



รายงานวิจัยฉบับสมบูรณ์

โครงการ สมบัติทางไฟฟ้าและวิศวกรรมโครงสร้างแถบพลังงานของวัสดุภายใต้สภาวะรุนแรง

โดย รองศาสตราจารย์ ดร.ธิตี บวรรัตนรักษ์

กรกฎาคม 2561

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

และจุฬาลงกรณ์มหาวิทยาลัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัยสกว. และจุฬาลงกรณ์มหาวิทยาลัยไม่จำเป็นต้องเห็นด้วยเสมอไป)

รหัสโครงการ: RSA5880058

ชื่อโครงการ: สมบัติทางไฟฟ้าและวิศวกรรมโครงสร้างแถบพลังงานของวัสดุภายใต้สภาวะรุนแรง

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ระยะเวลาโครงการ: 3 ปี

บทคัดย่อ

ความสัมพันธ์ระหว่างเสถียรภาพทางอุณหพลศาสตร์กับสมบัติความเป็นตัวนำยิ่งยวดของวัสดุเป็นประเด็นที่น่าสนใจสำหรับสาขาฟิสิกส์ธรณีฟิสิกส์และเคมีมาอย่างยาวนาน ตั้งแต่มีการค้นพบโครงสร้างที่มีความซับซ้อนสูงกว่าปกติเช่นโครงสร้างแบบไฮส เกส ในธาตุโลหะภายใต้ความดันสูงทำให้มีคำถามว่ากระบวนการใดที่ทำให้โครงสร้างของธาตุโลหะมีความซับซ้อนสูงและมีสภาพเหมือนมีการแยกตัวออกเป็นอะตอมที่มีโครงสร้างทางอิเล็กทรอนิกส์สองรูปแบบได้ ซึ่งหลายครั้งรวมไปถึงการเปลี่ยนแปลงสมบัติทางกายภาพสมบัติทางเคมีและโดยเฉพาะอย่างยิ่งสมบัติทางไฟฟ้าเช่นโครงสร้างแถบพลังงาน ดังนั้นงานวิจัยในสาขาฟิสิกส์สภาวะรุนแรงที่เกี่ยวข้องกับวัสดุพลังงานจึงมุ่งเน้นประเด็นไปที่การปรับปรุงโครงสร้างแถบพลังงานของวัสดุเหล่านี้โดยใช้กระบวนการความดันสูง ไม่เพียงแต่โครงสร้างทางอิเล็กทรอนิกส์เท่านั้นสมบัติเชิงกลก็เป็นประเด็นที่ได้รับการศึกษาอย่างกว้างขวาง โดยเฉพาะอย่างยิ่งการพัฒนาสมบัติความแข็งแรงยิ่งยวดในวัสดุหลากหลายประเภทเพื่อมาทดแทนเพชรในอุตสาหกรรม

งานวิจัยนี้ได้ทำการศึกษาเชิงทฤษฎีกับเซลล์สุริยะแบบเพอรอฟสไกต์ และสารกึ่งตัวนำในกลุ่มเทอเนอริย์ พร้อมทั้งวัสดุพลังงานอื่นๆโดยพุ่งเป้าไปที่วิศวกรรมโครงสร้างแถบพลังงานภายใต้สภาวะรุนแรงซึ่งในมุมมองของการศึกษาเชิงทฤษฎีไม่เพียงแต่จำเป็นจะต้องเลือกใช้ฟังก์ชันแนล ที่เหมาะสมเท่านั้นแต่จะต้องมีการศึกษาอย่างเป็นระบบซึ่งโครงการวิจัยนี้ได้พัฒนาขึ้นรวมถึงการศึกษาการเปลี่ยนแปลงสมบัติเชิงโครงสร้างในวัสดุเหล่านี้ด้วย

คำหลัก: การเลี้ยวเบนของรังสีเอกซ์ การเปลี่ยนแปลงโครงสร้าง ไดมอนด์แอนวิลเซลล์

ทฤษฎีฟังก์ชันแนลความหนาแน่น ความดันสูง

Project Code: RSA5880058

Project Title: Electrical Properties and Band Gap Engineering in Materials under Extreme Conditions

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Project Period: 3 years

Abstract

The relation between thermodynamically stable and superconductivity preparation is one of the fundamental questions in physics, geophysics and chemistry. Since the discovery of the novel structure, this has remained as one of the main questions regarding the very foundation of elemental metals. Needless to say this has also bearings on extreme conditions physics, where again the relation between structure and performance is of direct interest. Ternary compound semiconductors as well as Perovskite solar cell materials are energy materials which their energy band gap vary drastically under extreme conditions. Not only their electrical properties that highly sensitive to pressure but also their crystal structure as well as their mechanical properties. In this research, theoretical investigation of Perovskite solar cell and ternary compound semiconductors as well as other energy materials have been carried out. Band gap engineering mechanism exploit extreme conditions will also be proposed. The suitable functional for different type of materials have also been systematically studied. Structural phase transitions and their stability under various pressure have also been reported.

Keywords: X-ray diffraction, Structural phase transition, Diamond anvil cell, Density Functional Theory, High Pressure

หน้าสรุปโครงการ (Executive Summary)

ชื่อโครงการ สมบัติทางไฟฟ้าและวิศวกรรมโครงสร้างแถบพลังงานของวัสดุภายใต้สภาวะรุนแรง

Electrical Properties and Band Gap Engineering in Materials under Extreme Conditions

โครงการวิจัยนี้ต้องการใช้เทคนิคสภาวะรุนแรง ซึ่งได้แก่อุณหภูมิและความดันสูง ในการเหนี่ยวนำให้เกิดการเปลี่ยนแปลงโครงสร้างทั้งในเชิงโครงสร้างผลึกและเชิงอิเล็กทรอนิกส์ เพื่อให้วัสดุที่มีสมบัติเปลี่ยนไปตามที่ต้องการเช่น ใช้ความดันเป็นตัวแปรที่ทำให้ธาตุหรือวัสดุที่มีสมบัติทางกายภาพที่เปลี่ยนแปลงไปเช่นมีสมบัติเชิงกลที่ดีขึ้น ได้แก่ มีความแข็งแรงเพิ่มมากขึ้น หรือมีสมบัติทางไฟฟ้าที่เปลี่ยนแปลงไป เช่นกลายเป็นวัสดุที่มีสมบัติตัวนำยิ่งยวดที่อุณหภูมิต่างๆ หรือแม้แต่การเพิ่มเสถียรภาพและปรับขนาดช่องว่างแถบพลังงานของสารกึ่งตัวนำในตระกูล Perovskite เพื่อให้เหมาะสมกับการทำหน้าที่เป็น absorber ในเซลล์สุริยะ เป็นต้น

ในส่วนแรกของการดำเนินการวิจัย คณะผู้วิจัยได้ทำการศึกษาเชิงทฤษฎีในวัสดุสองประเภท โดยประเภทแรกนั้นได้ทำการศึกษาธาตุโลหะและสารประกอบเพื่อศึกษาถึงการเปลี่ยนแปลงโครงสร้างแนวโน้มการเปลี่ยนแปลงสมบัติเชิงพลังงาน เช่นโครงสร้างแถบพลังงาน สมบัติทางไฟฟ้า รวมทั้งการเปลี่ยนแปลงโครงสร้างผลึกที่มีผลโดยตรงต่อสมบัติเชิงกายภาพ และสมบัติทางไฟฟ้า โดยเฉพาะในโลหะลิเทียม และลิเทียมเพอออกไซด์ที่เป็นวัสดุสำคัญในการพัฒนาแบตเตอรี่แบบลิเทียม-แอร์ ผลการวิจัยในส่วนนี้จึงประกอบด้วยผลการพัฒนาระบบระเบียบการศึกษาเชิงทฤษฎีในวัสดุ โดยในเบื้องต้นมีผลงานที่ได้รับการตีพิมพ์ในวารสารที่มี Impact Factor สูงไปแล้วเป็นจำนวนทั้งสิ้น 7 ฉบับ และอยู่ระหว่างการพิจารณาอีก 3 ฉบับ

ส่วนที่สองนั้นผู้วิจัยได้ทำการศึกษาวัสดุที่เป็นตัวดูดกลืนในเซลล์สุริยะแบบไฮบริดซึ่งมีโครงสร้างแบบ Perovskite ซึ่งในกลุ่มนี้ผู้วิจัยได้ทำการศึกษาในสามประเด็น กล่าวคือในประเด็นแรกผู้วิจัยต้องการระบบการศึกษาเชิงทฤษฎีที่สามารถอธิบายปรากฏการณ์ได้แม่นยำที่สุด โดยคำนึงถึงการเลือกใช้ระดับของทฤษฎีที่เหมาะสม เนื่องจากระบบที่ศึกษาประกอบด้วยส่วนที่เป็นสารอินทรีย์ และสารอนินทรีย์ ซึ่งผู้วิจัยตั้งสมมุติฐานว่าแรงวานเดอร์วาลส์ อาจจะมีส่วนสำคัญในการคงเสถียรภาพของโครงสร้าง ผู้วิจัยจึงได้ทำการศึกษาเปรียบเทียบผลจากการคำนวณโดยการประมาณค่าและฟังก์ชันแนลแบบต่างๆ ประเด็นที่สองคือพยายามใช้ฟิสิกส์ทฤษฎีในการอธิบายเสถียรภาพของโครงสร้าง และจำลองพลวัตของอะตอมในโครงสร้าง ซึ่งที่ผ่านมาได้มีการรายงานถึงพลวัตในโครงสร้างและมีความเชื่อว่าอาจจะมีส่วนสำคัญในการทำให้เซลล์สุริยะชนิดนี้มีอายุการใช้งานต่ำ ส่วนในประเด็นสุดท้ายคือการทดลองเพิ่มความดันและศึกษาโครงสร้างผลึก และโครงสร้างแถบพลังงานที่เปลี่ยนแปลงไปกับความดันผลการศึกษาวิจัยในช่วงที่สองของ

โครงการนี้ได้รับการตอบรับให้ตีพิมพ์ในวารสาร Scientific Report ซึ่งมี Impact Factor 4.122 แล้ว รวมผลงานทั้งสองส่วนนี้จะมีผลงานตีพิมพ์จากโครงการนี้เป็นจำนวนทั้งสิ้น 11 ฉบับ

เนื้อหางานวิจัย

บทที่ 1 บทนำ

การทดลองทางฟิสิกส์เพื่อศึกษาโครงสร้างและสมบัติของวัสดุโดยการเปลี่ยนแปลงตัวแปรทางอุณหภูมิศาสตร์อันได้แก่อุณหภูมิและความดันเป็นที่สนใจของนักวิทยาศาสตร์จากหลายสาขาวิชามาเป็นเวลานานแล้ว ขณะที่การทดลองส่วนใหญ่มุ่งเน้นที่การเปลี่ยนแปลงอุณหภูมิเป็นตัวแปรสำคัญเนื่องจากเทคโนโลยีในการควบคุมอุณหภูมินี้มีการใช้งานอย่างกว้างขวางอย่างไรก็ตามในระยะสิบปีที่ผ่านมาการทดลองทางความดันมีการพัฒนาไปอย่างรวดเร็วโดยเฉพาะอย่างยิ่งการศึกษาปรากฏการณ์ทางฟิสิกส์สถานะของแข็งภายใต้สภาวะความดันสูงโดยใช้ Diamond Anvil Cell การทดลองโดยใช้ตัวแปรเป็นความดันนี้มีข้อดีในการศึกษาสมบัติทางฟิสิกส์และในการเกิดการเปลี่ยนแปลงโครงสร้างเมื่อเปรียบเทียบกับการใช้อุณหภูมิคือ การเพิ่มความดันนั้นเป็นการลดปริมาตรหรือกล่าวได้ว่าเป็นการนำอะตอมโมเลกุลของสารให้เข้ามาใกล้กันมากขึ้นโดยแรงทางกลศาสตร์เพียงอย่างเดียว ทำให้การเปลี่ยนแปลงสถานะหรือการสร้างพันธะเกิดจากการปฏิสัมพันธ์ระหว่างอะตอมที่ได้รับแรงกระทำให้อยู่ใกล้กันมากกว่าที่สภาวะความดันปกติ ในขณะที่การเพิ่มอุณหภูมินั้นเป็นการกระตุ้นให้เกิดการเปลี่ยนแปลงโครงสร้างโดยทางอ้อม กล่าวคือเมื่ออะตอมหรือโมเลกุลมีการสั่นมากขึ้นเนื่องจากการได้รับการกระตุ้นจากการเพิ่มอุณหภูมิก็นจะมีการเคลื่อนตัวเข้าใกล้กันและเป็นการเหนี่ยวนำให้เกิดการเปลี่ยนแปลงโครงสร้าง อย่างไรก็ตามในกรณีนี้พลังงานรวมของระบบจะถูกรบกวนอย่างมากจากการสั่นที่เพิ่มขึ้นทำให้อาจกล่าวได้ว่าการศึกษากการเปลี่ยนแปลงโครงสร้างนั้นตัวแปรที่มีผลโดยตรงและมีการรบกวนระบบน้อยกว่าคือความดัน ภายใต้สภาวะความดันสูงผลึกมีการเปลี่ยนแปลงสถานะและโครงสร้างซึ่งมีผลโดยตรงต่อสมบัติทางกายภาพและทางเคมีของผลึก การศึกษาโครงสร้างทางผลึกวิทยาของวัสดุภายใต้สภาวะความดันและอุณหภูมิสูงซึ่งรวมเรียกว่าสภาวะรุนแรง (Extreme Conditions) จึงเป็นกระบวนการสำคัญอันจะนำไปสู่ความเข้าใจฟิสิกส์ของวัสดุภายใต้สภาวะรุนแรง เช่น การเปลี่ยนแปลงของโครงสร้างแถบพลังงานและการจัดเรียงตัวของอิเล็กตรอนในลำดับชั้นต่าง ๆ อันเป็นผลเนื่องมาจากความดันและอุณหภูมิ ในปัจจุบันเมื่อความสนใจของการศึกษาและพัฒนาวัสดุมีมากขึ้นเพื่อสนองตอบความต้องการในการใช้งานประยุกต์ต่างๆ รวมทั้งการสังเคราะห์วัสดุระดับนาโน เหล่านี้ล้วนต้องการความเข้าใจในสมบัติทางฟิสิกส์ และ โครงสร้างของวัสดุที่ความดันและอุณหภูมิต่างๆ กัน โครงการวิจัยนี้ต้องการสร้างรากฐานงานวิจัยทางด้านฟิสิกส์ภายใต้สภาวะรุนแรงในประเทศไทยโดยมุ่งเน้นที่การนำเทคโนโลยีทางด้านนี้มาศึกษาโครงสร้างของโลหะ ซึ่งเป็นการนำเอาเทคโนโลยีในการวิจัยทางด้านนี้มาใช้ในการศึกษาทางด้านวัสดุศาสตร์ซึ่งเป็นสาขาที่ได้รับความสนใจสูง แต่การศึกษาโครงสร้างของวัสดุภายใต้ความดันนี้ยังมีน้อยมากในประเทศไทยเมื่อเทียบกับในระดับนานาชาติทั้งที่ผลการศึกษามีประโยชน์ต่อการพัฒนาเทคโนโลยีของวัสดุโดยเฉพาะกับวัสดุระดับนาโนได้อย่างชัดเจน

โครงการวิจัยนี้ทำการศึกษาเปลี่ยนแปลงโครงสร้างของวัสดุพื้นฐาน ซึ่งเป็นงานวิจัยต่อเนื่องจากงานวิจัยของหัวหน้าโครงการซึ่งมีผลงานตีพิมพ์ในระดับนานาชาติแล้วอย่างมากมาย โดยเฉพาะอย่างยิ่งคือการระบุโครงสร้างของ Sr ภายใต้ความดันสูงนั้นจำนวนสามโครงสร้างจากทั้งหมดที่มีการรายงานหัว

โครงสร้างเป็นผลงานวิจัยที่หัวหน้าโครงการ [1-3] ซึ่งในจำนวนนี้เป็นวารสารที่มี Impact Factor 3.475 ถึงสองบทความด้วยกัน นอกจากนั้นแล้วยังได้มีการขยายการศึกษาไปสู่สารกึ่งตัวนำ GaAs ซึ่งเป็นวัสดุต้นแบบที่นำไปพัฒนาเซลล์แสงอาทิตย์แล้วพบว่า เป็นเซลล์แสงอาทิตย์ที่มีช่วงกว้างของการตอบสนองต่อความยาวคลื่นแสงในช่วงต่างๆมากที่สุด [4] และมีผลงานตีพิมพ์ไปแล้วถึงสองบทความ [5-6] สำหรับในส่วนของการใช้ทฤษฎีและการคำนวณเพื่อทำนายสมบัติทางฟิสิกส์ของวัสดุนั้นนอกเหนือจากการอธิบายการเปลี่ยนแปลงโครงสร้างที่สังเกตได้จากการทดลองแล้วโครงการนี้ยังต้องการขยายขอบเขตการวิจัยไปสู่การทำนายสมบัติของธาตุโลหะหมู่ IA ในสถานะของเหลวภายใต้ความดันสูงอีกด้วย ผลที่ได้จากการวิจัยนี้สามารถนำไปบูรณาการกับศาสตร์อื่นๆ ได้อย่างกว้างขวางเนื่องจากเครื่องมือที่พัฒนานี้จะเป็นเครื่องมือสำคัญในการศึกษาและสังเคราะห์วัสดุอื่นๆ ภายใต้ความดัน เช่น โลหะ และสารกึ่งตัวนำที่จะได้นำไปพัฒนาเป็นอุปกรณ์ต่างๆต่อไป หรือแม้แต่นำไปพัฒนาให้มีโครงสร้างทางเคมีที่แตกต่างออกไปเพื่อปรับสภาพการออกฤทธิ์ในร่างกายมนุษย์ให้เหมาะสมซึ่งเป็นเทคนิคใหม่ที่ได้รับการสนใจสูงและเริ่มมีการทำวิจัยโดยใช้เทคนิคนี้แล้วกับการพัฒนายาบางชนิดในต่างประเทศ [7]

Diamond Anvil Cell เป็นอุปกรณ์ที่ใช้สร้างสภาวะความดันสูงสำหรับการทดลองในห้องปฏิบัติการที่ได้รับความนิยมมากที่สุดในงานวิจัยทางด้านความดันเนื่องจากเป็นอุปกรณ์ที่มีขนาดเล็ก มีความทนทานสูงและมีอายุการใช้งานยาวนานและสามารถนำไปประยุกต์ใช้กับการทดลองวัดค่าทางฟิสิกส์ได้หลายรูปแบบ[8] สำหรับในประเทศไทยการทดลองที่เกี่ยวข้องกับการเปลี่ยนแปลงสถานะและโครงสร้างเนื่องมาจากความดันยังมีน้อยมากและยังไม่มีงานวิจัยที่มีการตีพิมพ์ในระดับนานาชาติ การนำเอาเทคโนโลยีการทดลองทางด้านนี้มาใช้ในประเทศจึงมีความจำเป็นอย่างยิ่งในการพัฒนางานวิจัยทางด้านนี้ให้ทัดเทียมกับนานาชาติ ในระยะเวลาสิบปีที่ผ่านมาเทคโนโลยีทางด้านนี้ในระดับนานาชาติได้มีการพัฒนาไปอย่างมาก โดยเฉพาะอย่างยิ่งการศึกษาปรากฏการณ์ทางฟิสิกส์สถานะของแข็งภายใต้สภาวะความดันสูง[9] เนื่องจากการเข้าใจในโครงสร้างผลึกของวัสดุเป็นพื้นฐานที่สำคัญในการศึกษาสมบัติของวัสดุหรือนำไปสู่การทำนายสมบัติในกรณีที่มีการวัดค่าทางทดลองไม่สามารถกระทำได้ การศึกษาโครงสร้างผลึกภายใต้สภาวะความดันสูงจึงเป็นส่วนสำคัญสำหรับการวิจัยวัสดุที่อยู่ภายใต้ความดัน ในช่วงเวลาไม่นานมานี้การศึกษาโครงสร้างของธาตุโลหะและสารกึ่งตัวนำภายใต้สภาวะความดันสูงได้รับการสนใจอย่างมากเนื่องจากธาตุหลายชนิดมีการเปลี่ยนทั้งโครงสร้างและสมบัติต่างๆ ซิลิกอน(Si)เป็นธาตุหนึ่งที่ได้รับการสนใจอย่างมากจากการศึกษาโครงสร้างภายใต้ความดันสูงโดยมีรายงานการวิจัยพบว่าซิลิกอนมีโครงสร้างต่างๆ ที่ความดันสูงถึงหกโครงสร้างในช่วงความดันสูงถึง 50 GPa และมีการค้นพบว่าโครงสร้างสถานะที่สองที่ความดัน 12 GPa ซึ่งเป็นโครงสร้างแบบเตตระโกนอลนั้นมีสมบัติเป็นโลหะ[10,11] ปรากฏการณ์นี้สามารถอธิบายได้จากการที่ความดันมีผลทำให้อะตอมเคลื่อนตัวเข้ามาอยู่ใกล้กันมากขึ้นและมีการจัดเรียงตัวของลำดับชั้นของอิเล็กตรอนเปลี่ยนไปซึ่งนอกจากมีผลต่อการเปลี่ยนแปลงโครงสร้างของผลึกแล้วยังมีผลโดยตรงต่อการเปลี่ยนแปลงสมบัติการนำไฟฟ้าด้วย สำหรับการเปลี่ยนแปลงสมบัติภายใต้ความดันสูงนี้ ไฮโดรเจน (H) ซึ่งมีการทำนายว่าจะมีสมบัติเป็นโลหะที่ความดันสูงก็ได้รับการสนใจอย่างกว้างขวางในทางการทดลอง

[12] โดยที่ถ้าไฮโดรเจนกลายเป็นธาตุมีสมบัติเป็นโลหะจริงตามที่ได้รับการทำนายก็จะเป็นโลหะที่มีน้ำหนักเบามากและมีความเป็นไปได้สูงที่จะนำวัสดุเหล่านี้ไปใช้ในเชิงอุตสาหกรรม

สำหรับงานวิจัยศึกษาโครงสร้างผลึกภายใต้สภาวะความดันสูงของธาตุโลหะหมู่ IA และ IIA ได้รับความสนใจอย่างกว้างขวางจากทั้งนักทดลองและนักทฤษฎีเนื่องจากภายใต้ความดันสูงโลหะเหล่านี้จะเกิดการเปลี่ยนแปลงลำดับชั้นของอิเล็กตรอน กล่าวคือจากเดิมแบบที่มีลักษณะ s ไปเป็นแบบที่มีลักษณะ d [13-15] ซึ่งเป็นผลให้เกิดการเปลี่ยนแปลงรูปแบบของพันธะในโครงผลึกจากเดิมที่เป็นแบบไม่มีทิศทางมาเป็นแบบมีทิศทาง ส่งผลให้จากเดิมที่โครงสร้างผลึกเป็นแบบชิดกันมากที่สุด (close pack) มาเป็นโครงสร้างแบบที่อะตอมมิได้มีการจัดเรียงตัวแบบอยู่ใกล้กันมากที่สุดปรากฏการณ์นี้ทำให้ธาตุโลหะเหล่านี้เกิดการเปลี่ยนแปลงโครงสร้างอย่างมากภายใต้ความดันสูง อย่างไรก็ตามโครงสร้างทางผลึกวิทยาของธาตุเหล่านี้ภายใต้ความดันสูงมีความซับซ้อนมากและส่วนใหญ่ก็ได้รับการระบุโครงสร้างที่ชัดเจนเมื่อไม่นานมานี้ ยกตัวอย่างเช่น Li-III [16], Rb-IV and Rb-VI [17], Cs-V [18], Sr-III [2], Sr-IV [1], Sr-V [3] and Ba-IV [19] สำหรับโครงสร้างที่มีความแตกต่างจากกรณีทั่วไปคือในโครงสร้างของ Sr-V และ Ba-IV กล่าวคือจากการศึกษาโครงสร้างพบว่าอะตอมของธาตุเหล่านี้มีการแยกตัวออกเป็นสองประเภทหรือมีการจัดเรียงตัวของอิเล็กตรอนแตกต่างกันแล้วมีโครงสร้างแบบ Incommensurate ซึ่งมีลักษณะคล้ายกับโครงสร้างของซีโอไลต์และได้รับความสนใจอย่างมากเนื่องจากเป็นครั้งแรกที่มีการค้นพบว่าภายใต้ความดันสูงอะตอมของธาตุชนิดเดียวกันสามารถเปลี่ยนแปลงไปเป็นอะตอมที่มีการจัดเรียงตัวของลำดับชั้นของอิเล็กตรอนต่างกันและมีโครงสร้างของผลึกคล้ายกับโครงสร้างของสารประกอบที่มีส่วนประกอบของอะตอมมากกว่าหนึ่งชนิดได้

สำหรับงานวิจัยทางด้านการแพทย์และเภสัชศาสตร์นั้นมีการใช้ Diamond Anvil Cell ในการเปลี่ยนแปลงโครงสร้างของยา เช่นการปลูกผลึกของยาพาราเซตามอลที่ภายใต้ความดันสูงจากสารละลายพาราเซตามอล [20] พบว่ามีโครงสร้างคล้ายกับโครงสร้างที่อุณหภูมิต่ำ [7] รวมทั้งยังเสนอแนวทางสังเคราะห์สารที่มีโครงสร้างกึ่งเสถียรที่สภาวะปกติ ภายใต้ความดันอีกด้วย สาเหตุหลักของการเปลี่ยนแปลงโครงสร้างของสารเหล่านี้เกิดจากปัจจัยหลักประการหนึ่งคือการที่ลำดับชั้นของอิเล็กตรอนของอะตอมเกิดการเปลี่ยนแปลง การเข้าใจกลไกและระบบการเปลี่ยนแปลงโครงสร้างภายใต้ความดันสูงนี้เป็นส่วนสำคัญในการสังเคราะห์วัสดุที่มีสมบัติเฉพาะ และมีส่วนในการผลักดันการศึกษาทางทฤษฎีเกี่ยวกับการเปลี่ยนแปลงโครงสร้าง ดังนั้นการเสริมสร้างงานวิจัยทางด้านนี้จึงเป็นส่วนสำคัญในการพัฒนาเทคโนโลยีทางด้านวัสดุศาสตร์ โดยเฉพาะอย่างยิ่งในส่วนของโลหะและสารกึ่งตัวนำ หรือแม้แต่ในทางเภสัชศาสตร์และการแพทย์

บทที่ 2 ทฤษฎีพื้นฐาน

ในทางกลศาสตร์ควอนตัม สมการชโรดิงเงอร์ ประสบความสำเร็จในการอธิบายอนุภาคเดี่ยวในสภาวะต่างๆ สำหรับอนุภาคที่มีการเปลี่ยนแปลงตามเวลาจะถูกอธิบายด้วยสมการชโรดิงเงอร์ที่ขึ้นกับเวลา ซึ่งผลเฉลยมักจะถูกใช้ในการวิเคราะห์หาระดับพลังงานและคุณสมบัติอื่นๆ ของอิเล็กตรอนเดี่ยว อย่างไรก็ตามวิธีการนี้ไม่เหมาะสำหรับระบบที่ประกอบด้วยจำนวนอิเล็กตรอนมากๆ หรือที่เรียกว่า ระบบหลายอนุภาค กลศาสตร์ควอนตัมสำหรับระบบนิวเคลียสและอิเล็กตรอนที่มีอันตรกิริยาต่อกัน สามารถแก้ปัญหาโดยใช้สมการชโรดิงเงอร์หลายอนุภาค

$$\hat{H}\psi = E\psi \quad 2.1$$

โดย $\hat{H}$ คือ แฮมิลโทเนียนของระบบสามารถเขียนในรูปของตัวดำเนินการ

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{i,j(j \neq i)} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_I \frac{\hbar^2}{2M} \nabla_I^2 + \frac{1}{2} \sum_{I,J(I \neq J)} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} \quad 2.2$$

เมื่อ M และ m คือ มวลของนิวเคลียสและมวลของอิเล็กตรอน ตามลำดับ $\vec{R}$ และ $\vec{r}$ คือ ตำแหน่งของนิวเคลียสและตำแหน่งของอิเล็กตรอน ตามลำดับ พจน์ทางขวามือในสมการ 2.2 ประกอบด้วยพลังงานจลน์ของอิเล็กตรอน พลังงานศักย์ระหว่างอิเล็กตรอนกับนิวเคลียส พลังงานศักย์ระหว่างอิเล็กตรอนกับอิเล็กตรอน พลังงานจลน์ของนิวเคลียส และพลังงานศักย์ระหว่างนิวเคลียสกับนิวเคลียส ตามลำดับ แต่การแก้ปัญหของสมการนี้เป็นไปได้ยาก เนื่องจากระบบประกอบด้วยอนุภาค N ตัว จะทำให้ฟังก์ชันคลื่นมีระดับชั้นความเสรีถึง $3N$ จึงมีการเสนอแนวคิดที่นิวเคลียสเคลื่อนที่ช้ามากเมื่อเทียบกับอิเล็กตรอน ดังนั้น ψ จึงขึ้นอยู่กับเคลื่อนที่ของอิเล็กตรอนเท่านั้น เรียกการประมาณนี้ว่า การประมาณของบอร์น-ออปเพนไฮเมอร์ (Born-Oppenheimer approximation) [21] จากการประมาณของบอร์น-ออปเพนไฮเมอร์ ฟังก์ชันคลื่นสามารถเขียนอยู่ในรูปของผลคูณระหว่างฟังก์ชันคลื่นของอิเล็กตรอนกับฟังก์ชันคลื่นของนิวเคลียส ทำให้พจน์ของพลังงานระหว่างนิวเคลียสกับนิวเคลียสเป็นค่าคงที่ และให้ความสำคัญในส่วนของอิเล็กตรอน ดังนั้น แฮมิลโทเนียนของระบบอิเล็กตรอนที่นิวเคลียสอยู่นิ่งสามารถเขียนได้เป็น

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{i,j(j \neq i)} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad 2.3$$

ซึ่งแฮมิลโทเนียนนี้ยังไม่สามารถแก้ปัญหาได้โดยตรงเนื่องจากความซับซ้อนของฟังก์ชันคลื่นในระบบหลายอนุภาค การประมาณฟังก์ชันคลื่นของระบบหลายอนุภาคจึงเริ่มมีการคิดค้นโดยทฤษฎีของฮาร์ทรี (Hartree's theory) [22] ซึ่งลดรูปฟังก์ชันคลื่นของระบบหลายอนุภาคที่ซับซ้อนให้กลายเป็นผลคูณของฟังก์ชันคลื่นของอิเล็กตรอนเดี่ยว แต่ทฤษฎีฮาร์ทรีไม่สามารถอธิบายสมบัติปฏิสัมพันธ์ของฟังก์ชันคลื่นของอิเล็กตรอนได้ ต่อมาฮาร์ทรีและฟอกส์ได้เสนอฟังก์ชันคลื่นของระบบหลายอนุภาคให้อยู่ในรูปของSlater determinant ของฟังก์ชันคลื่นของอิเล็กตรอนเดี่ยวเพื่อแก้ปัญหามิติปฏิสัมพันธ์ของอิเล็กตรอน สามารถเขียนได้ในรูปเมทริกซ์ได้เป็น

$$\psi(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\bar{x}_1) & \psi_2(\bar{x}_1) & \cdots & \psi_N(\bar{x}_1) \\ \psi_1(\bar{x}_2) & \psi_2(\bar{x}_2) & \cdots & \psi_N(\bar{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\bar{x}_N) & \psi_2(\bar{x}_N) & \cdots & \psi_N(\bar{x}_N) \end{vmatrix} \quad 2.4$$

ซึ่งทฤษฎีของฮาร์ทรี่ฟอกค์สามารถอธิบายระบบเล็กๆที่มีสมบัติปฏิสมมาตรของฟังก์ชันคลื่นและอันตรกิริยาแลกเปลี่ยน แต่ยังไม่รวมผลของสหสัมพันธ์ ระเบียบวิธีของฮาร์ทรี่ฟอกค์จึงไม่เหมาะที่จะใช้แก้ปัญหาในระบบที่มีจำนวนอิเล็กตรอนมากๆ เนื่องจากใช้ทรัพยากรในการคำนวณมาก ดังนั้น ทฤษฎีฟังก์ชันนัลความหนาแน่น (Density Functional Theory) จึงมีความเหมาะสมมากกว่าที่จะใช้แก้ปัญหาในระบบหลายอนุภาคในของแข็งเนื่องจากทฤษฎีฟังก์ชันนัลความหนาแน่นประกอบด้วย พลังงานแลกเปลี่ยน-สหสัมพันธ์ ที่มีความใกล้เคียงกับระบบจริง

ฟังก์ชันนัลความหนาแน่นเป็นหนึ่งในเทคนิคที่ได้รับความนิยมและประสบความสำเร็จในการแก้ปัญหาในระบบหลายอนุภาค ซึ่งทฤษฎีฟังก์ชันนัลความหนาแน่นเป็นระเบียบวิธีที่ใช้กฎพื้นฐานทางฟิสิกส์ แต่มีการประมาณค่าในส่วนของพลังงานแลกเปลี่ยน-สหสัมพันธ์ โดยฟังก์ชันนัลความหนาแน่นเริ่มจากทฤษฎีบทโฮเซนเบิร์ก-โคห์น [23]

ทฤษฎีบทโฮเซนเบิร์ก-โคห์น (Hohenberg-Kohn Theorem)

ทฤษฎีบทโฮเซนเบิร์ก-โคห์นสำหรับระบบที่มีสถานะพื้น มีทั้งหมด 2 ข้อ คือ

1. สำหรับระบบที่มีอนุภาคที่มีแรงกระทำต่อกัน อยู่ภายใต้ศักย์ภายนอก $V_{ext}(r)$ พลังงานของระบบที่สถานะพื้นจะเป็นฟังก์ชันนัลแบบหนึ่งต่อหนึ่งของความหนาแน่นอิเล็กตรอน $n_0(r)$

$$E = E[n(r)] \quad 2.5$$

2. ค่าความหนาแน่นของอิเล็กตรอนที่แท้จริงของระบบเกิดจากค่าพลังงานที่ต่ำที่สุดของระบบ

$$E_0 = E[n_0(\bar{r})] \leq E[n(\bar{r})] \quad 2.6$$

ทำให้สามารถใช้ความหนาแน่นของอิเล็กตรอนแทนฟังก์ชันคลื่นในการแก้ปัญหасмการชโรดิงเงอร์ได้

สมการโคห์น-ชาม (Kohn-Sham equations)

จากทฤษฎีบทโฮเซนเบิร์ก-โคห์น โคห์น-ชาม [24] เขียนพลังงานรวมของระบบในรูปฟังก์ชันนัลได้ดังนี้

$$E[n] = T_s[n] + U[n] + E_{xc}[n] \quad 2.7$$

โดย T_s คือ พลังงานจลน์ของอิเล็กตรอน

U คือ พลังงานศักย์ที่ประกอบด้วยอันตรกิริยาระหว่างอิเล็กตรอนกับอิเล็กตรอน หรือ พลังงานฮาร์เทรี และพลังงานศักย์ภายนอกที่มาจากศักย์ลอมบ์ของนิวเคลียส

E_{xc} คือ พลังงานแลกเปลี่ยน-สหสัมพันธ์ที่เกิดจากอันตรกิริยาของอิเล็กตรอน

สำหรับพจน์พลังงานจลน์และพลังงานศักย์ของอิเล็กตรอนเป็นพจน์ที่สามารถเขียนได้ในรูปแบบเชิงวิเคราะห์ ส่วนผลทุกอย่างที่นอกเหนือจากนั้นจะรวมอยู่ในพจน์พลังงานแลกเปลี่ยน-สหสัมพันธ์ ซึ่งไม่สามารถหาค่าแม่นยำได้จึงมีการเสนอการประมาณค่าพลังงานแลกเปลี่ยน-สหสัมพันธ์ต่างๆ ซึ่งจะกล่าวในภายหลัง หลังจากนั้นโคห์นและซามได้หาค่าค่าสุดของฟังก์ชันนัลของสมการที่ 2.7 จะได้สมการที่มีลักษณะคล้ายกับชโรดิงเงอร์ เรียก สมการโคห์น-ซาม เขียนได้ดังนี้

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\vec{r}) \right] \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r}) \quad 2.8$$

ซึ่งเป็นการแก้ปัญหาระบบอิเล็กตรอนเดี่ยวที่อยู่ภายใต้ศักย์ยังผล (Effective potential) $V_{eff}(\vec{r})$ เท่านั้น โดยพจน์ศักย์ยังผลเขียนอยู่ในรูป

$$V_{eff}(\vec{r}) = V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}) \quad 2.9$$

โดย $V_{ext}(\vec{r})$ คือ ศักย์ภายนอกที่มาจากศักย์ลอมบ์ของนิวเคลียส

$V_H(\vec{r})$ คือ ศักย์ที่เกิดจากอันตรกิริยาระหว่างอิเล็กตรอนกับอิเล็กตรอนหรือศักย์ฮาร์เทรี

$V_{xc}(\vec{r})$ คือ ศักย์ที่เกิดจากการแลกเปลี่ยน-สหสัมพันธ์

เมื่อพิจารณาสมการโคห์น-ซาม จะพบว่าศักย์ยังผลขึ้นอยู่กับความหนาแน่นของอิเล็กตรอน ซึ่งความหนาแน่นของอิเล็กตรอนทราบได้จากฟังก์ชันคลื่น และฟังก์ชันคลื่นคำนวณจากสมการโคห์น-ซามที่ต้องทราบค่าศักย์ยังผลก่อน ดังนั้นจึงใช้วิธีการเซลฟ์คอนซิสแตนท์ฟิลด์ (self-consistent field) ในการแก้ปัญหสมการโคห์น-ซาม สำหรับระบบของแข็งที่มีลักษณะเป็นคาบ จะใช้ทฤษฎีบทของบลอค (Bloch's theorem) มาพิจารณาซึ่งฟังก์ชันคลื่นของอิเล็กตรอนจะอยู่ในรูปของผลคูณของคลื่นระนาบ ดังสมการ

$$\varphi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \quad 2.10$$

โดย $\vec{k}$ คือ เวกเตอร์คลื่น (wave vector) ซึ่งภายใต้เงื่อนไขของทฤษฎีบทของบลอค ค่าจะคงและฟังก์ชันคลื่น ต้องเป็นไปตามสมการ

$$E(\vec{k}) = E(\vec{k} + \vec{G}) \quad 2.11$$

โดย $\vec{G}$ คือ เวกเตอร์ของโครงผลึกส่วนกลับ (Reciprocal lattice vector) และค่า $\vec{G}$ ที่มากที่สุดสัมพันธ์กับพลังงานคัทออฟ (cut off energy)

$$E_{cut} = \frac{\hbar^2 \bar{G}_{max}^2}{2m} \quad 2.12$$

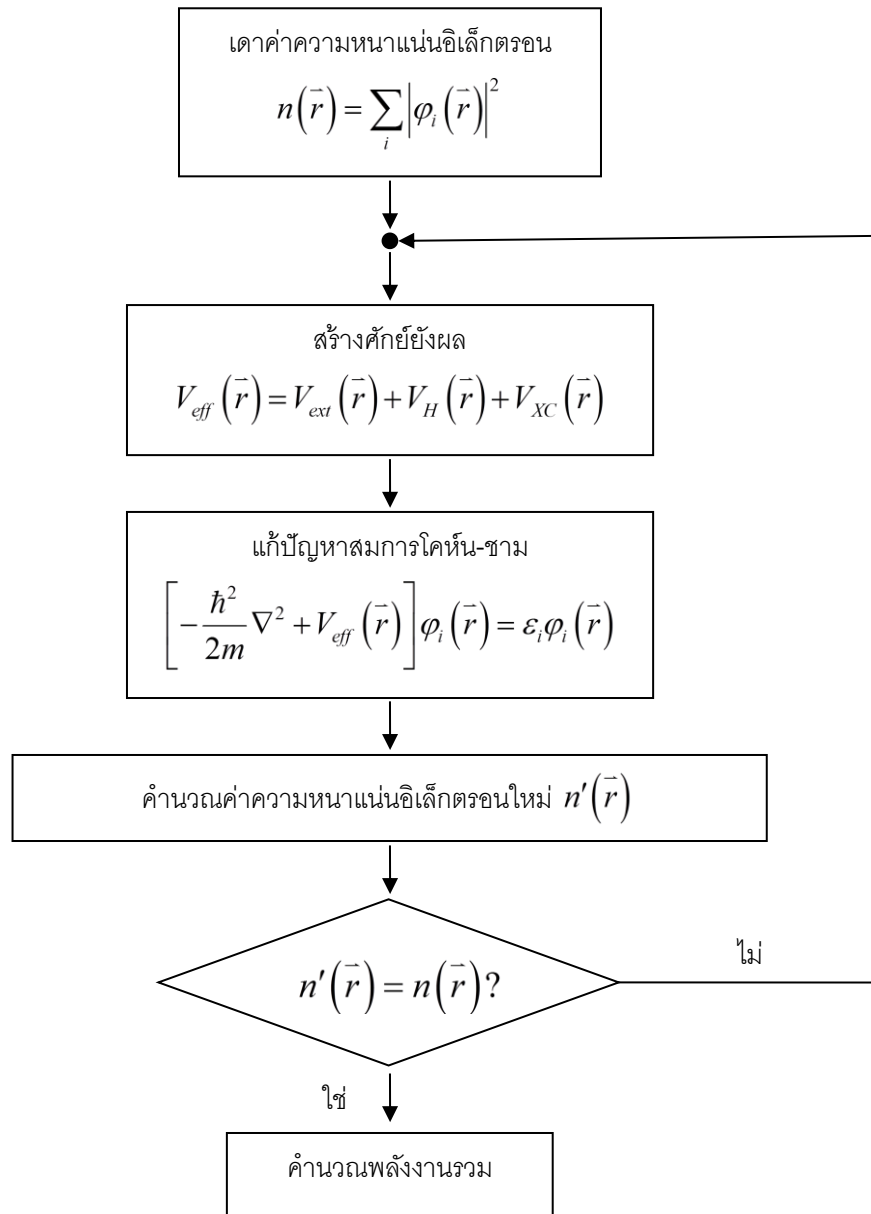
และฟังก์ชันคลื่นที่มีลักษณะเป็นคาบถูกให้นิยามเป็นผลรวมของเซตฐานคลื่นระนาบ จึงเขียนฟังก์ชันคลื่นได้ในลักษณะ

$$\varphi_k(\vec{r}) = \sum_j c_j(\vec{k}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \quad 2.13$$

โดย $c_j(\vec{k})$ คือ ค่าสัมประสิทธิ์ของฐานนั้นๆ ซึ่งค่าเริ่มต้นของค่า $c_j(\vec{k})$ จะสุ่มตัวเลขเพื่อนำมาคำนวณหาค่าความหนาแน่นอิเล็กตรอนจากสมการ

$$n(\vec{r}) = \sum_i |\varphi_i(\vec{r})|^2 \quad 2.14$$

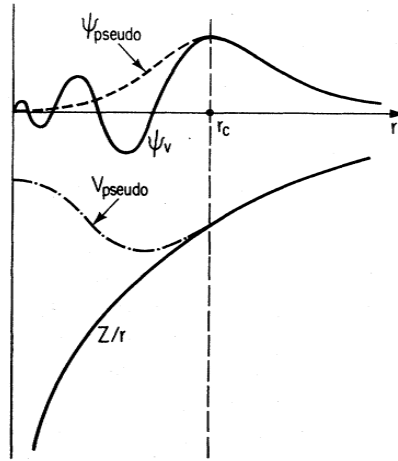
เพื่อนำไปสร้างศักย์ยังผลในสมการ 2.9 จากนั้นจึงแก้ปัญหасมารโคห์น-ฮามในสมการ 2.8 โดยใช้เมทริกซ์ ซึ่งจะได้ค่าเจาะจงออกมาและเซตคำตอบของ $\{c_j\}$ ใหม่ จึงนำไปคำนวณหาค่าความหนาแน่นของอิเล็กตรอนใหม่ในสมการ 2.14 แล้วเปรียบเทียบความหนาแน่นของอิเล็กตรอนใหม่กับความหนาแน่นของอิเล็กตรอนเก่า เมื่อความหนาแน่นของอิเล็กตรอนมีค่าไม่ต่างจากเดิม จะหยุดกระบวนการ และความหนาแน่นของอิเล็กตรอนนั้นจะเป็นค่าความหนาแน่นของอิเล็กตรอนที่สถานะพื้น หลังจากนั้นจะใช้ความหนาแน่นของอิเล็กตรอนนี้ไปคำนวณหาพลังงานรวมของระบบที่สถานะพื้นในสมการ 2.7 แต่ถ้าเปรียบเทียบความหนาแน่นของอิเล็กตรอนแล้วพบว่าค่าทั้งสองต่างกัน จะนำค่าความหนาแน่นของอิเล็กตรอนไปสร้างศักย์ยังผลและเข้าสู่กระบวนการทำซ้ำต่อไปจนกว่าค่าความหนาแน่นของอิเล็กตรอนมีค่าไม่ต่างจากค่าความหนาแน่นของอิเล็กตรอนในรอบก่อน สามารถแสดงเป็นแผนภาพได้ดังภาพที่ 2.4



ภาพที่ 2.4 แผนภาพแสดงกระบวนการวิธีเซลฟ์คอนซิสแตนท์ฟิลด์

การประมาณค่าศักย์เทียม

เนื่องจากอิเล็กตรอนวงนอก (valence electron) มักส่งผลต่อการเกิดปฏิกิริยาเคมีและสมบัติทางฟิสิกส์มากกว่าอิเล็กตรอนแกน (core electron) จึงมีการเสนอศักย์เทียมมาแทนศักย์ยังผล เพื่อลดจำนวนคลื่นระนาบที่ต้องใช้ โดยลักษณะของศักย์เทียมแสดงได้ดังภาพที่ 2.5 โดยศักย์เทียมจะมีลักษณะฟังก์ชันคลื่นหลังจากระยะอิเล็กตรอนแกนเหมือนกับฟังก์ชันคลื่นจริง และความหนาแน่นของอิเล็กตรอนของศักย์เทียมที่ระยะก่อนระยะอิเล็กตรอนแกนจะเท่ากับค่าความหนาแน่นของอิเล็กตรอนจริง เมื่อนำมาพิจารณาในสมการ 2.13 จะเห็นว่า ลักษณะฟังก์ชันคลื่นของศักย์เทียมเป็นผลรวมของคลื่นระนาบซึ่งใช้จำนวนคลื่นระนาบน้อยกว่าฟังก์ชันคลื่นจริง



ภาพที่ 2.5 เส้นที่แสดงฟังก์ชันคลื่นของอิเล็กตรอนทุกตัวและศักย์ที่เกิดจากนิวเคลียสกับอิเล็กตรอน เส้นประแสดงฟังก์ชันคลื่นเทียมและศักย์เทียมโดย r_c คือ ระยะของอิเล็กตรอนแกน (core electron) [25]

โดยทั่วไป ศักย์เทียม จะเขียนความหนาแน่นของอิเล็กตรอนวงนอกดังสมการ

$$n(\vec{r}) = \sum_n \left[\left| \phi_n(\vec{r}) \right|^2 + \sum_{ij} Q_{ij}(\vec{r}) \langle \phi_n | \beta_j \rangle \langle \beta_i | \phi_n \rangle \right] \quad 2.15$$

ซึ่ง β_i คือ ฟังก์ชันหลักที่ขึ้นอยู่กับตำแหน่งของนิวเคลียส และ $Q_{ij}(\vec{r})$ คือ ฟังก์ชันเสริมหาได้จาก

$$Q_{ij}(\vec{r}) = \phi_i^*(\vec{r}) \phi_j(\vec{r}) - \phi_j^*(\vec{r}) \phi_i(\vec{r}) \quad 2.16$$

โดย ϕ_i คือ ฟังก์ชันคลื่นของอิเล็กตรอนทั้งหมด และ ϕ_j คือ ฟังก์ชันคลื่นเทียม ในงานวิจัยชิ้นนี้ได้พิจารณาความแตกต่างในการเลือกใช้ศักย์เทียมแบบอัลตราซอฟท์ (ultrasoft pseudopotential) ซึ่งจะไม่พิจารณาเงื่อนไข $Q_{ij}(\vec{r}) = 0$ และแบบนอร์ม-คอนเซอเวทีฟ (norm-conservative pseudopotential) ที่พิจารณาเงื่อนไข $Q_{ij}(\vec{r}) = 0$ เข้าไปด้วย

การประมาณค่าพลังงานแลกเปลี่ยน-สหสัมพันธ์

ในส่วนของการประมาณแลกเปลี่ยน-สหสัมพันธ์เป็นพจน์ที่ไม่สามารถหาค่าแน่นอนตรงได้ ในงานวิจัยนี้ได้เลือกวิธีการประมาณแบบความหนาแน่นเฉพาะที่ (Local density Approximation) [24] และแบบผลต่างทั่วไป (Generalized Gradient Approximation) [26] สำหรับการประมาณแบบความหนาแน่นเฉพาะที่ (Local density Approximation) โดยสมมุติพลังงานแลกเปลี่ยน-สหสัมพันธ์ต่ออิเล็กตรอนที่ตำแหน่ง $\vec{r}$ มีค่าเท่ากับ

พลังงานแลกเปลี่ยน-สหสัมพันธ์ต่ออิเล็กตรอนที่ทราบค่าแล้วในอิเล็กตรอนแก๊ส สามารถเขียนในรูปทั่วไปคือ

$$E_{XC}^{LDA}[n(\vec{r})] = \int d^3r n(\vec{r}) \varepsilon_{XC}(n(\vec{r})) \quad 2.17$$

และ

$$\frac{\delta E_{XC}[n(\vec{r})]}{\delta n(\vec{r})} = \frac{\partial (n(\vec{r}) \varepsilon_{XC}(n(\vec{r})))}{\partial n(\vec{r})} \quad 2.18$$

กับ

$$\varepsilon_{XC}(n(\vec{r})) \equiv \varepsilon_{\text{homo}}[n(\vec{r})] \quad 2.19$$

โดย $\varepsilon_{\text{homo}}[n(\vec{r})]$ คือ พจน์ของพลังงานแลกเปลี่ยนสหสัมพันธ์ต่ออนุภาคของอิเล็กตรอนแก๊สที่มีความหนาแน่นสม่ำเสมอ ซึ่งมีการคิดค้นอธิบาย $\varepsilon_{XC}(n(\vec{r}))$ โดยใช้ระเบียบวิธีที่ต่างกันออกไป ในงานวิจัยนี้เลือกฟังก์ชันนัลชนิด CA-PZ (Ceperley, Alder - Perdew and Zunger) [27] และสำหรับพลังงานแลกเปลี่ยน-สหสัมพันธ์ต่ออิเล็กตรอนของการประมาณแบบผลต่างทั่วไป (Generalized Gradient Approximation) ซึ่งสามารถเขียนในรูปทั่วไปคือ

$$E_{XC}^{GGA}[n(\vec{r})] = \int d^3r n(\vec{r}) \varepsilon_{XC}(n(\vec{r}), \nabla n(\vec{r})) \quad 2.20$$

เป็นการพัฒนามาจากการประมาณแบบความหนาแน่นเฉพาะที่ (LDA) โดยการเพิ่มพจน์ของอนุพันธ์ของความหนาแน่นอิเล็กตรอน $\nabla n(\vec{r})$ โดยเลือกฟังก์ชันนัลชนิด PBE (Perdew, Burke, and Ernzerhof) [28]

พลังงานคัทออฟและ K-point

จำนวนของเซตฐาน (G_j) ถูกนิยามโดยพลังงานคัทออฟ ซึ่งถ้าจำนวนของเซตฐาน (G_j) มีมากมายไม่สิ้นสุดจะทำให้ได้ผลเฉลยจากสมการโคห์น-ชามที่ถูกต้องแม่นยำ แต่ในทางปฏิบัติไม่สามารถทำได้เนื่องจากขอบเขตของการคำนวณ ดังนั้นจึงต้องประมาณค่าพลังงานคัทออฟที่เหมาะสม

จำนวนของ k-point เป็นสัดส่วนกับปริมาตรของเซลล์พื้นฐาน (primitive cell) ในของแข็ง จำนวนของโคห์น-ชามออร์บิทัล (Kohn-Sham orbital) ขึ้นอยู่กับขนาดของการเลือกใช้จำนวน k-point สำหรับระเบียบวิธีของมองฮอร์สท์-แพ็ค (Monkhorst-pack method) [29] สามารถเขียนฟังก์ชัน $f(\vec{r})$ ตลอดทั้งเซลล์หน่วยพื้นฐานของโครงผลึกส่วนกลับ (first Brillouin zone) ได้ดังนี้

$$f(\vec{r}) = \frac{V}{8\pi^3} \int_{BZ} F(\vec{k}) d\vec{k} = \sum_j w_j F(\vec{k}_j) \quad 2.21$$

เมื่อ $F(\vec{k})$ คือฟูเรียร์ทรานสฟอร์มของ $f(\vec{r})$
 V คือ ปริมาตรของเซลล์
 w_j คือ ปัจจัยถ่วง

สามารถเขียนกระจาย k-point อย่างสม่ำเสมอในพื้นที่ได้เป็น $\vec{k}_j = x_{1j}\vec{b}_1 + x_{2j}\vec{b}_2 + x_{3j}\vec{b}_3$ โดย $\vec{b}_i$ คือเวกเตอร์ในปริภูมิส่วนกลับ (reciprocal space) การเลือกใช้จำนวน k-point ที่มากมายไม่มีที่สิ้นสุดจะทำให้ได้ผลเฉลยที่ถูกต้องแม่นยำ ซึ่งในทางปฏิบัติไม่สามารถทำได้ จึงต้องเลือกใช้จำนวน k-point ที่เหมาะสมในการคำนวณ

สมการสถานะ (Equation of state)

จากการแก้ปัญหามสมการโคห์น-แฮมจนได้ผลเฉลยเพื่อนำไปหาค่าพลังงานรวมของระบบที่ปริมาตรต่างๆ โดยพลังงานรวมสามารถเขียนอยู่ในรูปของปริมาตร เรียกว่า สมการสถานะ ซึ่งสมการสถานะที่นิยมใช้ในการศึกษาการเปลี่ยนแปลงโครงสร้างภายใต้ความดันสูงอุณหภูมิคงที่ คือ สมการสถานะของเบริช-เมอร์นาแกน (Birch-Murnaghan Equation of state) [30] โดยเริ่มจากเมอร์นาแกนคิดค้นสมการสถานะของเมอร์นาแกน (Murnaghan Equation of state) ดังแสดงในสมการ

$$E(V) = E_0 + \frac{B_0 V}{B'_0} \left[\frac{(V_0/V)}{B'_0 - 1} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} \quad 2.22$$

โดย E_0 คือ พลังงานรวมที่ความดันเป็นศูนย์
 V_0 คือ ปริมาตรที่ความดันเป็นศูนย์
 B_0 คือ ค่ามอดุลัสเชิงปริมาตรที่ความดันเป็นศูนย์
 B'_0 คือ อนุพันธ์ของมอดุลัสเชิงปริมาตรเทียบกับความดัน ที่ความดันเป็นศูนย์

หลังจากนั้นมีการพัฒนาสมการสถานะของเมอร์นาแกนโดยเบริชและเมอร์นาแกน ดังนี้

$$E(V) = E_0 + \frac{9B_0 V_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{2/3} \right] \right\} \quad 2.23$$

เรียกสมการนี้ว่า สมการสถานะของเบริช-เมอร์นาแกนลำดับที่สาม (the third order Birch-

Murnaghan equation of state) จาก $-\left(\frac{\partial E}{\partial V}\right)_T = P$ ทำให้ได้สมการสถานะซึ่งแสดงความสัมพันธ์ระหว่างความดันและปริมาตร คือ

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\} \quad 2.24$$

พลังงานเสรีกิบส์ (Gibbs free energy, G) เป็นตัวแปรสถานะทางอุณหพลศาสตร์ที่ใช้ในการบ่งบอกการเปลี่ยนแปลงโครงสร้างของวัสดุภายใต้ความดันสูงได้ จากสมการ

$$G = E + PV - TS \quad 2.25$$

และ

$$G = H - TS \quad 2.26$$

โดย S คือ เอนโทรปี

H คือ เอนทัลปี

สำหรับทฤษฎีฟังก์ชันัลความหนาแน่นซึ่งคำนวณที่อุณหภูมิเป็นศูนย์ ดังนั้นพลังงานเสรีกิบส์จะลดเหลือเพียงเอนทัลปี โดยโครงสร้างที่เสถียรที่ความดันต่างๆสามารถสังเกตได้จากเอนทัลปีที่ต่ำสุด การเปลี่ยนแปลงโครงสร้างลำดับที่หนึ่ง (first order phase transition) จะเกิดขึ้นภายใต้เงื่อนไข $\Delta G = 0$ และ $\left(\frac{\partial G}{\partial P}\right)_T = V$ โดยที่ปริมาตรจะต้องมีค่าไม่ต่อเนื่องกันระหว่างสองโครงสร้างที่พิจารณา ในขณะที่การเปลี่ยนแปลงโครงสร้างลำดับที่สอง (second order phase transition) ปริมาตรจะมีค่าต่อเนื่องกันระหว่างสองโครงสร้างที่พิจารณา

การคำนวณสมบัติทางไฟฟ้า

หลังจากการแก้ปัญหามสมการโคห์น-ฮาม จะได้ความหนาแน่นของอิเล็กตรอนที่สถานะพื้นและศักย์ยังผล ซึ่งทำให้แฮมิลโทเนียนมีความสมบูรณ์ในสมการ 2.8 และจากทฤษฎีบทของบลอค (Bloch's theorem) ระดับพลังงานอธิบายได้ในเซลล์หน่วยพื้นฐานของโครงผลึกส่วนกลับ ซึ่งระดับพลังงานในแต่ละเวกเตอร์คลื่น $\vec{k}$ สามารถหาได้โดย

$$\langle \psi_{nk} | H | \psi_{nk} \rangle = E_{nk} \quad 2.27$$

ซึ่งการอธิบายระดับพลังงานของอิเล็กตรอนที่ดำเนินไปตามทิศทางที่มีสมมาตรสูงในเซลล์หน่วยพื้นฐานของโครงผลึกส่วนกลับเรียกว่า โครงสร้างแถบพลังงาน และความหนาแน่นสถานะของอิเล็กตรอน (density of state) คือ จำนวนสถานะที่อิเล็กตรอนจะครอบครองได้ ซึ่งความหนาแน่นสถานะของอิเล็กตรอนที่ระดับพลังงานใดๆ สามารถหาได้จากผลรวมของโครงสร้างแถบพลังงานที่ระดับพลังงานนั้นๆ

การคำนวณสมบัติเชิงแสง

ในการคำนวณสมบัติเชิงแสง สามารถอธิบายได้ด้วยค่าคงที่ไดอิเล็กทริกสามารถเขียนในรูปเชิงซ้อนได้

$$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 = N^2 \quad 2.28$$

โดย ε_2 คือ ส่วนจินตภาพของค่าคงที่ไดอิเล็กทริก สามารถหาได้จาก

$$\varepsilon_2(\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{\mathbf{k},v,c} \left| \langle \psi_{\mathbf{k}}^c | \mathbf{r} | \psi_{\mathbf{k}}^v \rangle \right|^2 \delta(E_{\mathbf{k}}^c - E_{\mathbf{k}}^v - E) \quad 2.29$$

ซึ่ง ครรชนีหักห (N) คือ อัตราส่วนของความเร็วของคลื่นแม่เหล็กไฟฟ้าภายในวัสดุนั้นเทียบกับความเร็วของคลื่นแม่เหล็กไฟฟ้าในสุญญากาศสามารถอธิบายในรูปเชิงซ้อน คือ

$$N = n + ik \quad 2.30$$

ในส่วนของจินตภาพของครรชนีหักหจะสัมพันธ์กับสัมประสิทธิ์การดูดกลืน

$$\eta = \frac{k\omega}{c} \quad 2.31$$

ซึ่งสัมประสิทธิ์การดูดกลืนจะเป็นตัวบ่งบอกพลังงานที่สูญเสียไปเมื่อคลื่นเดินทางผ่านวัสดุ และสัมประสิทธิ์การสะท้อนของพื้นผิว หาได้จาก

$$R = \left| \frac{1-N}{1+N} \right|^2 = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad 2.32$$

บทที่ 3 ผลการศึกษาวิจัย

ผลการศึกษาในทัลเลียม (TI)

ธาตุทัลเลียมได้รับความสนใจในการศึกษาอย่างมากมาตลอดระยะเวลาที่ยืลืบปีเนื่องจากสมบัติเชิงพันธะที่สำคัญคือเป็นธาตุที่สามารถสร้างพันธะโลหะและโควาเลนต์ได้เนื่องจากโครงสร้างเชิงอิเล็กทรอนิกส์ของธาตุในหมู่นี้ อย่างไรก็ตามที่ผ่านมาการศึกษาเชิงทฤษฎียังประสบปัญหาอยู่มากเนื่องจากผลการวิจัยยังมีความไม่สอดคล้องกับการทดลองสูง การศึกษาวิจัยจึงมุ่งเน้นไปที่สองส่วน คือส่วนที่ทำการศึกษาถึงที่มาของการศึกษาเชิงทฤษฎีที่ทำให้ผลไม่สอดคล้องกับการทดลอง ได้แก่การรวมผลของสัมพันธภาพในการจำลองทางทฤษฎี ซึ่งผลการวิจัยได้ระบุว่ามีความจำเป็นสูงในการศึกษาโดยเฉพาะอย่างยิ่งภายใต้ความดันสูง ส่วนที่สองที่ได้ทำการศึกษาคือการทำนายการเปลี่ยนแปลงโครงสร้างผลึกภายใต้ความดันสูง โดยใช้เทคนิคการวิจัยที่ทำการพัฒนาจากส่วนแรกและทำการเปรียบเทียบผลการทำนายเชิงทฤษฎีกับผลการทดลองโดยการเลี้ยวเบนของรังสีเอกซ์ภายใต้ความดันสูง ซึ่งพบว่าทำให้ผลการทำนายโครงสร้าง และการศึกษาจากการทดลองสอดคล้องกันอย่างดีเยี่ยม ทำให้ผลงานวิจัยทั้งสองส่วนดังกล่าวได้รับการตีพิมพ์ในวารสารระดับนานาชาติที่มี Impact Factor สูงแล้วเป็นจำนวนทั้งสิ้นสองบทความ

ทัลเลียมในสถานะปกติมีโครงสร้างผลึกเป็นแบบเฮกซะโกนอลโคโลสแพค (h.c.p.) และมีการเปลี่ยนแปลงเป็นแบบเฟสเซนเตอร์คิวบิก (f.c.c.) ที่ความดันประมาณ 4 GPa. โดยโครงสร้างแบบคิวบิกดังกล่าวมีเสถียรภาพถึงความดัน 68 GPa. เมื่อไม่นานมานี้ได้มีการศึกษาโครงสร้างผลึกและการเปลี่ยนแปลงโครงสร้างผลึกที่ความดันสูงกว่า 120 GPa. โดยมีการเสนอว่าโครงสร้างผลึกแบบ h.c.p. มีการเปลี่ยนแปลงเป็นแบบ f.c.c. ที่ 3.5 GPa. ซึ่งมีเสถียรภาพถึง 125 GPa. จากการศึกษาโดยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ ประกอบกับการวิจัยเชิงทฤษฎีโดยกลุ่มวิจัยเดียวกันนี้ได้ทำนายว่าโครงสร้างผลึกแบบ h.c.p. มีการเปลี่ยนแปลงเป็นแบบ f.c.c. ที่ 8.8 GPa. ซึ่งมีเสถียรภาพไปจนถึงความดัน 4.3 TPa. ทำให้ผลการศึกษาดังกล่าวยังมีความไม่สอดคล้องกันสูงระหว่างการทดลองและการทำนายเชิงทฤษฎี ในการศึกษาทัลเลียมภายใต้ความดันสูงในโครงการวิจัยนี้จึงเริ่มต้นที่การพยายามอธิบายถึงที่มาของความคลาดเคลื่อนดังกล่าวโดยตั้งสมมุติฐานว่าอาจจะเกิดจากการไม่ได้มีการรวมผลของสัมพันธภาพกับการคำนวณ เนื่องจากทัลเลียมเป็นธาตุหนัก ดังนั้นคณะผู้วิจัยจึงได้ทำการสาธิตถึงผลของสัมพันธภาพจากระดับของทฤษฎีต่างๆที่ใช้ในการคำนวณใน Full Potential Local Orbital (FPLO) ผลของการคำนวณพบว่าสามารถทำนายการเปลี่ยนแปลงโครงสร้างจาก h.c.p. ไปยัง f.c.c. ได้อย่างแม่นยำ นอกจากนี้แล้วยังสามารถอธิบายได้ว่าการเกิด s-p hybridization และการซ้อนทับกันของอิเล็กตรอนในวาเลนซ์ และส่วนแกนกลาง ของ 6s และ 5d เป็นสาเหตุหลักที่ทำให้เกิดการเปลี่ยนแปลงโครงสร้างไปเป็น f.c.c. และสามารถยืนยันเสถียรภาพของโครงสร้างแบบเตตระโกนอล b.c.t. ที่ 83 GPa. โดยเทคนิค Evolutionary Algorithm ได้ด้วย นอกจากนี้แล้วยังสามารถทำนายการเปลี่ยนแปลงโครงสร้างกลับไปเป็น f.c.c. อีกครั้งที่ความดัน 800 GPa. ด้วย การค้นพบดังกล่าวทำ

ให้มีแนวโน้มว่าธาตุในกลุ่ม III-A เช่น แกลเลียม อินเดียม และทลเลียมนั้นน่าจะมีการเปลี่ยนแปลงจาก b.c.t. กลับไปเป็น f.c.c ได้อีกครั้งที่ความดันสูงมาก

ผลการศึกษาในออสเมียมเตตระโบไรด์ (OsB_4)

จากการศึกษาแบบแอบอิงนิโซโดยการคำนวณอย่างเป็นระบบในการค้นหาโครงสร้างด้วยอัลกอริทึมที่มีวิวัฒนาการ คณะผู้วิจัยได้ค้นพบโครงสร้าง P42/mmc ใน OsB_4 ซึ่งมีความแข็งแรงสูงมากและมีสมบัติเป็นสารกึ่งตัวนำ ในการศึกษาครั้งนี้การเปลี่ยนแปลงโครงสร้างจากโครงสร้างที่มีสมบัติเป็นโลหะไปสู่โครงสร้างที่มีสมบัติเป็นสารกึ่งตัวนำได้ถูกทำนายที่ความดันสูงกว่าที่ความดันปกติเพียงเล็กน้อย คือที่ 11 จิกะปาสกาล ดังนั้นโครงสร้าง P42/mmc นี้จึงมีความเป็นไปได้สูงที่จะเป็นโครงสร้างกึ่งเสถียรที่สภาวะความดันปกติด้วย ผลการคำนวณความแข็งแรงแบบวิกเกอร์และค่าช่องว่างแถบพลังงานคือ 60 จิกะปาสกาล และ 2.90 อิเล็กตรอนโวลต์ตามลำดับ ซึ่งการค้นพบนี้อาจกล่าวได้ว่าโครงสร้างแบบ P42/mmc อาจจะเป็นโครงสร้างที่มีสมบัติความแข็งแรงสูงมากพร้อมกับที่มีสมบัติเป็นสารกึ่งตัวนำ ซึ่งสามารถนำไปประยุกต์ใช้ในงานตัด และงานเจาะ หรือการเคลือบแข็ง และงานทางด้านเทคโนโลยีทางแสงได้ดี นอกจากนั้นแล้วเมื่อทำการเพิ่มความดันไปสูงถึง 300 จิกะปาสกาล พบว่าจะเกิดการเปลี่ยนแปลงโครงสร้างจากเดิมที่มีสมบัติความเป็นสารกึ่งตัวนำไปเป็นโลหะและมีสมมาตรเป็น P63/mmc ที่มีสมบัติเป็นโลหะที่ความดัน 134 จิกะปาสกาล และเป็นโครงสร้างที่มีสมบัติเป็นโลหะอีกโครงสร้างคือ Cmca ที่ความดันสูงกว่า 270 จิกะปาสกาล โดยเสถียรภาพของโครงสร้างทั้งสองนี้ได้รับการยืนยันจากการคำนวณทั้งเชิงพลวัตและเชิง

ผลการศึกษาในอาร์เซนิก (As)

อาร์เซนิกเป็นธาตุในหมู่ V ที่มีแนวโน้มการเปลี่ยนแปลงโครงสร้างไปเป็นโครงสร้างแบบโฮส เกส ในทำนองเดียวกับธาตุหมู่ V อื่นๆเช่น แอนทิโมนี และบิสมัท ทำให้เป็นที่น่าสนใจว่าโครงสร้างแบบโฮส เกสนี้น่าจะเป็นโครงสร้างที่ค้นพบธาตุโลหะหลายๆชนิดภายใต้ความดันสูง โดยอาร์เซนิกนั้นก็ที่สภาวะความดันสูง จะมีการเปลี่ยนแปลงโครงสร้างจากโครงสร้างแบบโฮส เกสไปเป็นโครงสร้างเป็นแบบบอดี้ เซ็นเตอร์คิวบิก ที่ความดัน 97 GPa ซึ่งทั้งสองโครงสร้างนี้เป็นโครงสร้างที่สนใจศึกษาในโครงการนี้ สาเหตุหลักเนื่องมาจากในธาตุโลหะใดหลายชนิดนั้นจะมีสมบัติทางไฟฟ้าที่เปลี่ยนแปลงไปมากเมื่อมีโครงสร้างแบบโฮส เกส เช่นมีสมบัติการเป็นตัวนำยิ่งยวดหรือมีอุณหภูมิวิกฤตที่สูงขึ้น

โลหะหลายชนิดมีแนวโน้มการเปลี่ยนแปลงไปเป็นตัวนำยิ่งยวดภายใต้ความดันสูงโดยมีอุณหภูมิวิกฤตสูงขึ้นซึ่งกลุ่มโลหะดังกล่าวได้แก่โลหะในหมู่ II-A เช่น Ca อุณหภูมิวิกฤต (T_c) 29 K ที่ความดัน 216 GPa และใน Sr กับ Ba มีการรายงานอุณหภูมิวิกฤต (T_c) เป็น 8 K ที่ความดัน 58 GPa และ 5 K ที่ 18

GPa ตามลำดับ นอกจากนี้แล้วธาตุในหมู่ III เช่น Y มีอุณหภูมิวิกฤตสูงถึง 20 K ที่ความดัน 115 GPa ส่วนในธาตุ Sc นั้นมีการตรวจพบอุณหภูมิวิกฤตที่ 19.8 K ภายใต้อุณหภูมิ 107 GPa สำหรับธาตุในหมู่ V นั้นพบว่า As มีอุณหภูมิวิกฤตสูงที่สุดคือ 2.7 K ที่ความดัน 24 GPa ส่วน Sb มีอุณหภูมิวิกฤต 3.6 K ที่ความดัน 3.5 GPa และใน Bi มีอุณหภูมิวิกฤตสูงที่สุดในหมู่นี้คือ 8.7 K ที่ความดัน 9 GPa

คณะผู้วิจัยได้ทำการศึกษาเชิงทฤษฎีของการเปลี่ยนแปลงโครงสร้างในธาตุแอตสไนทจากความดันปกติที่มีโครงสร้างแบบรอมโบฮีดรัล ไปสู่โครงสร้างแบบซิมเปิลคิวบิกที่ประมาณ 25 GPa จากนั้นเมื่อทำการเพิ่มความดันไปเรื่อยๆก็เกิดการเปลี่ยนแปลงโครงสร้างไปเป็นโครงสร้างแบบคิวบิก โซส เกส ที่ประมาณ 48 GPa และไปสู่โครงสร้างแบบซิมเปิลคิวบิกที่ประมาณ 97 GPa สำหรับในอาร์เซนิกนั้นสมบัติความเป็นตัวนำยิ่งยวดได้ถูกค้นพบที่โครงสร้างแบบโซส เกสและโครงสร้างแบบบอดีเซ็นเตอร์คิวบิก โดยจากการศึกษาอย่างละเอียดพบว่าโครงสร้างแบบโซส เกสเปลี่ยนแปลงไปเป็นโครงสร้างแบบบอดีเซ็นเตอร์คิวบิกที่ประมาณ 97 GPa และมีเสถียรภาพดีไปจนถึง 122 GPa ซึ่งการเปลี่ยนแปลงโครงสร้างนี้สืบเนื่องมาจากภายใต้ความดันสูงมีผลของ s-d hybridization

จากการทำนายโครงสร้างด้วยเทคนิค Ab initio random structure searching (AIRSS) คณะผู้วิจัยสามารถยืนยันได้ว่าโครงสร้างแบบโซส เกสและโครงสร้างแบบบอดีเซ็นเตอร์คิวบิกมีเสถียรภาพดี มีสมบัติทางกายภาพหลายประการคล้ายคลึงกัน และมีอุณหภูมิวิกฤต 4.2 K ที่ความดัน 150 GPa ผลการศึกษาวิจัยนี้เป็นการศึกษาเพื่อวางแผนการทำนายสมบัติการเป็นตัวนำยิ่งยวดโดยฟิสิกส์เชิงทฤษฎีอย่างเป็นระบบ และนำเสนอกลไกการเหนี่ยวนำให้เกิดเสถียรภาพของโครงสร้างแบบโซส เกส ซึ่งปัจจุบันผลงานวิจัยนี้ได้รับการตีพิมพ์ในวารสาร Scientific Report แล้วดังแสดงรายละเอียดในเอกสารแนบท้ายรายงานฉบับนี้

ผลการศึกษาในลิเทียม(Li) และลิเทียมเพอรอกไซด์ (Li_2O_2)

ลิเทียมจัดอยู่ในกลุ่มโลหะอัลคาไลน์ที่มีการเปลี่ยนวัฏภาคเชิงโครงสร้างภายใต้ความดันสูงที่หลากหลายมากเนื่องจากการเกิดการถ่ายโอนของอิเล็กตรอนจากชั้นอิเล็กตรอน (orbital) s ไปยังชั้น d รวมทั้งยังมีโครงสร้างที่ได้รับการค้นพบและเสนอว่าอาจจะมีเงื่อนไขในการมีเสถียรภาพที่อุณหภูมิและความดันต่างๆกัน แต่ยังไม่สามารถระบุสมมาตรที่ชัดเจนอีกเป็นจำนวนมาก งานวิจัยนี้ได้ทำการศึกษาการเปลี่ยนแปลงโครงสร้างโดยเทคนิค Ab initio random structure searching (AIRSS) และได้นำเสนอกลไกที่สำคัญที่ทำให้โครงสร้างแบบโซส เกส เป็นโครงสร้างที่เสถียรภายใต้ความดันสูงจากการศึกษาการกระจายตัวของอิเล็กตรอนโดยเทคนิค electron localization function (ELF) คณะนักวิจัยพบว่าการเกิดพันธะจาก p ที่มีการกระจุกตัวเฉพาะตำแหน่งมากขึ้น (Strongly localized p bond) สามารถอธิบายการมีเสถียรภาพที่ดีของโครงสร้างแบบโซส เกส ซึ่งการค้นพบดังกล่าวนี้ทำให้โครงสร้างแบบโซส เกสเป็นโครงสร้างภายใต้ความดันสูงที่ค้นพบในทุกธาตุในหมู่ IA

การศึกษาส่วนที่สองคือการศึกษาสารประกอบลิเทียมเปอร์ออกไซด์ซึ่งมีสมบัติเฉพาะที่โดดเด่นคือ ความจุออกซิเจนมากที่สุด (34.8 wt.%) สามารถเกิดปฏิกิริยากับคาร์บอนไดออกไซด์ภายใต้อุณหภูมิสูงกว่า 200 เซลเซียส ให้ผลิตภัณฑ์ 2 ชนิด คือ ลิเทียมคาร์บอเนต และออกซิเจน ซึ่งเป็นผลิตภัณฑ์ที่สามารถนำไปใช้ประโยชน์ได้ แต่เนื่องจากปฏิกิริยาดังกล่าวเกิดขึ้นที่อุณหภูมิสูง จึงต้องใช้ความร้อนในการกระตุ้นให้เกิดปฏิกิริยาทำให้สิ้นเปลืองพลังงาน จึงสนใจศึกษาผลของความดันต่อการดูดซับคาร์บอนไดออกไซด์ใน ลิเทียมเปอร์ออกไซด์ภายใต้ความดันสูง เนื่องจากการเพิ่มความดันให้กับคาร์บอนไดออกไซด์ส่งผลทำให้เพิ่มจำนวนครั้งในการชนระหว่างคาร์บอนไดออกไซด์กับลิเทียมเปอร์ออกไซด์ อาจทำให้เกิดปฏิกิริยาเคมีได้เช่นเดียวกับการเพิ่มอุณหภูมิ ในการทดลองโดยใช้เทคนิคการเลี้ยวเบนของรังสีเอกซ์ชนิดกระจายมุมและเทคนิคการวัดการกระเจิงแบบรามาน โดยใช้ไดมอนด์ แอนวิล เซลล์ เป็นอุปกรณ์เพิ่มความดัน และวัดความดันใช้เทคนิคการวัดการเลี้ยวเบนของความยาวคลื่นที่เกิดจากการฟลูออเรสเซนซ์ในผลึกของทับทิมเมื่อถูกกระตุ้นด้วยเลเซอร์ วิเคราะห์และปรับโครงสร้างด้วยวิธีการปรับตัวแปรโครงสร้างของริทเวลด และคำนวณด้วยทฤษฎีเชิงฟังก์ชันของความหนาแน่น (DFT) โดยใช้โปรแกรม VASP/CASTEP/Quantum Espresso ในการคำนวณเสถียรภาพของโครงสร้างที่ความดันต่าง ๆ ภายใต้อุณหภูมิต่ำ

ผลการ Optimized โครงสร้างของลิเทียมเปอร์ออกไซด์ ที่ความดันบรรยากาศและอุณหภูมิศูนย์องศาสัมบูรณ์ พบว่า ลิเทียมเปอร์ออกไซด์มีโครงสร้างของเซลล์หน่วยดังรูปที่ 1 โดยมีโครงสร้างแบบ Hexagonal มีหมู่สมมาตร P63/mmc มีแลตทิซพารามิเตอร์ $a=b=3.1850 \text{ \AA}$, $c=7.7170 \text{ \AA}$ ผลของความดันต่อการเปลี่ยนแปลงระยะห่างระหว่างอะตอมในเซลล์หน่วยของลิเทียมเปอร์ออกไซด์ ภายใต้ความดัน 0-70 GPa ที่อุณหภูมิศูนย์องศาสัมบูรณ์ พบว่า เมื่อความดันเพิ่มขึ้น ระยะห่างระหว่างอะตอมลดลงโมเลกุลของคาร์บอนไดออกไซด์สามารถผ่านเข้าเซลล์หน่วยของลิเทียมเปอร์ออกไซด์ได้ในช่องทางที่มีระยะห่างระหว่างอะตอมมากกว่า $3.4 \text{ \AA}$ เนื่องจากโมเลกุลของคาร์บอนไดออกไซด์เป็นแบบเส้นตรง มีความยาวประมาณ $3.4 \text{ \AA}$ ผลของความดันต่อการเปลี่ยนแปลงตำแหน่งอะตอมของออกซิเจนในเซลล์หน่วยของลิเทียมเปอร์ออกไซด์ภายใต้ความดันในช่วง 0-70 GPa พบว่า เมื่อเพิ่มความดันให้กับลิเทียมเปอร์ออกไซด์ ทำให้ตำแหน่งอะตอมของออกซิเจนในแนวแกน z มีการเปลี่ยนแปลงไปกับความดันทำให้ความยาวพันธะของออกซิเจนกับออกซิเจนลดลง ซึ่งอาจส่งผลต่อความสามารถในการเกิดปฏิกิริยาเคมีของลิเทียมเปอร์ออกไซด์

ผลการวิจัยทั้งสองส่วนนี้ได้รับการตีพิมพ์แล้วในวารสารสองฉบับคือ Scientific Report และ Physical Chemistry Chemical Physics ดังแสดงรายละเอียดในเอกสารแนบท้ายรายงานฉบับนี้

ผลการศึกษาใน Perovskite Materials

เพอร์อฟสไกต์เป็นวัสดุที่มีโครงสร้างสูตรทางเคมี ABX_3 โดยที่ A และ B เป็นตัวแทนของแคทไอออนและ X เป็นแอนไอออน โครงสร้างผลึกแบบอุดมคติของเพอร์อฟสไกต์คือโครงสร้างผลึกแบบลูกบาศก์ที่มี BX_6 ที่มี B เป็นศูนย์กลางรูปทรงแปดหน้าในแต่ละมุมและมี A ตั้งอยู่ที่กึ่งกลางของเซลล์ ในเพ

ออร์โอฟอสเฟตบ้างตัวอาจมีการเปลี่ยนจากโครงสร้างลูกบาศก์มาเป็นโครงสร้างที่มีสมมาตรต่ำกว่า เช่น โครงสร้างแบบเตตระโกนอล หรือออร์โธโรมบิกที่อุณหภูมิต่ำ งานวิจัยนี้ทำการศึกษาไฮบริดเพอโรฟสไกต์ อินทรีย์และอนินทรีย์ (Hybrid organic-inorganic perovskites, HOIPs) ซึ่งในตำแหน่งของ A จะถูกแทนที่ด้วย แคทไอออนจากสารอินทรีย์อย่างง่ายเช่นเมทิล แอมโมเนียมเป็นต้น เมื่อไม่นานมานี้ HOIPs ได้รับความสนใจ จากนักวิจัยอย่างเข้มข้นเนื่องจากการที่มีประสิทธิภาพสูง โดยมีค่าใช้จ่ายและราคาของส่วนประกอบในการ ผลิตค่อนข้างต่ำ โดยได้มีการนำ HOIPs ไปผลิตเป็นแผงเซลล์แสงอาทิตย์แล้วมีประสิทธิภาพ 20% ภายหลัง จากการค้นพบและการทำวิจัยอย่างเข้มข้นเพียงแค่ 5 ปี ในโครงการนี้จะมุ่งเน้นการศึกษาวิชาผลของความดัน ต่อโครงสร้างและการเปลี่ยนแปลงสมบัติเชิงกล และเชิงไฟฟ้า รวมทั้งประสิทธิภาพที่เปลี่ยนแปลงไปของ ไฮบริดเพอโรฟสไกต์อินทรีย์อนินทรีย์ที่มีเมทิลแอมโมเนียม (CH_3NH_3) เป็นไอออนบวกและตะกั่วไอโอ ไดด์ (PbI_2) เป็นโครงสร้างแบบกรงแปดด้านในโครงสร้างแบบลูกบาศก์ ซึ่งจากการวิจัยก่อนหน้านี้แสดงให้เห็นว่าส่วนอนินทรีย์ (PbI_2) นั้นมีบทบาทสำคัญในโครงสร้างทางอิเล็กทรอนิกส์ และระดับเฟอร์มิโดยที่ ระดับพลังงานของโมเลกุลอินทรีย์นั้นไม่มีผลกระทบโดยตรงกับวาลเลนซ์หรือกับแถบการนำ นอกจากนี้ยังมี รายงานที่แสดงให้เห็นอีกว่าทิศทางของการบิดไปของกึ่งกลางส่วนประกอบอินทรีย์นั้นส่งผลต่อโครงสร้าง ทางไฟฟ้าโดยรวมของวัสดุ

งานวิจัยนี้ประกอบด้วยสองส่วนทั้งการศึกษาเชิงการทดลองและการคำนวณที่ต่อเนื่องกัน ส่วนแรก จะทำการศึกษาลักษณะการแลกเปลี่ยนสัสมพันธ์ในการคำนวณเชิงทฤษฎีเพื่อความต้องการของการ คำนวณโครงสร้าง โดยความต้องการของการคำนวณที่จะใช้อ้างอิงต่อไปเพื่อเปรียบเทียบกับผลการทดลองนั้น จะเป็นวิเคราะห์โดยเปรียบเทียบผลงานวิจัยอื่นที่มีผู้ตีพิมพ์มาแล้วแต่มีความไม่สอดคล้องกันในหลายๆ ประเด็นซึ่งมีความขัดแย้งกับข้อมูลโครงสร้างผลึกจากการทดลอง ส่วนที่สองของการวิจัยจะเน้นบทบาท ของความดันที่ส่งผลต่อการเปลี่ยนแปลงโครงสร้างทั้งเชิงไฟฟ้าและโครงสร้างผลึก นอกจากนี้แล้วก็จะได้ ทำการศึกษาวัดพลังงานตระกูลโลหะไฮโดรด์โดยใช้เทคนิคทำนองเดียวกันด้วย

ผลการศึกษาวิชาเชิงทฤษฎีที่ผ่านมาของคณะผู้วิจัยพบว่างานวิจัยก่อนหน้านี้ส่วนมากมีปัญหาที่สำคัญ ที่ทำให้การทำนายเชิงทฤษฎีมีความไม่สอดคล้องกับผลการทดลองมากอย่างมีนัยสำคัญ เนื่องจากการ เลือกใช้ฟังก์ชันแนลที่ไม่เหมาะสม เนื่องจากในวัสดุไฮบริดนั้นการรวมผลของแวนเดอร์วาลส์จะมีผลมาก โดยเฉพาะอย่างยิ่งในการศึกษาเสถียรภาพของระบบที่มีพลวัตสูงของส่วนที่เป็นออกแกนิคส์ โดย ผลงานวิจัยนี้คณะผู้วิจัยคาดว่าจะสามารถผลิตผลงานเพื่อตีพิมพ์ได้สองฉบับ โดยฉบับแรกนั้นอยู่ระหว่างการ ปรับแก้ไขตามคำแนะนำของกรรมการผู้ทรงคุณวุฒิจาก Scientific Report และผลงานส่วนที่สองที่เน้นไปที่ โครงสร้างภายใต้ความดันสูงอยู่ระหว่างการเตรียมข้อมูลเพื่อเขียนบทความ

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บทความวิจัยที่ได้รับการตีพิมพ์



Pressure effects on hydrogen atoms near the metal plane in the HCP phase of rare-earth metal trihydrides

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ABSTRACT

Rare-earth metal trihydrides, REH₃ (RE=Sc, Y, La), in the hcp phase were investigated under high pressure by the *ab initio* method. We concentrated on the behavior of hydrogen atoms which is affected by pressure. Two-thirds of the hydrogen atoms near the metal plane (H_m) were found to displace away from the metal plane as pressure increases. The trajectory of these squeezed hydrogen atoms is from a site near the metal plane, and moves past the plane of the tetragonal sites, and heads toward the nearest octahedral site. However, the rate of displacement depends on the local environment. LaH₃ exhibits the least impediment on the H_m displacement while YH₃ and ScH₃ exhibit stronger impediment. Furthermore, our calculated Raman and IR active modes are in general agreement with the experimental data. The displacement of H_m can be used to explain the behavior of the O_ν peak in Raman spectra, where it exists at low pressure and disappears at higher pressure in YH₃ and ScH₃.

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1. Introduction

Rare-earth metal hydrides become more hydrogenated under high pressure, i.e. their hydrogen content increases up to six hydrogen atoms per metal atom [1]. At low pressure, these trihydride compounds appear to be in an hcp phase, except LaH₃ which is in an fcc phase [2,3]. The hcp phase transforms sluggishly through an intermediate phase to the fcc phase under high pressure [4–10]. Recently, it was pointed out that the transition pressures from the hcp phase to the intermediate phase decrease as the ionic radii of the rare-earth metals increase [10], as shown in Fig. 1. For illustration, the transition pressures (ionic radii [11]) of ScH₃, LuH₃, YH₃ and SmH₃ are 30 (88.5), 12 (100.1), 11 (104), and 2 (109.8) GPa (pm), respectively, whereas LaH₃, which has ionic radius as large as 117.2 pm, has no such phase transition. However, the transition pressures from the intermediate to the fcc phase do not follow this trend.

To accommodate the question of why the size of ionic radius is important, we need to look closer at the phase transition. First, we look for the possible structures of the hcp phase. According to recent calculations, there are three candidates, which are *P* $\overline{3}$ c1, *P*₆*3*cm and *P*₆*3* structures [12,13]. Along with the hexagonal packing of the metal

atoms, there are accompanying hydrogen atoms located at two distinguishable sites; near the metal plane (H_m) and near the tetrahedral site (H_t). Previous studies [14,15] showed that the bondings, electronic structures and symmetries can be distinguishable by the arrangements of the H_m atoms around the metal plane. ScH₃ is metallic, if all the H_m atoms are on the metal plane as in the *P*₆*3*/*mmc* structure. However, if the H_m atoms are appropriately distributed around the metal plane as in the *P*₆*3* structure, the band gap can be opened. The calculation of the *P*₆*3* band gap value is in good agreement with the value derived from the optical measurement [15–17]. In addition, the H_t atoms also arrange themselves correspondingly to the arrangement of the H_m atoms.

Under pressure, there are a few clues which suggest that the H_m atoms are squeezed out away from the metal plane. This is because in the metal plane which is a (001) plane, there are three metal atoms in the vicinity of an H_m atom. As pressure increases, the room in the vicinity of this H_m atom is reduced, or so-called squeezed, and these metal atoms exhibit stronger interaction with H_m. This is the reason why the ionic radii play an essential role under pressure. Kume et al. provided the first clue that the H_m atoms could be squeezed out of their low-pressure equilibrium locations near the metal plane and move toward the nearest octahedral site (O site), which has a larger room, at higher pressure [17,18].

Pakornchote et al. [19] have recently provided another clue. They have proposed a *Cm* structure for the intermediate phase of

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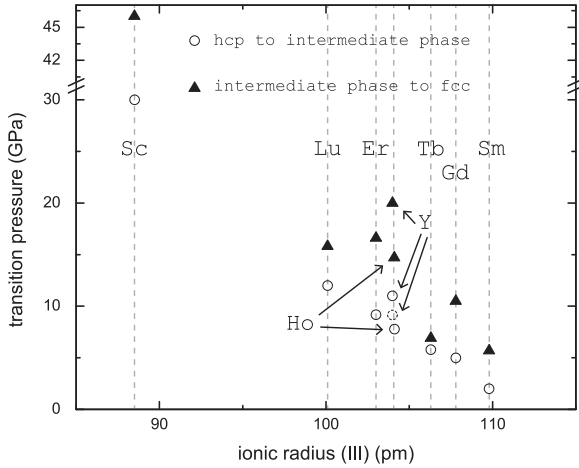


Fig. 1. The transition pressure with respect to the ionic radius of a metal atom.

ScH₃ and calculated the hcp to fcc transformation path using the *ab initio* method. This *Cm* structure reproduces all d-spacing derived from the x-ray diffraction (XRD). During the hcp to intermediate *Cm* to fcc transition under pressure, they also found that some H_m atoms are moving out of their equilibrium sites near the metal plane and heading toward the O site. It can be readily seen that the displacement of H_m atoms play an important role in the hcp to fcc phase transition. Thus, we aim to study the behavior of H_m in more detail.

It is worth mentioning here that there are some discrepancies in the determination of the intermediate phase. It was first proposed to be a long stacking structure [20]. However, theoretical studies show that the intermediate phase of YH₃, ErH₃ and HoH₃ is a *C2/m* structure [21,22]. In ScH₃, *C2/m* is not energetically favorable. Pakornchote et al. [19] proposed the *Cm* structure as mentioned earlier, but Ye et al. [16] discussed that the *Cm* and *C2/m* structures might be closely related.

The dynamical properties of ScH₃ and YH₃ have also been investigated. The neutron scattering experiment measured the phonon density of states (DOS), and Raman scattering measure Raman spectra under high pressure [17,23]. Pakornchote et al. [15] have calculated the phonon DOS and compared with the experimental data. Furthermore, they can identify the vibrational modes among the metal atoms and the hydrogen atoms. Kume et al. [18,17] performed Raman measurement and discussed the effects of the movement of the H_m atoms on broadening Raman peak. However, a more comprehensive explanation is required in order to fully understand the role of H_m in the hcp to fcc transition.

In this work, we perform the *ab initio* calculation of the hcp phase of ScH₃, YH₃ and LaH₃ under high pressure. We monitor the trajectories of the H_m atoms up to 100 GPa, which is beyond the hcp-fcc transition. This is to investigate the effect of the local environment along the trajectory of the H_m atoms. The role of H_m and their environment are established. Then, we calculate the phonon DOS and specify the corresponding eigenvectors, and also extract the Raman active modes. The calculation data is compared with available experimental data. The effect of H_m and their environment on the behavior of the phonon DOS and Raman peaks is discussed.

2. Method

The structural and dynamical properties of REH₃ have been investigated using CASTEP code which is based on the density functional theory [24–26]. The Perdew–Burke–Ernzerhof (PBE) functional

which is based on generalized gradient approximation (GGA) is used for the exchange–correlation function [27]. The unit cells are relaxed at every 5 GPa by Broyden–Fletcher–Goldfarb–Shanno (BFGS) optimization algorithm [28] with 24 atoms in a unit cell and the phonons are calculated by using the finite displacement method with 96 atoms. The “on-the-fly” pseudopotential based on Vanderbilt ultrasoft pseudopotential [29] is chosen to account for the effect of the core electron wave function under high pressure. For the accuracy of the calculation, the cut-off energy of 600 eV is used for phonon calculation and up to 800 eV is used for single-point energy calculation. The *k*-mesh interval is set to 0.02 Å^{−1} in Monkhorst-Pack scheme [30,31]. The hcp structure is chosen from several recent works. The most common candidates for ScH₃ and YH₃ are $P\bar{3}c1$, $P6_3cm$ and $P6_3$ structures [15,12,13].

3. Results and discussion

We perform the optimization of the hcp structures, i.e. $P\bar{3}c1$, $P6_3cm$ and $P6_3$, of ScH₃, YH₃ and LaH₃ at 0–100 GPa, and monitor the trajectories of the hydrogen atoms. We focus mostly on the displacement of the H_m atoms. The H_t atoms are in a larger cage of the tetrahedral site (T site) where each H_t atom is surrounded by four metal atoms, hence the H_t atom displaces only inside its cage. The squeezing has weaker effect on it.

As the chosen hcp structures have lower symmetry than $P6_3/mmc$, the H_m atoms can have as many as three variations, labeled as H_m¹, H_m² and H_m³ (see Fig. 2). For the $P\bar{3}c1$ and $P6_3cm$ structures, their H_m¹ and H_m² are at different locations but these locations are at the identical symmetry sites, so they are indeed indistinguishable (see Table 1). Their behaviors under pressure are the same. For the $P6_3$ structures, the three are all different (see Table 1). In Figs. 3 and 4(a), we plot the fractional coordinate (*fc*) in the *c*-axis of all three H_m atoms as a function of pressure.

Fig. 3 shows the results of ScH₃ with $P\bar{3}c1$, $P6_3cm$ and $P6_3$ structures. The H_m¹ atom of all three structures is located at 0.30*c* at 0 GPa, and moving up to 0.40*c*, which is on the same level as of H_t (dash-dot-dotted lines), at 60 GPa, and approaching to the level of the octahedral site at 0.50*c* at 100 GPa. The H_m² atom of $P\bar{3}c1$ and $P6_3cm$ is in the same symmetry site as its H_m¹, thus their behaviors are the same. The H_m³ atom of $P\bar{3}c1$ stays invariantly at 0.25*c*, exactly at the metal plane, at all pressures. The H_m³ atom of $P6_3cm$ and $P6_3$ is near 0.18*c* at 0 GPa, and displaces away from the *m* plane a little at pressure upto 50 GPa, and then move toward the *m* plane a little at pressure beyond 50 GPa. The H_m² atom of $P6_3$ is located at 0.26*c* at 0 GPa, and move up to 0.35*c* at 40 GPa. From this pressure onwards, the $P6_3$ structure becomes the $P6_3cm$ structure.

Fig. 3 exhibits a number of key features. First, at low pressure, the H_m¹ and H_m² atoms are squeezed out of the metal plane as the size of the room inside the equilateral triangle formed by three

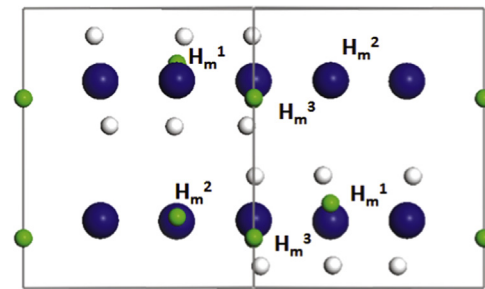


Fig. 2. (Color online) An illustration of positions of H_m¹, H_m² and H_m³ atoms on (110) plane in $P6_3$ structure when blue, white and green balls represent the metal, H_t and H_m atoms, respectively. The horizontal and vertical directions are [001] and [1 $\bar{1}$ 0] directions, respectively. It is worth noting that the H_m³ atom has disappeared from view because it is located behind the metal atom.

Table 1

The symmetry site of H_m^1 , H_m^2 and H_m^3 in each structure. The braces group the H_m^1 and H_m^2 atoms of $P\bar{3}c1$ and $P6_3cm$ structures with the same symmetry site, and thus indistinguishable. While the H_m^1 and H_m^2 atoms of $P6_3$ structure are not at the same symmetry site and, thus distinguishable.

space group	site
$P\bar{3}c1$	H_m^1
	H_m^2
	H_m^3
$P6_3cm$	H_m^1
	H_m^2
	H_m^3
$P6_3$	H_m^1
	H_m^2
	H_m^3

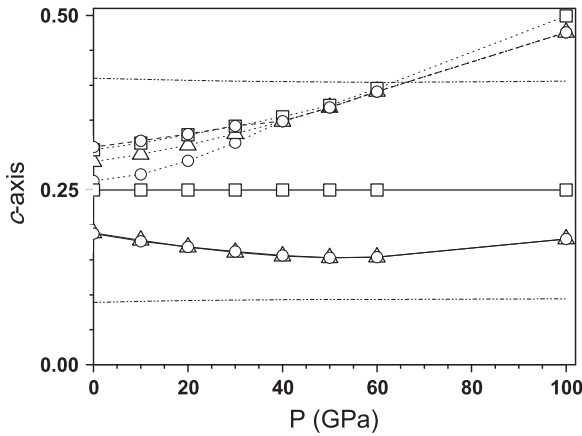


Fig. 3. The fractional coordinate in the c -axis of H_m with respect to pressure. They are separated into three symmetry sites; H_m^1 (dotted line), H_m^2 (dashed line) and H_m^3 (solid line). The symbols represent the $P\bar{3}c1$ (square), $P6_3cm$ (triangle) and $P6_3$ (circle) structures of ScH_3 . The levels of H_i atoms are represented by dash-dot-dotted lines, and the levels of metal plane and octahedral sites are at $0.25c$ and $0.5c$, respectively.

metal atoms surrounding H_m is reduced. This squeezing effect is much weaker for the H_m^3 atom as it does not displace at all in $P\bar{3}c1$, and displaces only a little in $P6_3cm$ and $P6_3$. Second, at higher pressure, the local environment also plays an important role. It can be easily seen that the squeezing effect cannot shoot H_m^1 and H_m^2 to the O site immediately. We found that it takes as high as 100 GPa in the ScH_3 case to complete the action. Thus the local environment rather impedes the displacement of H_m^1 and H_m^2 . This impediment depends on the type of the metal. This is shown in Fig. 4(a) where the fc in the c -axis of all three H_m atoms in $P6_3$ of ScH_3 , YH_3 and LaH_3 is compared between 0 and 100 GPa. In the $P6_3$ structure, the impediment is weakest in LaH_3 as it takes only 10 GPa to complete the action, and stronger in YH_3 (60 GPa), and strongest in ScH_3 (100 GPa). Fig. 4(b) shows the nearest atomic distance between the metal and hydrogen atoms. It can be readily seen that the atomic distance seems to slightly change under pressure, despite large changes in the displacement of H_m . This shows that the hydrogen atom avoids getting too close to the metal atom, even at pressure as large as 100 GPa.

The displacement of H_m plays an important role in the hcp to fcc transition as well. Pakornchote et al. [19] derived the transformation path from the experimental data. They found that the phase transition occurs via a sliding movement of the hcp basal plane of the metal atoms, and the hydrogen atoms have to move accordingly. In general, the hydrogen atoms move from their symmetry sites in the hcp phase to their new nearest symmetry sites in the fcc phase. In the fcc structure, there are a number of octahedral sites similar to those of the hcp structure. However, in the case of ScH_3 , half the number of the O sites in the fcc are originated from the O sites of the hcp. We shall call these O sites as the permanent O sites. Another half the number of the O sites form only when the transformation is about to complete. Pakornchote et al. [19] showed that some of H_m move from the sites near m plane to the permanent O sites, instead of the nearest T sites of the fcc. They called this behavior as site switching. From our calculation, it is obvious that the local impediment of H_m also have an effect on this site switching behavior as well. This means that site switching cannot occur easily. This would explain why the phase transition is so sluggish.

Next, we calculated the phonon frequencies of ScH_3 and YH_3 using the finite displacement method with 96 atoms in a supercell. We found that the $P6_3$ structures of ScH_3 and YH_3 are dynamically stable at 0 and 10 GPa. Fig. 5 shows the phonon DOS of (a) ScH_3 and (b) YH_3 .

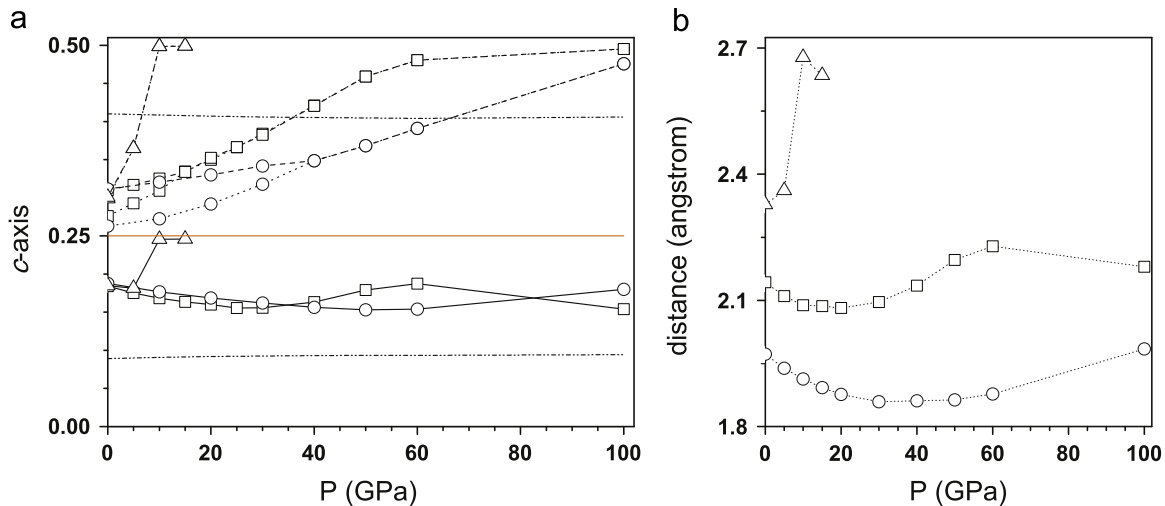


Fig. 4. (Color online) (a) The fractional coordinate in the c -axis of H_m atoms of ScH_3 , YH_3 and LaH_3 with respect to pressure which is separated into three symmetry sites; H_m^1 (dotted line), H_m^2 (dashed line) and H_m^3 (solid line). The orange line and dash-dot-dotted lines are levels of the metal plane and H_i atoms, respectively. (b) The nearest neighbor distances between H_m and metal atoms with respect to pressure. The symbols represent ScH_3 (circle), YH_3 (square) and LaH_3 (triangle).

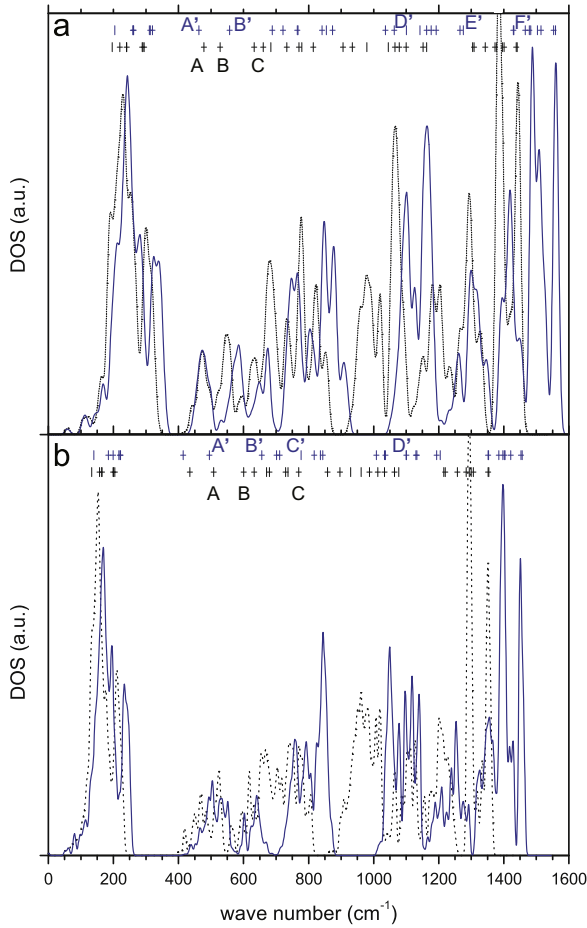


Fig. 5. (Color online) The phonon DOS of (a) ScH_3 and (b) YH_3 at 0 GPa (black) and 10 GPa (blue). The integration is over the Brillouin zone. The Raman and IR active modes at a gamma point ($k=0$) are marked by vertical and horizontal bars, respectively, above each figure (black bars for 0 GPa and blue bars for 10 GPa). A–C are Raman/IR active modes at 0 GPa. A'–F' are Raman/IR active modes at 10 GPa.

which are integrated from the phonon frequencies over the Brillouin zone. The phonon frequencies can be divided into 2 regions: at 0–400 cm^{-1} are the vibrational modes of metal atoms and at 400–1600 cm^{-1} are the vibrational modes of H_t and H_m atoms. The details of H_t and H_m modes can be seen elsewhere [13,15]. The high pressure does not change the peak profiles of Sc and Y modes but slightly shifts them to higher frequencies. The H_t and H_m modes are most effected by high pressure as well as Raman and IR active modes [13,15].

Furthermore, the Raman active modes, marked by vertical bars, and infrared (IR) active modes, marked by horizontal bars in Fig. 5, are extracted using group theory at a gamma point ($k=0$). The numerical values of Raman and IR modes are listed in Table 2 for ScH_3 and Table 3 for YH_3 , and compared with the peak values of Raman and IR spectra from experiments. For the active modes that can be directly compared with the experiment, we assign the letters A–F for each active mode in the ascending order of the frequencies. The unprime symbols are for the active modes at 0 GPa, and the prime symbols are for the active modes at higher pressure, which is normally 10 GPa unless otherwise stated.

In ScH_3 case, we are certain that $P6_3$ is the strongest candidate [19]. In YH_3 case, we give the numerical values in $P\bar{3}c1$ and $P6_3cm$ for comparison as well. This is because there are some discrepancies in the structure determination in the literature [13]. However, the $P6_3cm$ structure of YH_3 contains some unstable modes, i.e. imaginary frequencies, at 0 GPa, but it becomes stable at 10 GPa.

Table 2

Raman and IR active modes (cm^{-1}) of ScH_3 under high pressure compared with the experimental data.

	$P6_3$	Raman [17]	IR [17]
A	478	481	
A'	463	469	
A*		498	
A'*		514	
B	528	553	
B'	558	574	
C	633	649	
C'*		668	
D'	1064		1064
E'	1265		1243
F'	1466		1464

Table 3

Raman active modes (cm^{-1}) of YH_3 under high pressure compared to the experiment.

	$P\bar{3}c1$	$P6_3cm$	$P6_3$	Raman [18]
A		504	507	487
A'		485	495	451
A*				556
B	593	609	600	573
B'	631	658	656	645
C	775	776	769	783
C'	843	848	844	844
D'	1092,1097	1100	1100	1094

For ScH_3 , Raman active modes are between 450 and 700 cm^{-1} . At 0 GPa, we label the first two modes by A and B modes. The A mode is dominated by the c -polarization of the H_m^1 or H_m^2 atom and the ab -polarization of the H_t atom, while the B mode is dominated by the c -polarization of the H_m^3 atom and the ab -polarization of the H_t atom. As the pressure increases to 10 GPa, these two peaks evolve to A' and B' modes. We found that A' mode is softer than A mode. This is because the H_m^1 and H_m^2 are squeezed out of the metal plane, and the interaction among them is weakened a little. It can be deduced that A' mode will be disappearing eventually as $\text{H}_m^{1,2}$ move toward the O sites. On the other hand, B' mode is harder than B mode. This is a natural response of most vibrational modes under high pressure, and the H_m^3 atom displaces only a little around its equilibrium between 0 and 10 GPa. These A (A') and B (B') modes are in good agreement with the Raman experiment at 0 GPa (8.3 GPa) [17], as shown in Table 2. However, the experimental spectra exhibit the A* and A'* modes which cannot be matched with our calculation. The next calculated active mode is labeled as the C mode. This mode contains a frequency of 633 cm^{-1} at 0 GPa. At 10 GPa, the C' mode disappears. The Raman measurement shows a different behavior. The peak at 649 cm^{-1} appears at 0 GPa, and becomes the peak at 668 cm^{-1} at 8.3 GPa, but this high pressure peak is very broad and contains large uncertainty [17].

Moreover, Kume et al. performed IR spectroscopy of ScH_3 under pressure [17]. The IR peaks are between 600 and 1800 cm^{-1} . Thus, we compare our calculation at 10 GPa with the IR peaks at 9.9 GPa, as shown in Table 2. The IR active modes at 1064, 1265 and 1466 cm^{-1} from our calculation are labeled as D', E', and F', respectively. These active modes can be matched with 1064, 1243 and 1464 cm^{-1} peaks from experiment. The D', E', and F' modes come from the abc -polarization of the H_t atoms, the c -polarization of H_t atoms, and the ab -polarization of the H_m atoms, respectively.

For YH_3 , the Raman peaks are between 400–800 cm^{-1} . Under high pressure, there is an additional peak at 1000 cm^{-1} [18]. Table 3 shows the comparison between the experimental data [18]

and the numerical values from the three possible structures. Again, the unprime symbols are for the peaks at 0 GPa, and the prime symbols are for the peaks at higher pressure, which is normally 10 GPa unless otherwise stated.

It can be seen from Table 3 that the Raman modes of the $P6_3cm$ and $P6_3$ structures are generally in excellent agreement with the experiment. A mode is soft and evolve to A' mode at 10 GPa, similar to that of ScH_3 . The other modes are getting harder. We cannot find any modes that are related to the A mode in the $P\bar{3}c1$ structure. This would make $P\bar{3}c1$ least favorable. Furthermore, the experiment peak at 556 cm^{-1} has no match in all three structures.

From Raman and IR spectra, we can see the essence of the H_m atoms. Kume et al. have recently discovered that the O_v mode becomes more dispersive as the pressure increases [17]. They suggested that this is the effect of the displacement of the H_m atoms. At sufficiently high pressure, the O_v mode disappears. This is consistent with our finding where the $H_m^{1,2}$ atoms gradually displace away from the metal plane and move toward the O site under pressure. The O_v peak exists as long as the H_m atoms are in the vicinity of the metal plane. The peak is also very broad relative to other experimental peaks. This broadening effect could come from the strong coupling of the H_m atoms to the H_t atoms, as pointed previously out by Pakornchote et al. [15].

Acknowledgments

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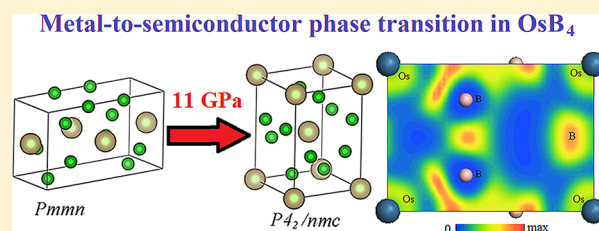
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Superhard Semiconducting Phase of Osmium Tetraboride Stabilizing at 11 GPa

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S Supporting Information

ABSTRACT: Employing a systematic first-principles investigation with crystal structure searching based on an evolutionary algorithm, we have uncovered the novel phase ($P4_2/nmc$) of OsB_4 with a novel superhardness and semiconducting state. In this investigation, metal-to-semiconductor phase transition is predicted at only a few gigapascals above ambient pressure, i.e., 11 GPa. As a result, the $P4_2/nmc$ phase should potentially become a metastable phase at ambient pressure. The Vickers (polycrystalline) hardness and the band gap of the semiconducting phase are calculated to be 60 GPa and 2.90 eV, respectively. These findings indicate that the $P4_2/nmc$ phase might be a promising superhard-semiconducting material which could be used in cutting and drilling tools, material coating, and other advanced optical technologies. Moreover, under further compression up to 300 GPa, the semiconducting phase transforms into a metallic $P6_3/mmc$ phase at 134 GPa, and then another predicted metallic phase with a $Cmca$ symmetry emerges beyond 270 GPa. Both dynamic and elastic stabilities are fully investigated to ensure the existence of the predicted phases.



INTRODUCTION

Osmium (Os), at ambient pressure, is a metallic element that exhibits large incompressibility and has the highest cohesive energy among the known elements.¹ Dubrovinsky et al. have compressed Os up to 770 GPa, but it retains a hexagonal close-packed structure (*hcp*) up to the highest recorded compression.² Despite having very low compressibility with bulk modulus in the range of 395–462 GPa,^{3–5} Os holds a low Vickers hardness (H_V) of only 4 GPa^{3,6,7} due to an intrinsic behavior of nondirectional metallic bonding. Incorporating light atoms such as boron (B) into the metallic osmium has been investigated in order to enhance its hardness value. A number of studies on OsB_2 have indicated a hardness of 21–37 GPa^{8,9} and bulk modulus of 297–395 GPa.^{9,10} While its hardness could be increased due to strong and directional covalent bonds of both networking boron atoms and Os–B interaction,¹² it does not exceed the threshold of superhard material ($H_V \geq 40$ GPa). An approach to enhance the hardness of transition-metal boride compounds (TM–B) is to increase the number of boron atoms in the unit cell. The formation of a three-dimensional (3D) boron-rich network, which carries a large degree of directional covalent bonding, could significantly contribute to the hardness and compressibility of TM–B materials.

Recent studies on TMB_4 's have reported some potential candidates for superhard materials. As reported by experiments, WB_4 , a promising incompressible and superhard material, has a hardness of 43.3 GPa and bulk modulus of 339 GPa.^{13,14} Niu et al. theoretically proposed that CrB_4 exhibits a superhard material with a hardness of 48 GPa.¹¹ Kolmogorov et al. predicted that the novel phase of FeB_4 is an orthorhombic structure (e.g., $Pnnm$),¹⁵ and Gou et al. synthesized this phase and measured its microhardness and bulk modulus as 43 and 252 GPa, respectively.¹⁶ Intriguingly, recent works have also predicted high pressure phases of FeB_4 . A metal-to-semiconductor phase transition with a transition pressure of 48–55 GPa has been predicted in this material, and the predicted semiconducting phases have $I4_1/acd$ and $P4_2/nmc$ symmetries.^{17–19} The superconducting temperature of the ambient phase of FeB_4 was reported at around 2.9 K by both theoretical and experimental studies.^{16,17} For OsB_4 , this material has been predicted at ambient pressure as a hard metallic $Pmmn$ phase with a hardness of 28 GPa²⁰ and suggested to have a high-pressure phase with MoB_4 -type structure ($P6_3/mmc$) at 33.7

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GPa.²¹ However, the previous theoretical high-pressure study of OsB₄ was limited to a few selected structures from the literature. Therefore, the present study aims at theoretically investigating the high-pressure behaviors of OsB₄ up to 300 GPa. To search the high-pressure phases of OsB₄ by using an unbiased method based on an evolutionary algorithm, one should guide the high-pressure behaviors and propose possible applications of OsB₄.

COMPUTATIONAL METHODS

To investigate the higher pressure phase transitions of OsB₄, the evolutionary algorithm within the USPEX code^{22,23} with an interface to the VASP code^{24,25} was used to search for minima enthalpy phases. The searches were performed by varying cell size up to 8 formula units per cell (fu/cell) and operated at 0, 25, 50, 75, 100, 150, 200, and 300 GPa. Further details of these searches as well as other candidate phases from previous searches of other TMB₄s can be found in the Supporting Information.²⁶ Other candidate phases were also chosen from previous searches of other TMB₄s as listed in the Supporting Information.²⁶ The CASTEP code²⁷ with the generalized gradient approximation functional (GGA-PBE)²⁸ and ultrasoft pseudopotential with the electronic configurations of Os, 5s²5p⁶5d⁶6s², and B, 2s²2p¹, was used for the full optimization of all selected phases. The cutoff energy of 600 eV and dense k-point meshes (spacing between k-points of $0.03 \times 2\pi \text{ \AA}^{-1}$) were verified for all calculations to ensure the energy convergence of 1 meV/fu. The Birch–Murnaghan equation of state (BM-EOS)²⁹ was used to fit the energy–volume curves to determine the thermodynamic stability phases at pressure ranges within 0–300 GPa. The elastic constants were calculated to evaluate the mechanical stability according to Born criteria.³⁰ Bulk modulus (*B*), shear modulus (*G*), and Young modulus (*E*) were estimated by using the Voigt–Reuss–Hill approximation,³¹ and Vickers hardness (*H_V*) was estimated by using the empirical model of Chen et al.³² Phonon dispersion based on supercell and finite displacement approaches as used in Phonopy code³³ was performed to confirm the dynamic stability.

RESULTS AND DISCUSSION

In analyzing the structural prediction determined by using USPEX, we found that the candidate structures consist of *Pmmn*, *P4₂/nmc*, *P6₃/mmc*, *Cmca*, *Cmcm*, *R3m*, and *R3m*. All predicted and selected structures of other TMB₄s²⁶ are fully optimized up to 300 GPa. By including spin-polarization, all structures do not exhibit a magnetic phase. The crystal structures of all candidates are presented in Table S1.²⁶ Figure 1 shows the relationship between energy and volume (*E*–*V* curve) of some selected structures. It indicates that the *Pmmn* structure is the most stable structure at ambient pressure, as previously predicted by Zhang et al.²⁰ For high-pressure phases, the two tetragonal structures, *P4₂/nmc* and *I4₁/acd*, also emerge in OsB₄, as is similar to FeB₄. In contrast to FeB₄, *P4₂/nmc* is more favorable than *I4₁/acd* as shown in the inset of Figure 1. Additionally, it is found that the structures of *P6₃/mmc* and *Cmca* energetically prefer to be the high-pressure phases of OsB₄ under further compression up to 300 GPa.

Figure 2 demonstrates the relative enthalpy and pressure of those phases. The predicted transformation pathway of OsB₄ within 300 GPa is *Pmmn* → *P4₂/nmc* → *P6₃/mmc* → *Cmca* with transition pressures of 11, 134, and 270 GPa, respectively.

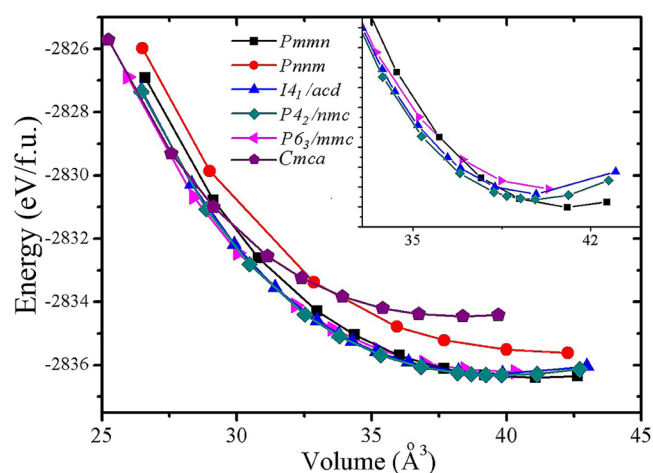


Figure 1. Energy–volume curves of some selected structures with the individual lowest volume corresponding to pressure of 300 GPa. The inset illustrates the *E*–*V* curves of *Pmmn*, *P4₂/nmc*, *I4₁/acd*, and *P6₃/mmc* to magnify energy differences.

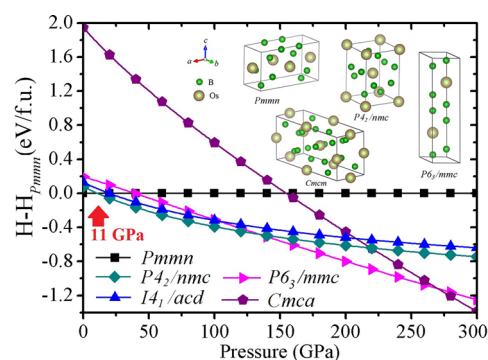


Figure 2. Relative enthalpy of *Pmmn*, *P4₂/nmc*, *I4₁/acd*, *P6₃/mmc*, and *Cmca* phases as a function of pressure (referenced to *Pmmn* structure). The crystal structures with atomic configurations of the predicted phases are given in the inset.

It is important to point out that the *Pmmn* → *P4₂/nmc* phase transition occurs at the lowest pressure among the TMB₄ group both in predictions and experiments. The enthalpy difference of *Pmmn* and *P4₂/nmc* phases at zero pressure is about 15.7 meV/atom corresponding to a temperature of 182 K, indicating that the *P4₂/nmc* phase might be energetically stable at ambient temperature as well. Moreover, Wang et al.²¹ investigated the possible reactive routes of the *Pmmn* phase of OsB₄ at high pressure. They found that the *Pmmn* phase possesses negative formation enthalpy when compared to the Os–B solid system, but the *Pmmn*–OsB₂ could be initially formed because it has much lower formation enthalpy than others. However, a possible reactive route of the *Pmmn* phase of OsB₄ was reported to be the route of OsB + α -B (rhombohedral) at pressure exceeding 25 GPa. Therefore, it is reasonable to claim that the *P4₂/nmc* phase should be initially obtained before the *Pmmn* phase along the same route reported in a previous study.²¹

The inset of Figure 2 displays the crystal structures of four calculated phases. The *Pmmn* phase has OsB₁₀ dodecahedron and B–Os–B sandwiches stacking order along the *a*-axis; more details are provided in ref 20. For the *P4₂/nmc* phase, there are two sets of B atoms (consisting of 4 and 8 for B¹ and B², respectively) that form as a 3D B₁₂ network surrounding a

centering Os atom, as shown in the inset of Figure S1.²⁶ The $P6_3/mmc$ phase is in a MoB_4 -type structure in which the Mo atoms are packed in a hcp structure with the networks of B atoms as presented in the previous study.³⁴ The $Cmca$ phase is composed of the ABAB stacks of Os, which are inserted between the double layer of borons, as presented in Figure S2.²⁶

The lattice constants of the predicted phases and the fitting parameters using BM-EOS are listed in Table 1. By considering

Table 1. Lattice Constants and the Fitting Parameters Consisting of Volume (V_0), Bulk Modulus (B_0), and Pressure Derivative of Bulk Modulus (B'_0) at Zero Pressure of the $Pmmn$, $P4_2/nmc$, $P6_3/mmc$, and $Cmca$ Phases

phase	lattice constants (Å)			V_0 (Å ³ /fu)	B_0 (GPa)	B'_0
	a	b	c			
$Pmmn$	7.106	2.886	4.006	41.06	296	3.95
$P4_2/nmc$	3.837		5.409	39.82	331	3.92
$P6_3/mmc$	2.955		10.671	40.30	284	3.99
$Cmca$	3.451	9.847	4.517	38.31	328	3.78

the high bulk moduli of the predicted phases, we found that they reflect the incompressible behavior of them. It is possible that the $P4_2/nmc$ phase is favorable at a wide range of pressures. The fractional lattice constants of the $P4_2/nmc$ phase under compression are presented in Figure S1.²⁶ There is a small anisotropy in the compressibility of the $P4_2/nmc$ phase under increasing pressure. By considering only Os atoms within the $P4_2/nmc$ phase, we discovered that their positions display a body-centered tetragonal structure having $c/a = 1.410$ within calculated pressures. This c/a is very close to the ideal value of the face-centered cubic ($c/a = \sqrt{2}$) (i.e., a close packed structure). This result suggests that the intrinsic atomic positions and crystal structure of the $P4_2/nmc$ phase play an important role in its low compressibility and low anisotropy. As shown in Table 2, this low anisotropic compressibility also corresponds to the high Young modulus of this phase (around 313 GPa at ambient pressure).

The elastic constants C_{ij} of the $Pmmn$, $P4_2/nmc$, $P6_3/mmc$, and $Cmca$ phases at stable pressures are shown in Table 2. These constants can be used to indicate the elastic stability and mechanical properties of solids. By using Born criteria,³⁰ the sufficient conditions of each crystal system were listed in the recent literature.³⁵ We found that all phases are elastically stable under the respective Born criteria at all calculated pressures. The main diagonal components of C_{11} , C_{22} , C_{33} , and C_{44} of the $P4_2/nmc$ phase at 0 GPa are highest compared to those of the others, indicating that the $P4_2/nmc$ phase probably is the

hardest phase in OsB_4 . B , G , and E values are also listed in Table 2. The $Pmmn$ phase at 0 GPa shows $B = 293$ GPa, $G = 217$ GPa, and $E = 521$ GPa, which are consistent with the values found in a previous study.²⁰ G and E values of the $P4_2/nmc$ phase are highest, indicating that this is the stiffest phase. The H_V values of the proposed phases are also reported in Table 2. The H_V of the $Pmmn$ phase at 0 GPa is around 30 GPa, which is in agreement with the reported values of Zhang et al. of 28.0 GPa²⁰ and Wang et al. of 31.3 GPa.²¹

Surprisingly, the calculated H_V of the $P4_2/nmc$ phase at ambient pressure is 60 GPa. Note that until now there have been no experimental techniques capable of measuring the hardness of materials under high pressure. Nevertheless, it might be useful to provide this information for guiding the use of a given material under high pressure. Therefore, the H_V of the $P4_2/nmc$ phase at 100 GPa is estimated to be 41 GPa, indicating that it still exhibits a superhard material at high pressure as well. At ambient pressure, the H_V of the $P4_2/nmc$ phase is extremely high compared to the calculated H_V of OsB_2 (37 GPa),⁸ ReB_2 (48 GPa),³⁶ and other TMB_4 's such as FeB_4 (~24 GPa),¹⁶ CrB_4 (~48 GPa),¹¹ and WB_4 (~43 GPa).¹⁴ However, the empirical model is obtained from the corresponding polycrystalline hardness, which is the average hardness of all crystal directions. Recently, stress response calculations (SRCs), which bring insight into the deformation behavior of a certain direction of a single crystal, were proposed. Several studies revealed that SRC give lower hardness compared to those of the empirical model, such as in the case of CrB_4 (~27 GPa)³⁷ and FeB_4 (~17 GPa).³⁸ Even though the SRCs are not presented in this study, in comparison with CrB_4 and FeB_4 , the H_V of the $P4_2/nmc$ phase is estimated to be around 35–45 GPa. On the basis of the tendency of increasing hardness with increasing shear modulus, it obviously indicates that the H_V of the $P4_2/nmc$ phase ($G = 313$ GPa) of OsB_4 must be higher than that of the $Pmmn$ phase of CrB_4 ($G = 261$ GPa) and FeB_4 ($G = 177$ GPa).¹¹

The B/G ratio of 1.75 is the critical value for indicating whether a given material is brittle (lower) or ductile (higher).³⁹ It is found that the $Pmmn$ and $P4_2/nmc$ phases are brittle, which is a result of the 3D boron network structure or covalent bonded solid. On the other hand, the $P6_3/mmc$ and the $Cmca$ phases are ductile, which is a result of the layered boron structure or metallic solid.

The phonon dispersions of the predicted phases show that all phases are dynamically stable at individual pressure ranges as shown in Figure 3a–d. This confirms that all calculated phases would exist because they are not only dynamically stable as proven by phonon dispersion but also elastically stable, as discussed previously. Moreover, as the $P4_2/nmc$ phase is

Table 2. Calculated Elastic Constants (C_{ij}), Bulk Modulus (B), Shear Modulus (G), Young Modulus (E), B/G Ratio, and the Vickers Hardness (H_V) of the Calculated Phases at Various Pressure

phase	P (GPa)	elastic constants (GPa)									moduli and hardness (GPa)				
		C_{11}	C_{12}	C_{13}	C_{23}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	B	G	E	B/G	H_V
$Pmmn$	0	613	124	248	55	572	630	152	340	180	293	217	521	1.35	30
	15	710	164	310	85	671	735	166	387	195	355	240	589	1.48	
$P4_2/nmc$	0	805	66	66			615	388		181	289	313	690	0.92	60
	15	932	108	108			703	426		188	354	340	773	1.04	
	100	1459	300	300			1115	574		194	643	438	1071	1.47	
$P6_3/mmc$	150	1272	538	497			1890	382			823	411	1058	2.00	
$Cmca$	300	2071	823	1043	904	2047	1899	619	648	667	1284	597	1551	2.15	

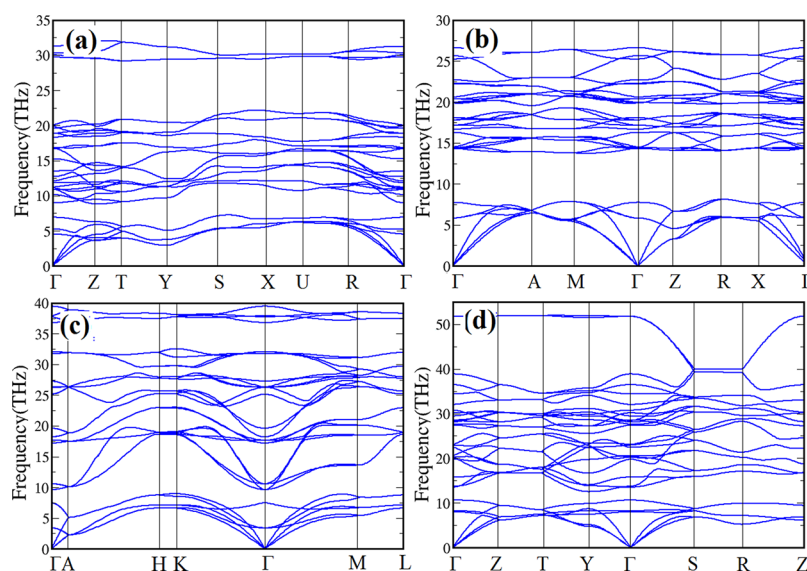


Figure 3. Phonon dispersion of (a) *Pmmn* phase at 0 GPa, (b) *P4₂/nmc* phase at 15 GPa, (c) *P6₃/mmc* phase at 150 GPa, and (d) *Cmca* phase at 300 GPa.

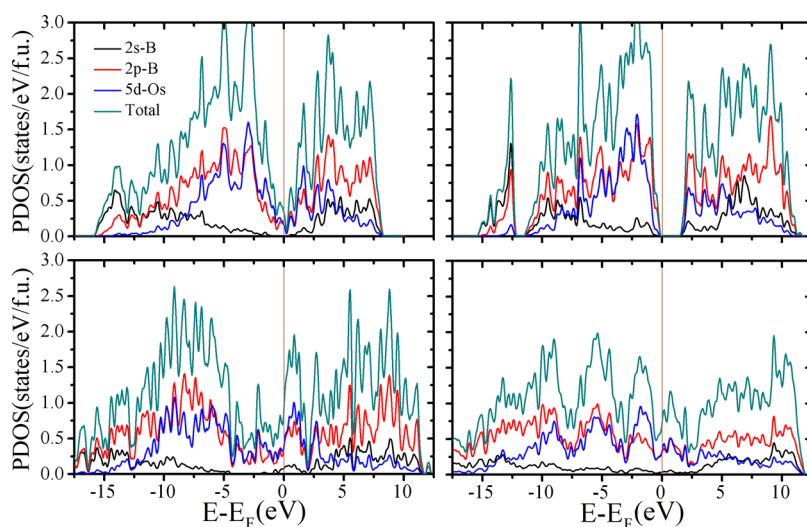


Figure 4. Partial density of state (PDOS) of (a) *Pmmn* phase at 0 GPa, (b) *P4₂/nmc* phase at 15 GPa, (c) *P6₃/mmc* phase at 150 GPa, and (d) *Cmca* phase at 300 GPa.

dynamically stable at ambient pressure (Figure S3²⁶), it is important to re-emphasize that this superhard phase would be a metastable phase at ambient pressure.

To elucidate the phase transitions in OsB₄ and incompressible and superhard behaviors of the *P4₂/nmc* phase, Mulliken population analysis (MPA), electronic band structure, and density of state (DOS) are calculated and analyzed. From the MPA at 0 GPa of the *Pmmn* and the *P4₂/nmc* phases, approximately 1.1e of the 2s-B state is promoted to an unfilled 2p-B state, and net electrons of 2s-B and 2p-B states are 0.9e and 2.3e, respectively. This finding implies the possibility of the formation of sp² or sp³ hybridization in B, which are consistent with orbital hybridizations of carbon in the form of graphite or diamond phases, respectively. Moreover, the MPA also reveals that most electrons in 6s² of Os transfer to 5d-Os by 0.6e and to 3p-B by 0.2e per atom, resulting in net charges of +0.80e in Os. Less charge transfer, i.e., lower than approximately 1.0e, might occur due to the slight differentiation in the electronegativity of Os and B (2.20 for Os and 2.04 for B). This

analysis reveals that the electronic density of states (DOS) at around the Fermi level are mainly contributed by 5d-Os, 2s-B, and 2p-B as shown in Figure 4. The DOS of the *Pmmn* phase at 0 GPa (Figure 4a) displays a pseudogap due to the separation of bonding and antibonding states at Fermi energy. The mixing of the 5d-Fe and 2p-B states is responsible for the valence band maximum, and the mixing of the s- and p-B state is formed by the energy between −17.5 and −5.0 eV.

Intriguingly, Figure 4b shows that the PDOS of the *P4₂/nmc* phase at 15 GPa has a semiconducting feature similar to those of the *P4₂/nmc* and *I4₁/acd* phases predicted in FeB₄.^{17,18} According to Figure 5a, the band structure displays an indirect band gap in which the valence band maximum (VBM) and conduction band minimum (CBM) are at different wave vectors. The band gap of the *P4₂/nmc* phase at 15 GPa is 2.02 and 2.90 eV, as calculated by using GGA-PBE and the hybrid functional of HSE06,⁴⁰ respectively. In Figure 5b, the band gaps obtained by both functionals are almost constant within small variations of 4% under increasing pressure up to 150 GPa. The

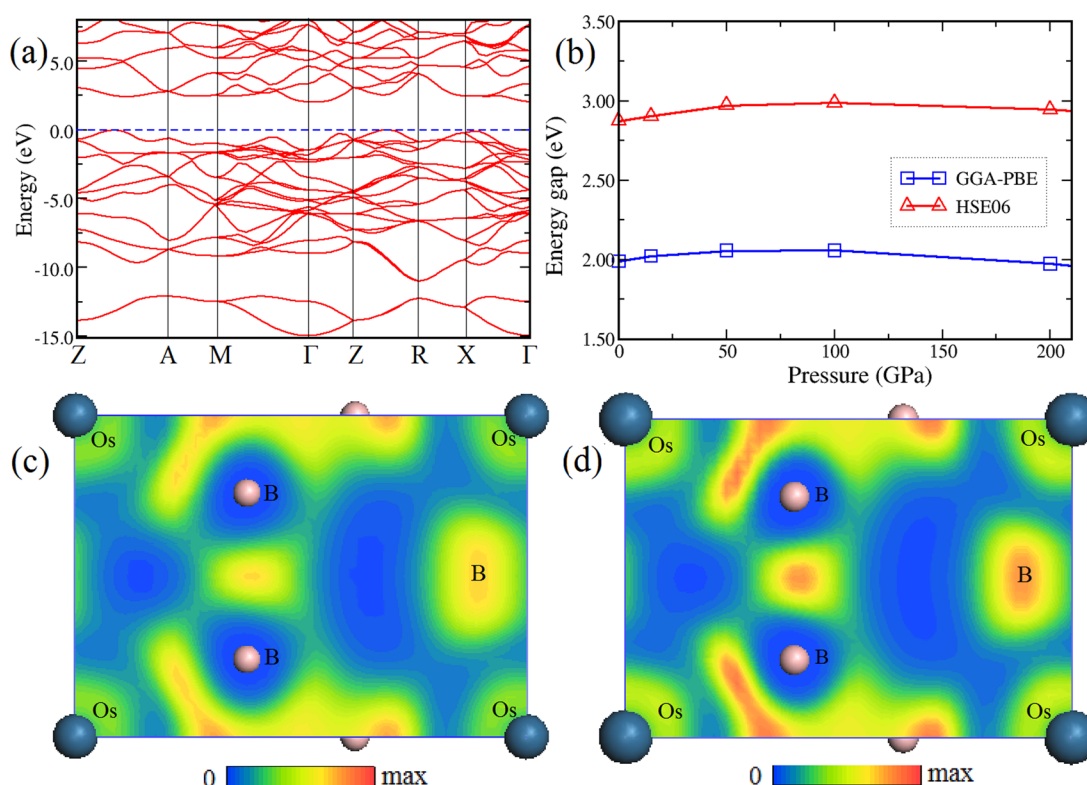


Figure 5. (a) Electronic band structure of the $P4_2/nmc$ phase at 15 GPa using GGA-PBE, in which the Fermi energy is set as zero. (b) Indirect band gaps of the $P4_2/nmc$ phase, calculated by GGA-PBE and HSE06, versus pressure from 0 to 200 GPa. Electron localization function in (100) plane of the $P4_2/nmc$ phase at 15 and 150 GPa are represented by (c) and (d), respectively.

unique band gap at widespread pressure is a result of its low compressibility with $B_0 = 331$ GPa.

The difference between PDOS of the $P4_2/nmc$ and the $Pm\bar{m}n$ phases could be a result of the differences in orbital hybridizations of them. The 2s-B state significantly emerges at both VBM and CBM as shown in Figure 4b. It is possible that the sp-d mixing states are formed during the bonding of B-Os in the $P4_2/nmc$ phase. Furthermore, we found that the 3D boron network in the $P4_2/nmc$ phase is a result of the distortion of sp^3 hybridization. One can notice evidence of the distorted sp^3 hybridization by monitoring a splitting peak of PDOS at the energy range of -15 to -12 eV, which is compatible with the two energy dispersion bands at that energy range, as illustrated in Figure 4a. In Figure S4,²⁶ the PDOS of the 3D boron network (Figure S4c), without the Os of the $P4_2/nmc$ phase, is compared with the PDOSs of the diamond (Figure S4a) and graphite (Figure S4b) phases of carbon. It is more compatible with the PDOS of the diamond phase than of another phase. The band gap of the pure 3D boron network (Figure S4c) is opened by the association of charge transfer and interaction with an intercalated Os atom. This confirms the distorted sp^3 hybridization in the 3D boron network as well. By considering the two-dimensional plot of the electron localization function (ELF) in Figure 5c,d, we found that there are strongly large populations of localized electrons at regions between B and B as well as Os and B. This is revealed in the strong covalent bonds in both B-B and Os-B bondings. Therefore, the ELFs confirm that the $P4_2/nmc$ phase of OsB_4 is a promising semiconducting superhard material. In summary, the strong covalent bondings of the 3D boron network constructed by distorted sp^3 hybridization and of Os and B due to sp-d mixing states play significant roles in the semiconducting and

superhard behavior of the $P4_2/nmc$ phase. These bondings, alongside the advantageous properties in the $P4_2/nmc$ phase of OsB_4 , uncover a novel multifunctional material. Therefore, this finding should substantially induce further experimental investigation.

The $P6_3/mmc$ and $Cmca$ phases exhibit a metallic phase, as presented in Figure 4c,d. In the $Cmca$ phase, the large antibonding, resulting from the mixing of 5d-Os and 2p-B states, is below the Fermi level. The sharpness of PDOS at -7.5 eV in Figure 4d indicates a separation between bonding and antibonding in the $Cmca$ phase. It typically occurs in solids under compression, which is a direct consequence of shortening the bond lengths of paired atoms. The metallic ELF features of $P6_3/mmc$ at 150 GPa and $Cmca$ phases at 300 GPa are demonstrated, respectively, in Figure S5a,b.²⁶

CONCLUSION

In this investigation, we used a systematic first-principles study in order to examine structural phase transitions and related physical properties of OsB_4 under high pressure. The metal-to-semiconductor phase transition from the $Pm\bar{m}n$ to the $P4_2/nmc$ phase has been predicted to be 11 GPa. The two metallic phases of the $P6_3/mmc$ and the $Cmca$ symmetry have been predicted to be 134 and 270 GPa, respectively. The calculated Vickers hardness of the semiconducting $P4_2/nmc$ phase is 60 GPa at ambient pressure, and it still exhibits a superhard material until it reaches a pressure of 100 GPa. Both the semiconductivity and superhardness of the semiconducting $P4_2/nmc$ phase are contributed to by the strong covalent bondings of B-B and Os-B pairs. Bearing in mind the calculated wide-bandgap value of the $P4_2/nmc$ phase, as well as the calculated hardness in the wide pressure range, we found

that it should be a promising material for cutting and drilling tools, hard material coating, and other advanced optical technologies.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b07976.

Optimized lattice parameters of the calculated structures at 0 GPa; fractional lattice parameters, a/a_0 and c/c_0 of the $P4_2/nmc$ phase; crystal structure and atomic arrangements of the $Cmca$ phase at 300 GPa; phonon dispersion of the $P4_2/nmc$ phase at 0 GPa; the PDOSs of diamond, graphite and the $P4_2/nmc$ phase; electron localization function (ELF) of the $P6_3/mmc$ at 150 GPa and $Cmca$ phase at 300 GPa (PDF)

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Notes

The authors declare no competing financial interest.

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High pressure-induced distortion in face-centered cubic phase of thallium

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The complex and unusual high-pressure phase transition of III-A (i.e. Al, Ga, and In) metals have been investigated in the last several decades because of their interesting periodic table position between the elements having metallic and covalent bonding. Our present first principles-based electronic structure calculations and experimental investigation have revealed the unusual distortion in face-centered cubic (f.c.c.) phase of the heavy element thallium (Tl) induced by the high pressure. We have predicted body-centered tetragonal (b.c.t) phase at 83 GPa using an evolutionary algorithm coupled with ab initio calculations, and this prediction has been confirmed with a slightly distorted parameter ($\sqrt{2} \times a - c$) lowered by 1% using an angle-dispersive X-ray diffraction technique. The density functional theory (DFT)-based calculations suggest that *s-p* mixing states and the valence-core overlapping of 6*s* and 5*d* states play the most important roles for the phase transitions along the pathway h.c.p. $\rightarrow$ f.c.c. $\rightarrow$ b.c.t.

thallium | high pressure | phase transition | distorted face-centered cubic | first principle study

High-pressure phase transitions of the metals with semicore *d* electrons among III-A elements has become a challenging problem because of these metals' unusual atomistic mechanisms driven by pressure. The first three III-A elements, Al, Ga, and In, have been widely investigated both experimentally and theoretically for the last several years (1–7). The lightest one among these elements is Al, which has shown a transition at room temperature from face-centered cubic (f.c.c.) to hexagonal close-packed (h.c.p.) at 217 ± 10 GPa (1). For Ga, there was an isostructural phase transformation from body-centered tetragonal (b.c.t.) to f.c.c. that had been observed around 120 ± 10 GPa using the powder X-ray diffraction (XRD) method (2). In the case of In, the predicted transition pressure from b.c.t. to f.c.c. was found to be around 800 GPa (4). However, there was also a reported body-centered orthorhombic (b.c.o.) phase that might exist as the high-pressure phase of In (5). The double-well feature of the total energy based on the first principles electronic structure calculations for b.c.t. $\rightarrow$ f.c.c. transition in the case of Ga and In had been explored successfully, in good agreement with the experimental results (2, 3). However, the heavy element of this group Tl has rarely been investigated in both experiment and theory to date. Tl also is an important element in the high-temperature superconducting compounds and has potential in various technological advances (8). For pure crystalline Tl, the superconducting temperature (T_c) has been experimentally found as 2.39 K at ambient pressure (9). At ambient pressure and temperature, the crystal structure of Tl is h.c.p with low bulk modulus (B_0) of 35.3 GPa. Tl is isothermally crystallized as f.c.c. phase around 4 GPa (10), and this closed-packed structure

remains unchanged up to 68 GPa (11). The lack of theoretical investigation of Tl under high pressure opens up the possible investigation that can contribute to our understanding of both mechanical and electronic behaviors of this element. This work aimed to investigate the structural phase transformations of Tl under high pressure based on combined density functional theory (DFT) and in situ XRD. Here, an evolutionary algorithm, coupled with DFT, has been used to predict the high-pressure phase of Tl as a distorted f.c.c. phase at 83 GPa, and this phase is confirmed with the experimental counterpart as well.

Results and Discussion

From the structural prediction using USPEX, the four lowest enthalpy phases that are found between 60 and 90 GPa are b.c.t (*I4/mmm*), b.c.o. (*Immm*), face-centered orthorhombic (f.c.o.) (*Fmmm*), and monoclinic (*C2/m*). A subsequent complete reoptimization of these structures with accurate force convergence criteria using VASP (energy cutoff of 500 eV and spacing between *k*-points of $0.2 \text{ \AA}^{-1}$) demonstrates that the relaxed b.c.o., f.c.o., and monoclinic structures are quite close to each other and to f.c.c. (distorted) as a competing phase with b.c.t. (average $c/a = 1.375$) configuration. However, the structural predictions at 100, 150, and 200 GPa reveal that the b.c.t. phase prevails as the most stable phase with the lowest enthalpy. We have calculated the total energy of h.c.p., f.c.c., and b.c.t. phases

Significance

The III-A metals (i.e. Al, Ga, and In) have displayed complexity of structural phase transitions under high pressure. The contribution of *d* electrons to valence states has been investigated previously and has been suggested to be responsible for that behavior. Here, another III-A metal, Tl, is predicted to be an unusual distorted f.c.c. structure (b.c.t.) at high pressure and then is confirmed by using the angle-dispersive X-ray diffraction method. The enhancement of *sp-d* mixing states at valence bands with the increasing pressure is suspected to be the cause of distortion in Tl. The transformation pathway of Tl is intended to be h.c.p. $\rightarrow$ f.c.c. $\rightarrow$ b.c.t. under compression. Tl is an important element in high-temperature superconducting compounds; thus the present study has great implications in the area of superconductivity.

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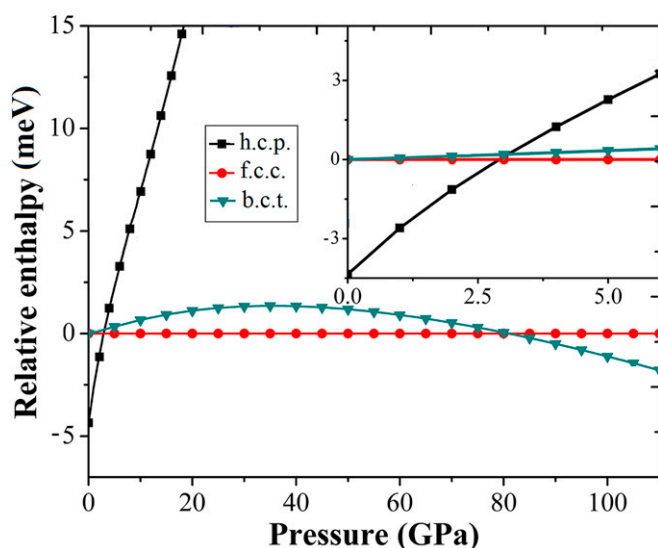


Fig. 1. Relationship of relative enthalpies of calculated phases that are referenced by enthalpy of the f.c.c. phase versus pressure from 0 to 110 GPa. The *Inset* magnifies the pressure range of 0–7.5 GPa, to magnify the first phase transition of TI from the h.c.p. to f.c.c. phase.

by changing the cell volume corresponding to the pressure range of 0–200 GPa. The lattice parameter c/a is fixed at 1.598 and 1.375 for h.c.p. and b.c.t. phase, respectively. The calculations are performed using full-potential local-orbital minimum-basis (FPLO) code with full relativistic approach. Fig. 1 shows the complete profile of relative enthalpies with respect to the pressure. The first phase transition from h.c.p. to f.c.c. has been predicted around 3 GPa; this transition pressure is in good agreement with the experimental results (10, 11). The fitting parameters consisting of volume (V_0), bulk modulus (B_0), and pressure derivative of bulk modulus (B'_0) at zero pressure are $V_0 = 27.23 \text{ \AA}^3$, $B_0 = 40.80 \text{ GPa}$, and $B'_0 = 6.30$ for the h.c.p. phase and $V_0 = 26.95 \text{ \AA}^3$, $B_0 = 42.94 \text{ GPa}$, and $B'_0 = 6.20$ for the f.c.c. phase. These parameters are also in good agreement with experimental results (10, 11). The enthalpy of f.c.c. phase is the lowest between 3 and 83 GPa with a slightly higher one (i.e., the b.c.t. phase). At a pressure greater than 83 GPa, the calculation indicates that the predicted b.c.t. phase is the most stable phase with the lowest enthalpy. The relative enthalpy between b.c.t. and f.c.c. phase is significantly lower than equivalent thermal energy at room temperature ($\sim 26 \text{ meV}$). The structural parameters of b.c.t. phase are fitted to be $V_0 = 26.92 \text{ \AA}^3$, $B_0 = 45.30 \text{ GPa}$, and $B'_0 = 5.52$.

The dynamical stability of b.c.t. phase has been determined at a selected pressure of 80–200 GPa, as shown in Fig. 2. The value of c/a is below $\sqrt{2}$ for the fully optimized structures based on VASP results. The $3 \times 3 \times 3$ supercell consisting of 54 atoms has been constructed to calculate the phonon dispersion along the symmetrical path $\Gamma \rightarrow X \rightarrow P \rightarrow \Gamma \rightarrow T$. The absence of negative phonon frequencies of the b.c.t. phase in different pressures supports the fact of dynamical stabilities of the corresponding crystal structures.

To confirm the phase transitions of Tl under high pressures, we also performed in situ XRD on Tl at room temperature. Selected XRD patterns are displayed in Fig. 3A. At pressures between 3.1 GPa and 4.6 GPa, a phase transition from h.c.p. structure has been confirmed, and the high pressure phase after h.c.p. phase has found to be stable up to 129 GPa, which is the highest attainable pressure in the experiment. In previous high pressure XRD studies, energy dispersive experiments by Schulte and coworkers (11, 12) and Olsen et al. (10) and a

laboratory-based angle-dispersive experiment by Leger et al. (13) came to the same conclusion that a phase transition from h.c.p. to f.c.c. occurred at about 4 GPa, and the f.c.c. phase was stable to 68 GPa (10). However, detailed analysis of our experimental data using angle-dispersive XRD with synchrotron radiation shows that the f.c.c. phase is not perfect. Full width at half maximum (FWHM) of the f.c.c. phase has been checked at high pressures, as depicted in Fig. 4A. Although the high-pressure phase of TI could be indexed using f.c.c. structure, the peaks 111 and 222 have significantly smaller FWHM than other f.c.c. index peaks, indicating a distorted f.c.c. structure rather than a perfect one. Our theoretical results suggest that the distorted structure is undergoing the b.c.t. phase, because when a f.c.c. structure is slightly distorted to a b.c.t. structure, each of the f.c.c. index peaks would split into two or more b.c.t. structure peaks, except those peaks with f.c.c. index hkl ($h = k = l = 1, 2, 4 \dots$). Therefore, our XRD results indicate that the high-pressure phase after the h.c.p. phase is a b.c.t. structure. For a better understanding of this distortion, all of the XRD patterns after 4 GPa are fitted using the b.c.t. structure model, as shown in Fig. 3A. The b.c.t.-type distortion of TI is very small, to characterize this distortion quantity, and the parameter $(\sqrt{2} \times a - c)/c$ is investigated at high pressures, where a and c are lattice parameters of the b.c.t. structure. When $\sqrt{2} \times a = c$, the symmetry of the b.c.t. structure has become an f.c.c. structure. Fig. 3B shows the distortion parameter as a function of pressure, which indicates that, in general, the distortion is very small ($<1\%$) and enlarged after phase transition from the h.c.p. structure to ~ 35 GPa, whereas after the transition, the distortion stays the same at $\sim 0.7\%$ up to 129 GPa in this study. In addition, the pressure-volume curve (P-V curve) from the experiment is shown in Fig. 4B. The fitting parameters of b.c.t. phase using the Birch-Murnaghan equation of state are $V_0 = 28.4 \text{ \AA}^3$, $B_0 = 35 \text{ GPa}$, and $B'_0 = 5.7$.

To understand the phase transition of TI under high pressure, the electronic band structures and partial density of states (PDOSs) of the h.c.p. and f.c.c. phases of TI at selected pressures are depicted in Fig. 5. For the h.c.p. phase at 0 GPa (Fig. 5A), the major contribution of $6p$ above -3 eV influences the electrical conductivity. The density of states (DOS) and energy dispersions below the Fermi level between -10.0 to -4.0 eV are dominantly occupied by $6s$ states. A small separation between $6p$ and $6s$ states has been observed around 3 eV below the Fermi level. The band structure indicates the p states prevail along $\Gamma \rightarrow \text{M} \rightarrow \text{K} \rightarrow \Gamma$ and $\text{L} \rightarrow \text{H}$ directions; meanwhile, s - p mixing states are seen along $\Gamma \rightarrow \text{A} \rightarrow \text{L}$ and $\text{H} \rightarrow \text{A}$ directions. In the lower energy range between -15 and -10 eV, the spin-orbit (SO) splitting evidently is attributable to two energy levels $5d_{5/2}$ and $5d_{3/2}$ being present around -10.24 eV and -12.55 eV, respectively. This splitting is in reasonable agreement with the

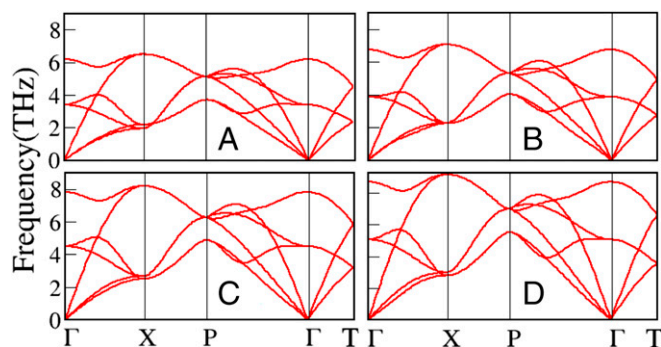


Fig. 2. Phonon dispersions of the b.c.t. phase at pressures of 80 GPa (A), 100 GPa (B), 150 GPa (C), and 200 GPa (D).

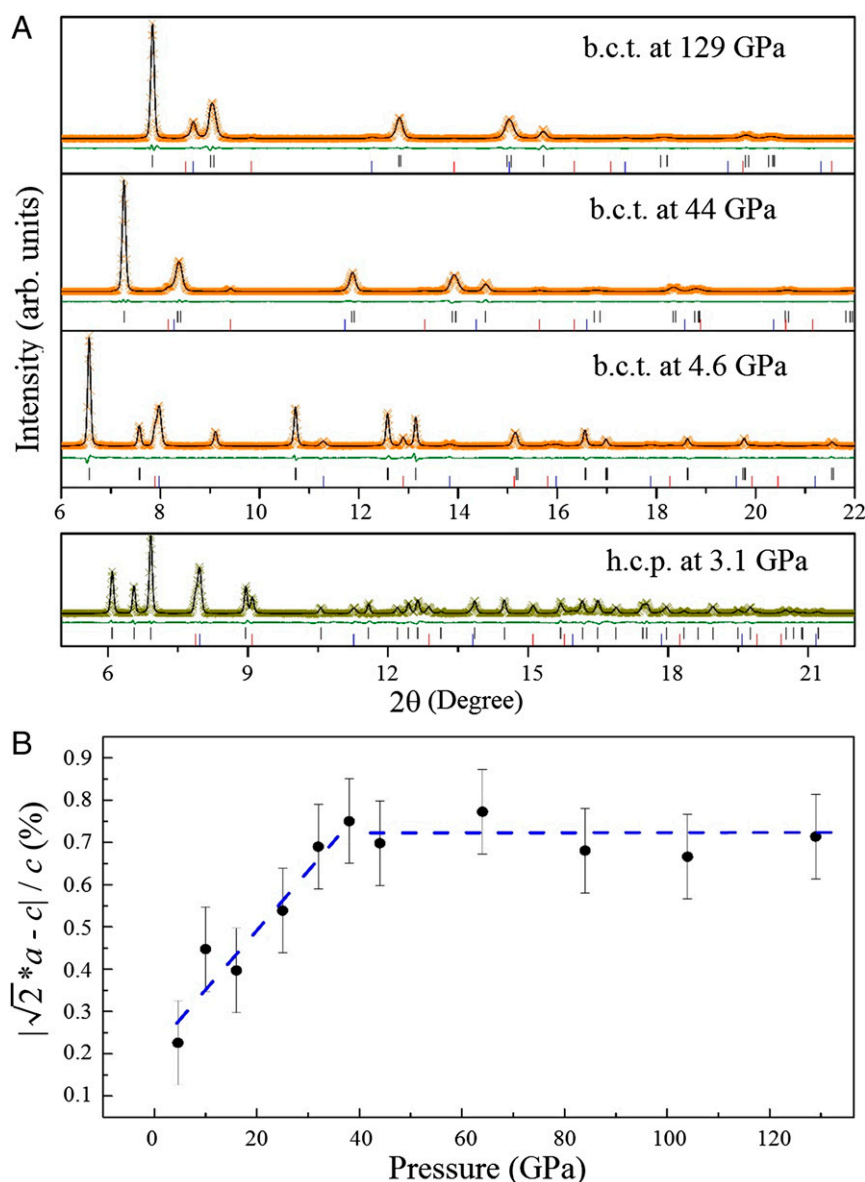


Fig. 3. XRD study of TI under high pressure. (A) Selected in situ angle-dispersive XRD patterns of TI at room temperature during compression. Experimental data are indicated by orange or green crosses; full-profile refinements, black curves; difference patterns, green curves; and tick marks, peak positions calculated from the refined lattice parameters of different phases: TI, Pt, and W with colors of black, red, and blue, respectively. (B) b.c.t. distortion of TI under high pressure. The dashed line serves guide to the eye.

previous experiments (14, 15). Furthermore, an overlap of 6s and 5 $d_{5/2}$ at Γ -point is observed at the ambient pressure. Therefore, the overlap might indicate that the electronic structure of the h.c.p. phase is dominated by the mostly by p - p bonding states and less by s - p mixing states. At the transition pressure of 3 GPa, band structures and PDOSs of h.c.p. and f.c.c phase are shown in Fig. 5 B and C, respectively. There are mainly two distinct features for the PDOSs compared with the h.c.p. phase at 0 GPa: (i) the separation between 6p and 6s states is zero; and (ii) the d states are increasingly contributed to the valence state as shown in the inset of PDOS panels. Both features are directly influenced by compressed volume that might cause to increase of s - p mixing and valence-core overlap of 6s and 5 $d_{5/2}$ states. This finding suggests that the external pressure increases s - p mixing of valence states and partial-valence states of 5d, the primary reason for h.c.p. $\rightarrow$ f.c.c. phase transformation. This finding corresponds to the f.c.c. phase

formation in III-A metal group, consisting of Ga and In, as reported in previous investigations (4–6). The PDOS of the f.c.c. phase still indicates that this phase comprises the majority of p - p bonding states and the minority of s - p mixing and valence-core overlapping states. The flat band, below the Fermi level, that lies along the $X \rightarrow K$ and $L \rightarrow W \rightarrow X$ directions is identified to be the s band, which is under the p band. Under more compression, it is found that the width of energy dispersions of the f.c.c. phase is increased. At 50 GPa (Fig. 5D), the s and p states are crossing at the midway $X \rightarrow K$ and $L \rightarrow W$ paths individually. Moreover, there is a s - p hybridization that has been observed in the deeper energy states corresponding to $5d_{3/2}$ states, and this increases the d state contribution to the valence band. These effects reshape the PDOS that has not been theoretically observed in the case of 3 GPa. Our calculations suggest that the f.c.c. $\rightarrow$ b.c.t. phase transition is influenced by enhancement of sp - d mixing states with the increasing pressure.

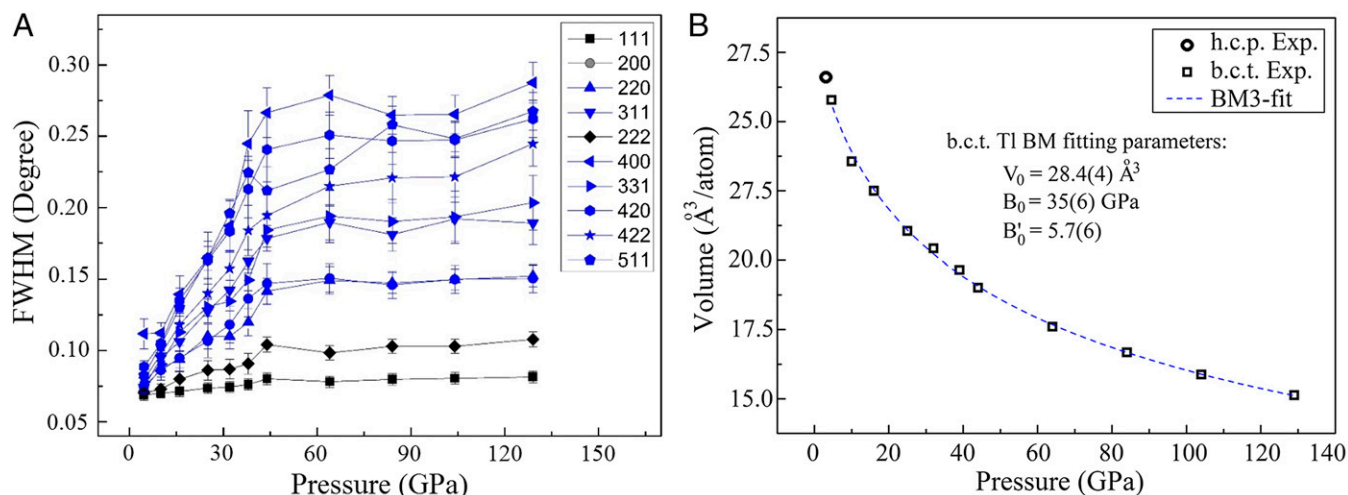


Fig. 4. (A) FWHM of TI XRD peaks at high pressures (>4 GPa). FWHM is measured based on the f.c.c. structure index. (B) Pressure–volume curve of thallium up to 129 GPa. Data points of h.c.p. and f.c.c. phases are represented by circle and rectangles, respectively. The dashed line is the tendency of plotting the equation of state of the b.c.t. phase.

Conclusions

In summary, we have done an extensive investigation of the high-pressure phase transition of TI based on systematic first principles electronic structure calculations and the in situ XRD method. The first phase transition from h.c.p. to f.c.c. at high pressure with our calculations has been validated with already-existing literature. Using an evolutionary algorithm, we have proposed another high-pressure phase (i.e., b.c.t. structure) at ~80 GPa. Our experimental investigation shows that the f.c.c.

phase is imperfect with a distortion of parameter $(\sqrt{2} \times a - c)/c$ within 1%. Additionally, the complete phase transformation pathway h.c.p. $\rightarrow$ f.c.c. $\rightarrow$ b.c.t. has been elucidated based on the electronic band structure and density of state. It has been found that the phase transition is contributed by increasing s - p mixing of valence states and partial-valence states of $5d$ states in h.c.p. $\rightarrow$ f.c.c. phase transition. The transition from the f.c.c. to b.c.t. phase is assumed to occur due to the enhancement of sp - d mixing states at valence bands with the increasing pressure.

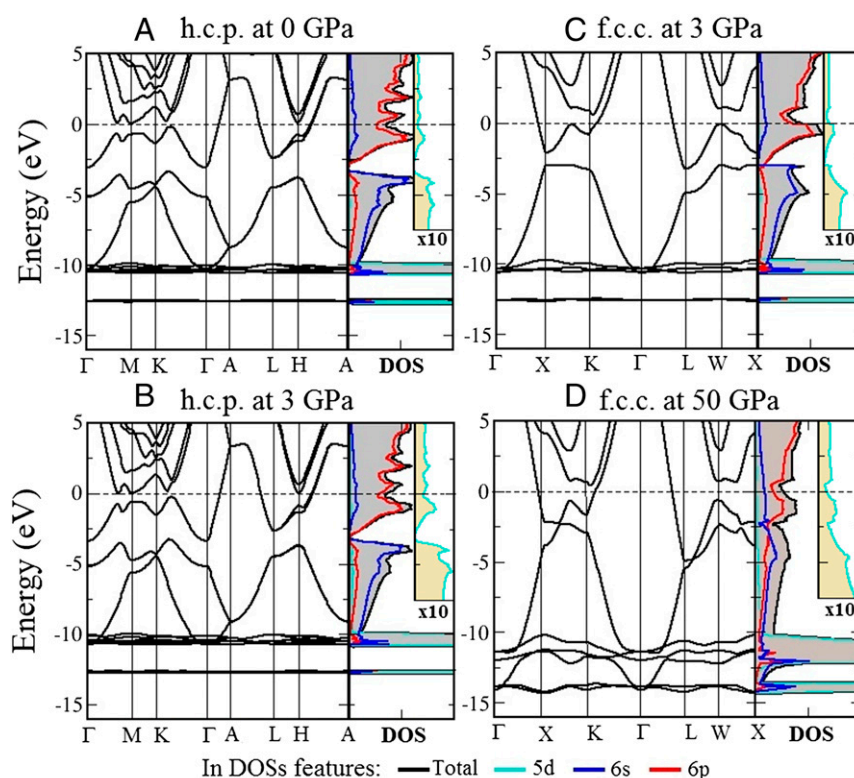


Fig. 5. Comparison of electronic band structure and PDOS of h.c.p. phase at 0 GPa (A) and 3 GPa (B) and the f.c.c. phase at 3 GPa (C) and 50 GPa (D). In the Inset, the contribution of 5d-DOS has been shown in a magnified scale to have a clear demarcation.

Materials and Methods

The calculations have been performed using ab initio calculation based on DFT formalism. The local spin-density approximation (LSDA-PW92) with the full relativistic approach implemented within the FPLO code (16, 17) has been used. The h.c.p. $\rightarrow$ f.c.c. phase transformation was carefully determined using $19 \times 19 \times 12$ and $16 \times 16 \times 16$ converged k-points for the h.c.p. and f.c.c. phase, respectively. We have also predicted the high-pressure phases at 60, 70, 80, 90, 100, 150, and 200 GPa, by using the evolutionary algorithm based on structural search implemented in USPEX code (18, 19) interfacing with VASP code (20, 21). The phase with the lowest enthalpy is the b.c.t. phase, which has been calculated with converged $19 \times 19 \times 16$ k-point mesh. To determine the most stable phase at high pressure, the third-order Birch–Murnaghan equation of state has been used to fit the energy–volume curve (22). The lowest enthalpy among all of the calculated phases is corresponding to the thermodynamically most stable phase. The phonon dispersion of the predicted phase has been calculated to confirm the dynamical stability using Phonopy code (23).

A Mao-type symmetric diamond anvil cell (DAC) has been used to generate high pressures. The culet of diamond anvil is 100 μm beveled to 300 μm with 8.5° beveled angle. Tungsten foil with initial thickness of 250 μm has been used as a gasket. A hole is drilled into the center of the preindented gasket using the laser-drill system (24). Polycrystalline thallium (99.9%; Alfa Aesar) has been loaded into the sample chamber without a pressure transmitting medium. The sample loading has been carried out inside a glove box with an Ar atmosphere to avoid reaction with oxygen and water. A small amount of

Pt powder is placed next to the sample in the sample chamber as a pressure marker. Pressures have been determined by measuring the XRD of Pt using the metal's equation of state (25). All experiments are carried out at room temperature on beam line 16-BMD of the High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source (APS), Argonne National Laboratory. The beam size is about 6 μm by 9 μm , and the X-ray wavelength is 0.3100 Å. In situ XRD patterns are recorded using a Mar-CCD detector, integrated using the Fit2D software and analyzed using the General Structure Analysis System (GSAS) Le-Bail fit (26).

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Role of relativity in high-pressure phase transitions of thallium

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We demonstrate the relativistic effects in high-pressure phase transitions of heavy element thallium. The known first phase transition from h.c.p. to f.c.c. is initially investigated by various relativistic levels and exchange-correlation functionals as implemented in FPLO method, as well as scalar relativistic scheme within PAW formalism. The electronic structure calculations are interpreted from the perspective of energetic stability and electronic density of states. The full relativistic scheme (FR) within L(S)DA performs to be the scheme that resembles mostly with experimental results with a transition pressure of 3 GPa. The *s-p* hybridization and the valence-core overlapping of 6s and 5d states are the primary reasons behind the f.c.c. phase occurrence. A recent proposed phase, i.e., a body-centered tetragonal (b.c.t.) phase, is confirmed with a small distortion from the f.c.c. phase. We have also predicted a reversible b.c.t. → f.c.c. phase transition at 800 GPa. This finding has been suggested that almost all the III-A elements (Ga, In and Tl) exhibit the b.c.t. → f.c.c. phase transition at extremely high pressure.

High-pressure induced phase transition in thallium (Tl) was envisaged over last couple decades^{1,2}. A structural phase transition of Tl from a hexagonal close packed (h.c.p.) structure to a face-centered cubic (f.c.c.) structure occurs around 4 GPa², and the f.c.c. structure is stable with compressing up to 68 GPa¹. In recent year, two independent high-pressure studies in Tl over 120 GPa have been reported^{3,4}. Cazorla *et al.* confirmed the first phase transition from the h.c.p. to f.c.c. structure at 3.5 GPa, and the f.c.c. phase was persistently stable up to 125 GPa based on angle-dispersive x-ray diffraction (ADXRD) method. They also found that the h.c.p. to f.c.c. phase transition was at 8.8 GPa and the f.c.c. phase stabilized up to 4.3 TPa by using the projector augmented wave and generalized gradient approximation (PAW-GGA) method^{5,6} with including spin-orbit (SO) coupling based on density functional calculations³. In contrast to the Cazorla's report, Kotmool *et al.* have theoretically studied and predicted the high-pressure phases of Tl up to 200 GPa. The h.c.p. → f.c.c. phase transition has been confirmed at 3 GPa by using L(S)DA with full relativistic calculation based on full-potential with local-orbital minimum-basis set (FPLO) method^{7,8}. A body-centered tetragonal (b.c.t.) phase has been predicted around 80 GPa, and their experimental results by using the ADXRD method have also insisted the existence of a small distortion of the f.c.c. phase with $|(\sqrt{2} \times a - c)/c| < 1\%$ up to 128 GPa⁴.

The subtle difference of two previous studies^{3,4} needs to be clarified in order to have a complete picture of the high-pressure phase transition of the III-A group. As a known b.c.t. → f.c.c. phase transition in gallium (Ga)^{9,10} and indium (In)¹¹, here an hypothesis of the possible b.c.t. → f.c.c. phase transition beyond 200 GPa in Tl is established. Moreover, as seen in the previous results, a thorough investigation is still needed to make more understanding in high-pressure behavior of this element. Therefore, the present study aims at theoretically investigating the high-pressure phase transitions of Tl up to 1 TPa. The various methods of calculations are employed to find the most appropriate one to represent electronic structure of Tl. An evolutionary algorithm, which is an unbiased method, is used to search the high-pressure phases of Tl beyond 200 GPa up to 1 TPa to proof the initial hypothesis as well.

Results and Discussion

Figure 1, shows the relative enthalpy, determined with all considered methods, of the f.c.c. phase from 0 to 15 GPa, with the h.c.p. phase as reference. The results indicate that the relativistic scheme has a strong effect

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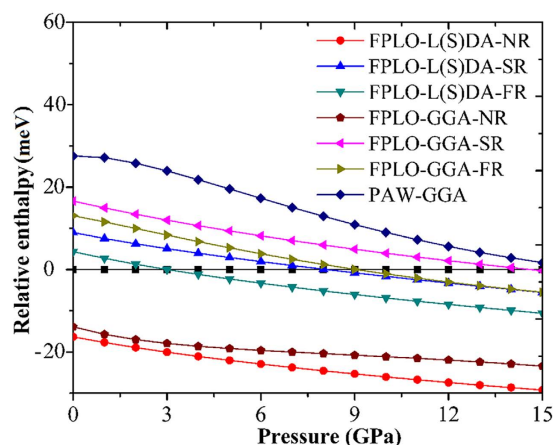


Figure 1. Relationship of relative enthalpies of the f.c.c. phase with grounded by enthalpy of the h.c.p. phase, versus pressure. The calculations are performed using various basis sets, exchange-correlation functionals, and relativistic levels.

Methods	P_t (GPa)	h.c.p.			f.c.c.			Reference
		$V_0(\text{\AA}^3)$	$B_0(\text{GPa})$	B'_0	$V_0(\text{\AA}^3)$	$B_0(\text{GPa})$	B'_0	
FPLO-LSDA-NR	—	29.52	41.63	5.99	29.29	43.02	5.99	this work
FPLO-LSDA-SR	8.1	27.19	41.16	6.30	26.95	42.75	6.20	this work
FPLO-LSDA-FR	3.0	27.23	40.80	6.30	26.95	42.94	6.20	this work
FPLO-GGA-NR	—	32.62	31.59	5.60	32.27	36.22	4.84	this work
FPLO-GGA-SR	14.8	31.50	24.51	5.96	31.23	24.61	6.11	this work
FPLO-GGA-FR	8.0	31.45	25.97	5.55	31.23	24.68	6.11	this work
PAW-GGA-SR	16.8	31.96	22.21	5.91	31.39	24.63	5.84	this work
PAW-GGA-FR	8.8	29.36	38.9	4	28.84	44.78	3.94	3
ADXRD	3.5	28.7	31	4	28.2/28.8	48/50	4/3.2	3
EDXRD	4.0	28.5	35.3	6.2	28.1	29.4	6.3	1

Table 1. Illustration of fitting parameters consisting of volume (V_0), bulk moduli (B_0), and pressure derivative of bulk modulus (B'_0) at zero pressure, as well as transition pressures from h.c.p. to f.c.c. phase using various calculated methods, and experiment.

upon the structural phase transition from the h.c.p. to f.c.c. But this dependence can not be seen in case of NR calculation within both L(S)DA and GGA schemes. This is because of the fact that the enthalpy of the f.c.c. phase is lower than the h.c.p. phase in that range of pressures. In other cases that consider the SR and FR effects, the h.c.p. $\rightarrow$ f.c.c. phase transition can be revealed. The result using FPLO with L(S)DA and FR shows reasonable agreement with the experimental outcomes^{1–4} with a transition pressure of 3 GPa, whereas, the other methods yield the overestimating transition pressures. Interestingly, the transition pressure using GGA and FR within FPLO method is higher than that from the L(S)DA and the PAW-GGA reveals the transition pressure as three times higher than the experimental value. This issue will be discussed later. The fitting parameters and transition pressures of both the phases calculated with other methods are shown in Table 1. For fitting parameters, the results agree following the conventional trend that GGA overestimates the volume and underestimates the bulk modulus, but they are different while using L(S)DA scheme. It is found that the fitting parameters using FPLO with L(S)DA and FR also mostly agree with experiments as well. Therefore, this scheme will be reliable and appropriate option to perform the structural and mechanical properties of thallium.

The electronic band structures and density of states (DOSs) of the h.c.p. and f.c.c. phase of Tl at selected pressures as depicted in Fig. 2 show the influence of relativistic effects in particular L(S)DA method. For the h.c.p. phase at 0 GPa (top row), the 6p states are the majority across the Fermi level. The DOS shapes for the FR and SR consideration are different in terms of smoothness as it is less smooth between 1.0 and 2.0 eV energy range in the former case. This difference also reflects in the energy dispersion of zone-boundary at M- and K-points, where crossing of dispersion lines in the SR is observed, while a small splitting right at H-point in the FR is seen. The DOS and energy dispersions in case of the SR and FR are similar below the Fermi level between -4.0 and -10.0 eV, dominantly occupied by 6s states. There is a separation between 6p and 6s states that is observed around 3 eV below the Fermi level. It leads to the conclusion that there is no s-p hybridization, but only bonding of the p states exist that forms the h.c.p. phase at ambient condition. In contrast to this separation in case of the SR and FR, both 6p and 6s states play the important role of bonding electrons in the NR case. This leads to the disagreement with experiment regarding the phase transformation of the h.c.p. $\rightarrow$ f.c.c. in cases of NR calculations. In

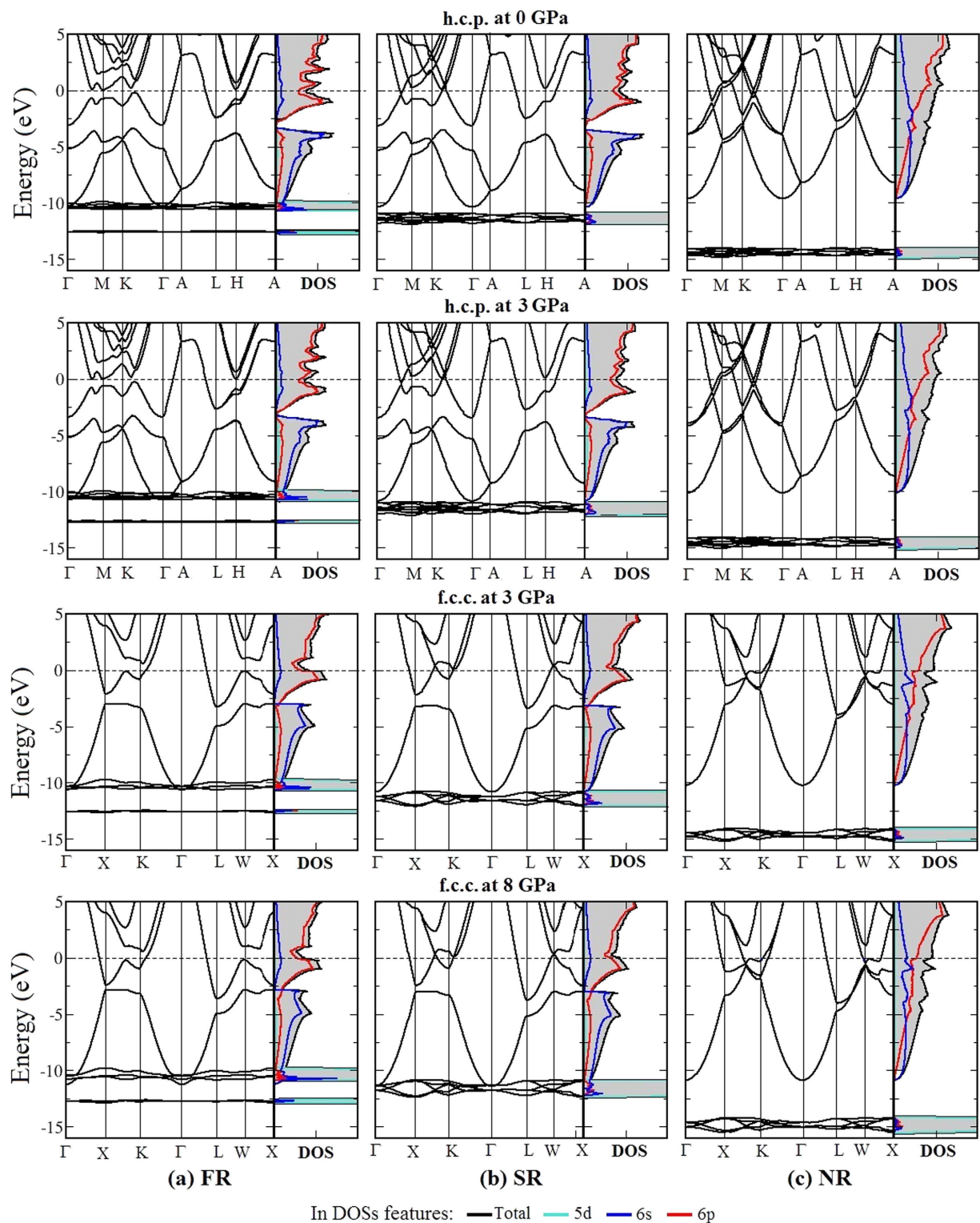


Figure 2. Comparison of electronic band structures and DOSs of h.c.p. phase at 0, and 3 GPa, and f.c.c. at 3 and 8 GPa, by using various relativistic levels, consisting of (column (a)) fully relativistic (FR), (column (b)) scalar relativistic (SR), and (column (c)) non-relativistic (NR) within LS(D)A. The horizontal lines in DOS panels at energy range of -15 to -10 eV, are cut peaks of 5d states in which their height are in range of 10–30 state/eV.atom, meanwhile shown scales of DOSs are in range of 0–1 state/eV.atom.

the lower energy range between -15 and -10 eV, an apparent difference in relativistic levels is contributed by 5d states, which originates together at around -11.8 eV and -14.0 eV in the SR and NR, respectively. But in the FR case, there is a splitting of 5d states into $5d_{5/2}$ and $5d_{3/2}$ states as allocated at -10.24 eV and -12.55 eV. This

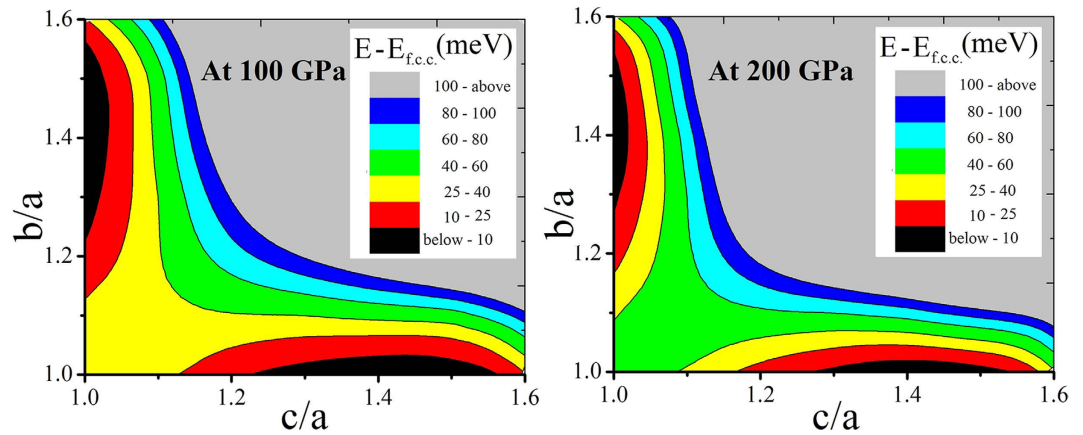


Figure 3. The contour plot of enthalpy of Tl by varying b/a and c/a at given volumes corresponding to 100 GPa (left panel) and 200 GPa (right panel).

splitting is resulted due to the spin-orbit (SO) coupling in this case, and is in good agreement with the previous experiments^{12,13}. Furthermore, an overlap of $6s$ and $5d_{5/2}$ at Γ -point is observed in case of FR. The evidences of the h.c.p. $\rightarrow$ f.c.c. transformation are revealed at 3 GPa, as shown in second and third row of Fig. 2 for h.c.p. and f.c.c., respectively. For the first one, a mixing state between $6s$ and $6p$ appears in the h.c.p. and f.c.c. phase at this pressure for both SR and FR. In contrast, the second evidence of a valence-core overlap of $6s$ and $5d_{5/2}$ state appears in the FR case only. The transition pressure for the h.c.p. $\rightarrow$ f.c.c. phase transition of the FR calculation has been determined as 3 GPa. For the SR calculation, it has been found that the valence-core overlap arises at 3 GPa for the h.c.p. phase and increases with increasing pressure. The bottom row of Fig. 2 displays the band structures and DOS of the f.c.c. phase at 8 GPa (the transition pressure in the SR case) and the overlap of $6s$ and $5d$ states is also appearing in the SR case. In the NR case, the valence-core overlap is unobserved up to 8 GPa as the energy tail of $6s$ states being still far from the $5d$ states.

The calculation results using both FPLO and PAW approach with GGA functional reveal the similar tendency in accord with the previous discussion. But, due to the overestimation of volume and as a consequence to the change in the electronic band structure, the transition pressure is also overestimated using GGA. Moreover, it is found that the use of GGA and FR within FPLO obtains the compatible transition pressure with previous reports using GGA and including SO coupling within PAW method³.

The bonding in case of the h.c.p. phase originates from $6p$ states and the valence-core overlapping of $6s$ and $5d_{5/2}$ states is appeared. The external pressure induces s - p mixing of valence state and partial-valence state of $5d$ electrons leading to the h.c.p. $\rightarrow$ f.c.c. phase transformation. This finding corresponds to forming the f.c.c. phase in III-A metal group, consisting of Ga and In as reported in previous investigations^{11,14,15}. It should be emphasized here that the electronic structure of Tl strongly depends on the level of relativistic application.

We have done further calculations to confirm the existence of the b.c.t. phase. at high pressure reported by Kotmool *et al.* Firstly, in order to search the other possible distorted f.c.c. phases, primarily a body-centered orthorhombic (b.c.o.) phase, which has been found with more structural distortion than the b.c.t. phase, is considered. The calculations while varying b/a and c/a in range of 1.0 to 1.8 at 100 GPa and 200 GPa are reported as depicted in Fig. 3. The both contours have a diagonal symmetry. The lowest enthalpy zone is represented by the black area of contours as lay on the middle of the axes. The shape of the black zones along both the axes confirm the probability of existence of the b.c.t. phase, rather than the lower symmetry b.c.o. phase. Secondly, we also predict the high-pressure phases of Tl using USPEX code from 300 GPa to 1 TPa. At 300–600 GPa, the b.c.t. phase still prevails as the most stable phase with lowest enthalpy comparing to the f.c.c., b.c.o. and monoclinic (i.e., C2/m) phases. But the f.c.c. phase emerges to be the most stable once again at 800 and 1000 GPa. The relationships between relative energy and c/a at fixed volumes are calculated using FPLO with L(s)DA and FR calculation as shown in Fig. 3. The results confirm the previous reports^{1–4} that the f.c.c. phase (20 GPa, Fig. 4(a)) is induced by increasing pressure to be the b.c.t. phase (Fig. 4(b–f)) with a small distortion of $|\sqrt{2} \cdot a - c|/c < 1\%$. Intriguingly, at 800 GPa (Fig. 4(g)), the lowest energy is corresponding to the f.c.c. phase with $c/a = \sqrt{2}$ which is in agreement with the prediction. These results indicate that the perfect f.c.c. phase can be recovered by pressure of 800 GPa. This finding is quite important because it is a fulfillment suggesting that almost the III-A elements (Ga, In and Tl) exhibit the b.c.t. $\rightarrow$ f.c.c. phase transition under high pressure.

Conclusion

In this work, we have thoroughly investigated the influence of the relativistic effects on the high-pressure phase transition of Tl. The transformation of the h.c.p. to f.c.c. phase is carried out by using various relativistic levels and exchange correlation functionals. It has been found that the relativistic effect strongly controls the transition pressure and structural parameters under high pressure. The transition pressure has been found in range of 3 to 16 GPa with the scalar and fully relativistic (SR and FR) schemes, which is in reasonable agreement with experimental result, specially with L(S)DA coupled with FR. Moreover, the SO coupling has been found to have inevitable role behind the h.c.p. $\rightarrow$ f.c.c. phase transformation. The previously reported b.c.t. phase has also been

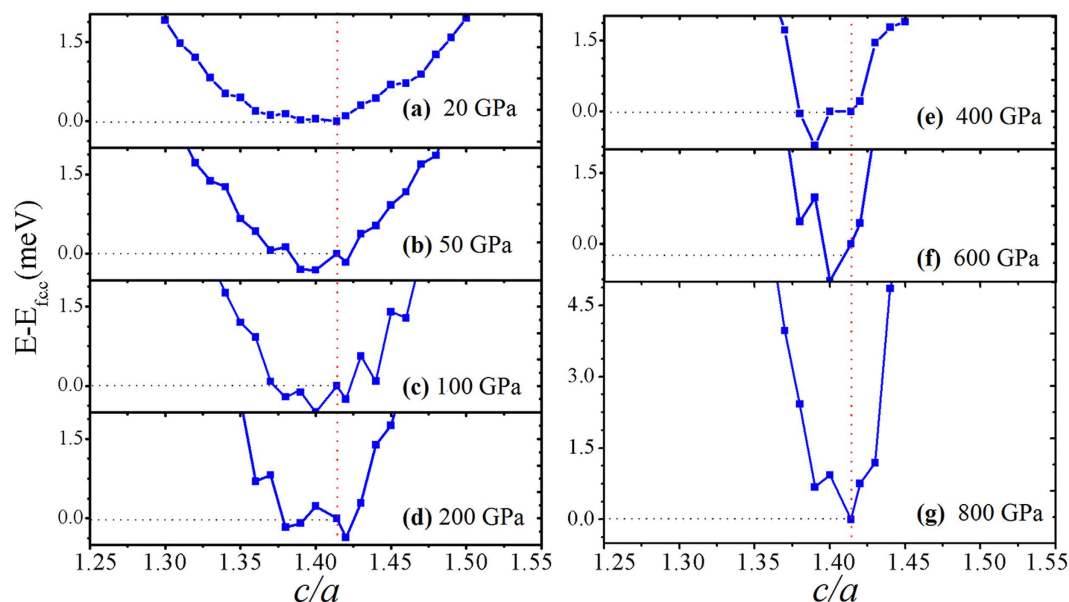


Figure 4. Relative energy respecting the f.c.c. phase ($c/a = \sqrt{2}$) versus varying c/a of the b.c.t. phase of Tl at given volumes corresponding to (a) 20 GPa, (b) 50 GPa, (c) 100 GPa, (d) 200 GPa, (e) 400 GPa, (f) 600 GPa and (g) 800 GPa.

confirmed in this work. The search for high-pressure phase up to 1 TPa envisages the re-occurrence of the f.c.c. phase, that has been recovered at 800 GPa.

Methods

We have performed all the electronic structure calculations based on density functional theory (DFT) formalism. In addition to the local spin-density approximation (L(S)DA-PW92)¹⁶ and generalized gradient approximation (GGA-PBE)⁶, the non-relativistic (NR), scalar relativistic (SR) and full relativistic (FR) schemes have also been considered. We have employed full-potential with local-orbital minimum-basis set implemented FPLO package^{7,8} and projector augmented wave (PAW)⁵ implemented Vienna *Ab initio* Simulation Package (VASP)^{17,18} for performing all the calculations. By using the FPLO method, the converged k-points were set to be $19 \times 19 \times 12$, $16 \times 16 \times 16$ and $19 \times 19 \times 16$ for the h.c.p., f.c.c. and b.c.t. phase, respectively. For using VASP calculation, energy cutoff of 500 eV is used and the automatic k-point mesh with setting spacing between k-points of $0.2 \text{ \AA}^{-1}$ is considered (corresponding $10 \times 10 \times 6$ and $11 \times 11 \times 11$ for the h.c.p. and f.c.c. phase, respectively). All the setup values of VASP and FPLO methods are verified for all the calculations to ensure the energy convergence of 1 meV/atom. The third-order Birch-Murnaghan equation of state has been used to fit the energy change with volume¹⁹.

The structural searching method based on the evolutionary algorithm, which has been implemented in USPEX code^{20,21} interfacing with VASP code, has been used to extend the previous prediction up to 1 TPa (i.e., 300, 400, 600, 800 and 1000 GPa). The searches are performed by varying cell size up to 8 atoms per cell. During the prediction, number of initial randomized structures in the 1st generation is set as 40 structures. The next is carried out 30 population structures by heredity and mutations of the lowest enthalpy structure of the previous generation by 50% and 30% respectively, and remaining 20% of populations are obtained by randomization. The prediction would be done when a lowest enthalpy structure would be continuously survival within 30 generations.

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Author Contributions

R.A. designed the research; all authors performed research, analyzed the results and wrote the manuscript.

Additional Information

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Effect of Pressure on the Stability and Electronic Structure of $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$

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Effect of Pressure on the Stability and Electronic Structure of $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$

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Structures and high-pressure phase transitions in $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ have been investigated using density functional theory calculations. The previously proposed structures of $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ which are chalcopyrite ($I42d$), rocksalt ($Fm3m$), wurtzite ($P6_3mc$) and CuAu-I ($P4m2$) have been fully investigated. Stabilities of these materials have been systematically studied up to 40 GPa using various approaches. We have confirmed the stability of the chalcopyrite structure up to 30 GPa for which the CuAu-I structure has been previously proposed. However, our calculation revealed that CuAu-I is not a stable structure under 32 GPa and 33 GPa for both $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$, respectively, which could explain the failure in several attempts to fabricate these materials under such conditions. We have also examined the pressure-dependence of the bandgap and electronic structure up to 30 GPa. We can conclude from our PDOS analysis that the applied pressure does not change the atomic state characters of electronic states near the top of valence and the bottom of conduction bands, but mainly modifies the dominant Zn-3d atomic state of the deep Bloch state at -1 eV below Fermi level.

Key words: Phase stability, elastic properties, high pressure, II–VI ternary alloys

INTRODUCTION

From the viewpoint of blue spectral range optoelectronic devices, the II–VI group semiconductors have recently drawn significant interest from scientists of various disciplines for their possibility of substituting the III–V group semiconductors, which have previously dominated the scene. This is due to their wide band gap property. In addition, the $\text{ZnO}_x\text{S}_{1-x}$ and $\text{ZnO}_x\text{Se}_{1-x}$ ternary alloys have also been synthesized for electronic and optical devices with a wide range of applications. There have been reports from researchers that changes in the concentration of anions in ternary alloys affect their electronic properties. Therefore, this would play a

crucial role in the future of band gap engineering.^{1–3} In the III–V group, it has been shown that a small amount of N doping results in a drastic reduction of the fundamental band gap.^{4,5} The band-anticrossing (BAC) model has been used to describe the electronic band structure of mismatched alloys. From the BAC, the anticrossing interaction between N localized states and conduction band states in a host semiconductor causes the band gap bowing effect.^{6,7} The larger bowing parameters of ZnOS and ZnOSe compared with those of GaNP and GaNAs was expected to be due to large differences in electronegativity of O, S and Se.⁸ Therefore, this could lead to a more adjustable energy gap range. $\text{ZnO}_x\text{S}_{1-x}$ and $\text{ZnO}_x\text{Se}_{1-x}$ were synthesized as typical II–VI ternary alloys for investigating the properties of this alloy group. However, to the best of our knowledge, there has so far been no experimental report on the crystal structure of these alloys in the concentration

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range of $0.4 < x < 0.6$.^{1,2} In addition, Rozale et al. reported the theoretical structure and electronic properties of $\text{ZnO}_x\text{S}_{1-x}$ for $0 < x < 1$ at ambient pressure using the Landau–Lifshitz theory of order–disorder transformations.⁹ They found that both chalcopyrite and CuAu-I are indistinguishable lowest energy structures of $\text{ZnO}_{0.5}\text{S}_{0.5}$. Fan et al. also investigated the structure and thermal stability of $\text{ZnO}_x\text{S}_{1-x}$ using the SQS method. In the case of $\text{ZnO}_{0.5}\text{S}_{0.5}$, they reported that the chalcopyrite structure was the lowest formation enthalpy at ambient condition.¹⁰ Although there have been such theoretical reports, it is still unclear which structure is stable at ambient condition owing to insufficient dynamical information of the system, e.g., phonon dispersion and structural dynamics at nonzero temperature.^{9,10} Moreover, the effects of pressure on their structural stability and electronic properties are still in doubt and need more research.

With this in mind, in this work, we investigate the structural stability of $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ ternary alloys and the corresponding electronic properties of the stable structures both at ambient and

high pressure using *ab initio* calculations. To confirm the stability of the two lowest enthalpy structures, the phonon dispersion, molecular dynamics and elastic constant calculations were also performed along with the pressure-dependent energy band gap. Knowledge of these properties would benefit electronic device designing and/or II–VI group ternary alloy synthesis.

CALCULATION DETAIL

Ab initio calculations were performed using the self-consistent field (SCF) method as implemented in Cambridge Serial Total Energy Package (CASTEP) code.^{11,12} The ground state properties of a unit cell such as electron density and total energy were obtained by solving the Kohn–Sham equation. The general gradient approximation of Perdew–Burke–Ernzerhof^{13,14} is used as the exchange–correlation term in the Kohn–Sham equation. The ultrasoft pseudopotentials¹⁵ are used for the representation of the ionic cores. The initial values of lattice parameters for ternary alloy semiconductors are obtained through Vegard’s law,¹⁶ which is

Table I. The lattice parameters, energy cutoffs and k -points of the four structures

Structure	a (Å)	c (Å)	Energy cutoff (eV)	k -points
Chalcopyrite	5.0411	10.055	700	$10 \times 10 \times 6$
Rocksalt	5.9155		700	$10 \times 10 \times 10$
Wurtzite	3.5760	5.8394	700	$10 \times 10 \times 10$
CuAu-1	3.6256	4.8386	700	$11 \times 11 \times 8$

Table II. The atomic positions of the $\text{ZnO}_{0.5}\text{S}_{0.5}$ ternary alloy

Wurtzite structure spacegroup $P6_3mc$ (156)			
O	0.666667	0.333333	0.840750
S	0.333333	0.666667	0.334673
Zn_1	0.333333	0.666667	0.334673
Zn_2	0.666667	0.333333	0.499143
Chalcopyrite structure spacegroup $I4_2d$ (122)			
O_1	0.000000	0.000000	0.000000
O_2	0.750000	0.250000	0.500000
S_1	0.500000	0.500000	0.000000
S_2	0.250000	0.750000	0.500000
Zn_1	0.375000	0.322245	0.447245
Zn_2	0.875000	0.927755	0.552755
Zn_3	0.677775	0.125000	0.052755
Zn_4	0.072245	0.625000	0.947245
Rocksalt structure spacegroup $Fm3m$ (225)			
O	0.000000	0.000000	0.000000
Zn_1	0.250000	0.250000	0.250000
Zn_2	0.750000	0.750000	0.750000
S	0.500000	0.500000	0.500000
CuAu-I structure spacegroup $P4m2$ (115)			
O	0.500000	0.500000	0.500000
Zn_1	0.500000	0.000000	0.706295
Zn_2	0.000000	0.500000	0.293705
S	0.000000	0.000000	0.000000

$$a(A_{1-x}B_xC)_{\text{alloy}} = (1-x)a_{AC} + xa_{BC} \quad (1)$$

where AC stands for ZnO and BC stands for ZnS or ZnSe . The lattice parameters of all the unit cells were obtained by the structural optimization at a given pressure and 0 K by means of the Brodyden–Fletcher–Goldfarb–Shanno,¹⁷ minimization scheme. The optimal lattice parameters of all the unit cells and calculation setting, i.e., energy cutoffs and Monkhorst–Pack grid sizes,¹⁸ are listed in Table I. The converged calculations were obtained within the following criteria: a total energy difference less than 5×10^{-7} eV/atom, Hellman–Feynman forces less than 0.01 eV/Å, the maximum ionic displacement within 0.0005 Å, and all the stress components within 0.02 GPa. The phonon dispersions were obtained by performing the calculation using the finite displacement,¹⁹ method with $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells for chalcopyrite and CuAu-I structures, respectively. The elastic constants, the average isotropic bulk modulus (B) and shear modulus (G) were obtained by applying the Voigt–Reuss–Hill (VRH) method,^{20,21} which is based on single-crystal elastic constants.

RESULT AND DISCUSSION

To study the structural evolution under high pressure, we first compares the total enthalpy, $H = E + PV$, of the II–VI group ternary alloys with four different structures, namely, chalcopyrite ($I\bar{4}2d$), rocksalt ($Fm\bar{3}m$), wurtzite ($P6_3mc$) and CuAu-I ($P\bar{4}m2$) at various pressures. The symbols in parentheses after the structure names stand for the space group symmetry symbol following the International Tables for Crystallography. In the process of selecting the structural model, we performed the special quasi-random structure (SQS)²² for a number of structures with two supercell sizes, i.e., $1 \times 1 \times 2$ and $1 \times 2 \times 2$ supercells, as given in Tables SI and SII in the supporting information. From the SQS result, the structures that represent a better randomness of the alloy (smaller P_i values) have significantly higher enthalpies than the chalcopyrite structure. Despite the fact that the chalcopyrite structure is poorer in representing the randomness (larger P_i values) than the others, it has the lowest enthalpy. Moreover, the structures that are better at representing the randomness have significantly higher enthalpies than the chalcopyrite structure, which is ~ 0.4 eV. Therefore, we can conclude that the chalcopyrite structure is the preferred structure of $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ in nature at ambient condition. The atomic positions of all four structures are shown in fractional coordinates for the primitive cell in Table II.

By considering the total enthalpy differences between the chalcopyrite and the other structures, we found that the lowest enthalpy structure of both $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ in the low-pressure

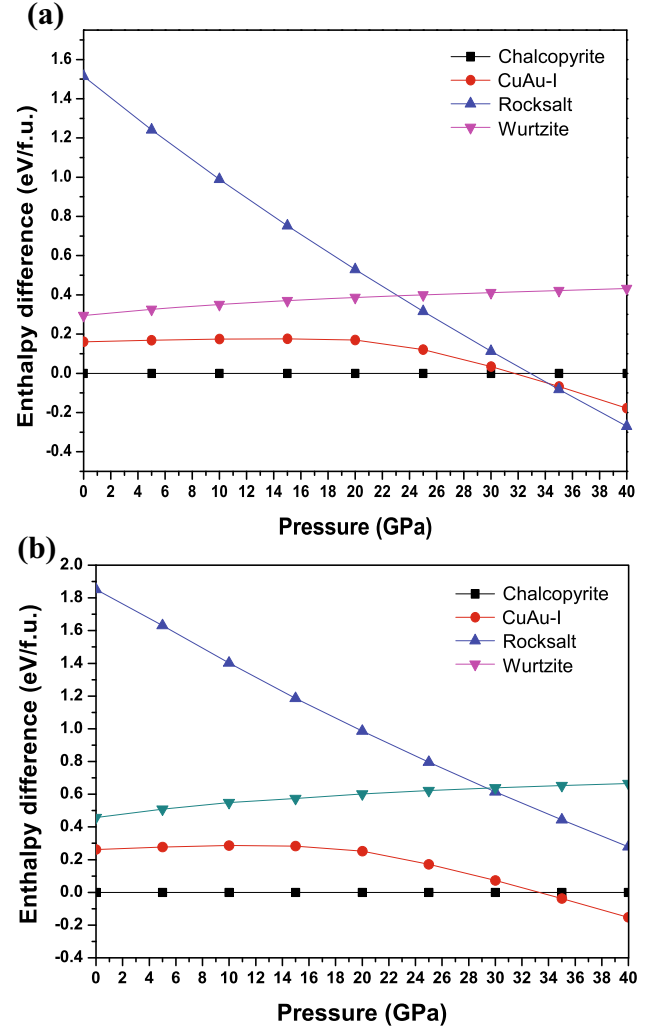


Fig. 1. The total enthalpy difference compared with the chalcopyrite structure per formulae unit versus pressure of (a) $\text{ZnO}_{0.5}\text{S}_{0.5}$ and (b) $\text{ZnO}_{0.5}\text{Se}_{0.5}$.

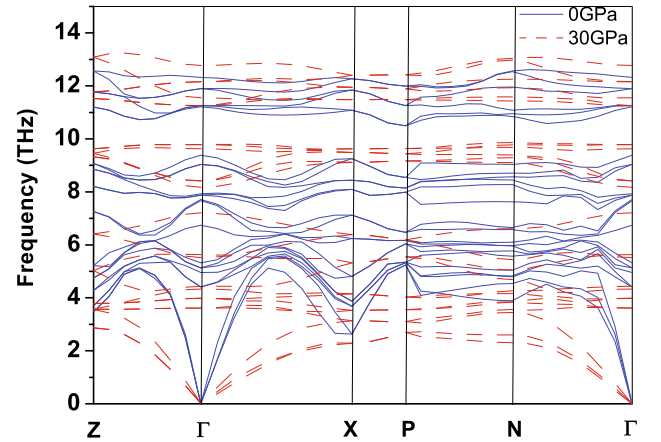


Fig. 2. The phonon dispersion of the $\text{ZnO}_{0.5}\text{S}_{0.5}$ chalcopyrite structure with various pressures.

regime is the chalcopyrite, and then they transform to CuAu-I at high pressure (see Fig. 1). The transition pressures are 32 GPa and 33 GPa for $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$, respectively. However, these results are only from the energetic point of view and it has to be noticed that the CuAu-I enthalpy is approximately 0.2 eV above chalcopyrite for both $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$. Therefore, they can be two candidates for a possible structure that exists in nature in this relatively low-pressure regime. Therefore, to justify which one is the most stable structure, the phonon calculation (for dynamical stability) has been performed and has also been checked for the elastic stiffness condition (for mechanical stability).²³ It was found that the chalcopyrite structure is stable up to 30 GPa for both $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$. According to Fig. 2, the chalcopyrite $\text{ZnO}_{0.5}\text{S}_{0.5}$ phonon dispersion shows the phase transition signal with the increasing pressure through softening of the acoustic phonon around the Z, X, P and N points. Nevertheless, up to 30 GPa, it never reaches a negative value. We note here that it is the same for chalcopyrite $\text{ZnO}_{0.5}\text{Se}_{0.5}$. In conclusion, for the relatively low-pressure regime, we found no imaginary phonon frequency and a non-negative value of the elastic stiffness constant for chalcopyrite up to 30 GPa. However, for CuAu-I, there exists the unsatisfactory elastic stiffness constant, C_{66} , (see Fig. 2 and Table III). Therefore, chalcopyrite is the only stable structure of $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ at ambient, which is in excellent agreement with the previous reports.^{9,10,24} As mentioned before, from the lowest enthalpy viewpoint and the acoustic phonon softening, the stable structure in the high-pressure regime (above the enthalpy transition pressures) for $\text{ZnO}_{0.5}\text{Se}_{0.5}$ above 33 GPa should be CuAu-I. For $\text{ZnO}_{0.5}\text{S}_{0.5}$ at

high pressure, above 32 GPa, the stable structure should be CuAu-I and then the rocksalt structure above 34 GPa. In contrast, the calculated phonon dispersions and elastic stiffness constants of chalcopyrite at high pressure satisfy the stability conditions, whereas those of CuAu-I do not, as there exist negative C_{66} and also an imaginary phonon frequency (see Fig. 3 and Table III). At 34 GPa, negative values of phonon frequencies of the rocksalt structure are also observed (see Fig. SI in supporting information). Thus, we can conclude that both the CuAu-I and rocksalt structures are not stable at high pressure. In order to confirm this result, the MD calculations were established. NPT²⁵ Gamma-point (Γ -point) MD calculations were employed for the chalcopyrite structure (Zn 108, O and S 54 atoms) and the CuAu-I structure (Zn 54, O and Se 27 atoms) systems at 300 K under 30 GPa.

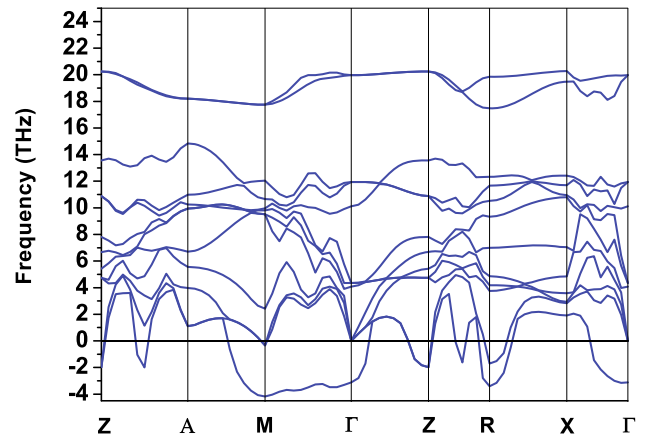


Fig. 3. The phonon dispersion of the CuAu-I structure at 32 GPa of $\text{ZnO}_{0.5}\text{S}_{0.5}$.

Table III. The elastic stiffness constant and bulk modulus of the chalcopyrite and CuAu-I structures with various pressures of $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$

Pressure (GPa)	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B (GPa)
$\text{ZnO}_{0.5}\text{S}_{0.5}$ Chalcopyrite							
0	145.2	100.8	104.7	152.1	66.4	57.5	117.9
10	178.7	141.4	146.7	185.0	58.5	46.9	156.6
20	208.9	186.0	192.5	233.5	48.0	38.3	197.0
30	235.2	230.8	236.5	278.5	40.3	33.6	232.7
$\text{ZnO}_{0.5}\text{S}_{0.5}$ CuAu-I							
25	308.9	196.5	162.1	127.6	26.7	-1.9	117.9
30	357.3	224.2	172.8	145.6	20.4	-36.3	137.4
35	395.2	248.7	184.0	170.5	18.2	-65.1	169.0
$\text{ZnO}_{0.5}\text{Se}_{0.5}$ Chalcopyrite							
0	84.5	60.3	48.7	117.0	44.5	43.1	66.3
10	143.7	115.6	120.9	163.8	31.4	46.7	128.2
20	198.7	177.3	186.4	232.3	52.5	49.6	188.0
30	207.6	199.5	207.2	256.1	60.2	63.2	203.3
$\text{ZnO}_{0.5}\text{Se}_{0.5}$ CuAu-I							
25	302.8	196.1	152.0	126.8	-1.2	-40.5	118.0
30	342.1	218.7	161.5	150.9	2.3	-81.6	149.9
35	372.2	237.1	173.9	176.3	14.9	-204.2	176.3

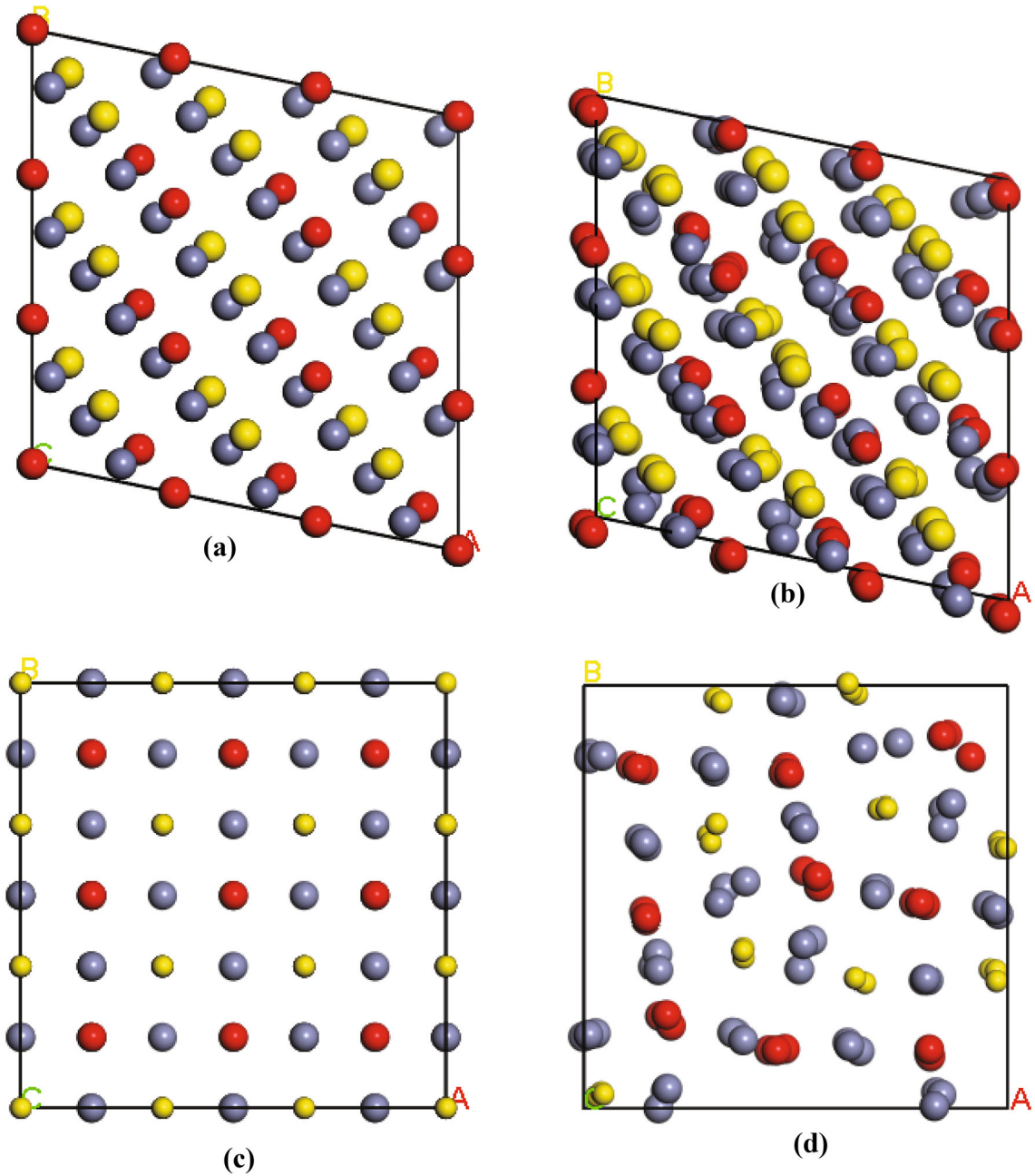


Fig. 4. (a) The initial optimum supercell of $\text{ZnO}_{0.5}\text{S}_{0.5}$ in the chalcopyrite structure at 0 GPa and 0 K. (b) The final supercell at 30 GPa and 300 K. (c) The initial optimized supercell of $\text{ZnO}_{0.5}\text{S}_{0.5}$ in the CuAu-I structure at 0 GPa and 0 K. (d) The final supercell at 32 GPa 300 K.

The results from the MD calculations of the chalcopyrite and CuAu-I structures of $\text{ZnO}_{0.5}\text{S}_{0.5}$ at 30 GPa and 300 K are shown in Fig. 4a–d. By comparing with their respective initial structures (Fig. 4a and c), Zn (gray) S (yellow) and O (red) atoms fluctuate about their equilibrium point owing to the temperature effect; this result converged within 1 ps simulation time. Nevertheless, they are still in the same crystal plane as the initial supercell. In contrast, for CuAu-I structure, Zn (gray) atoms in Fig. 4 [100] and [010] planes in the

final supercell (Fig. 4d) are distorted and tend to change the supercell into another structure after 5 ps of MD calculation time, which shows that this structure is not vibrationally stable. This indicates that the chalcopyrite structure was stable at 30 GPa and 300 K even under the temperature effect, as demonstrated by the MD calculation. Combining this result with the non-negative elastic stiffness constant and the phonon dispersion, these are the strong evidence which enables us to conclude that the chalcopyrite structure is the most stable high-

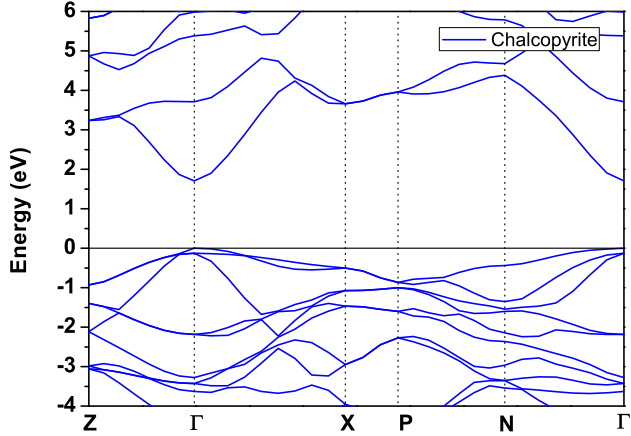


Fig. 5. The electronic band structure of the chalcopyrite structure at 0 GPa (a) $\text{ZnO}_{0.5}\text{S}_{0.5}$.

Table IV. The energy gap of $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ with various pressures

Pressure (GPa)	$\text{ZnO}_{0.5}\text{S}_{0.5}$ Band gap (eV)	$\text{ZnO}_{0.5}\text{Se}_{0.5}$ Band gap (eV)
0	1.19, 2.83, ²⁷ 1.44, ⁹ 1.39 ²⁴	0.68, 0.694 ²⁴
10	1.48	1.00
20	1.70	1.26
30	1.92	1.48

pressure structure up to at least 30 GPa. These results are also in excellent agreement with the ternary alloys such as $I\text{-III-VI}_2$ and $II\text{-IV-V}_2$ in which they tend to be stable in the chalcopyrite structure at ambient pressure and room temperature.²⁶ In addition, the phonon softening and decreasing of C_{66} with the increasing pressure of the chalcopyrite phase suggest a high possibility of phase transition at a higher pressure than our calculated ones.

Besides identifying the stable structure under pressure, we also calculated the electronic structure of chalcopyrite $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ at ambient and high pressure up to 30 GPa using the GGA exchange correlation functional. The results are shown in Fig. 5. We found that both the chalcopyrite $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ are direct band gap semiconductors at the gamma point. Their corresponding energy gaps at 0 GPa are 1.193 eV and 0.675 eV for $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$, respectively. In addition, our calculated energy gaps of chalcopyrite $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ at various pressures compared to those obtained from previous works are listed in Table IV.

Furthermore, we investigated the atomic state characters of the electron Bloch wave function in both valence and conduction band at ambient pressure and 30 GPa by computing the total density of states (DOS) and the partial density of states

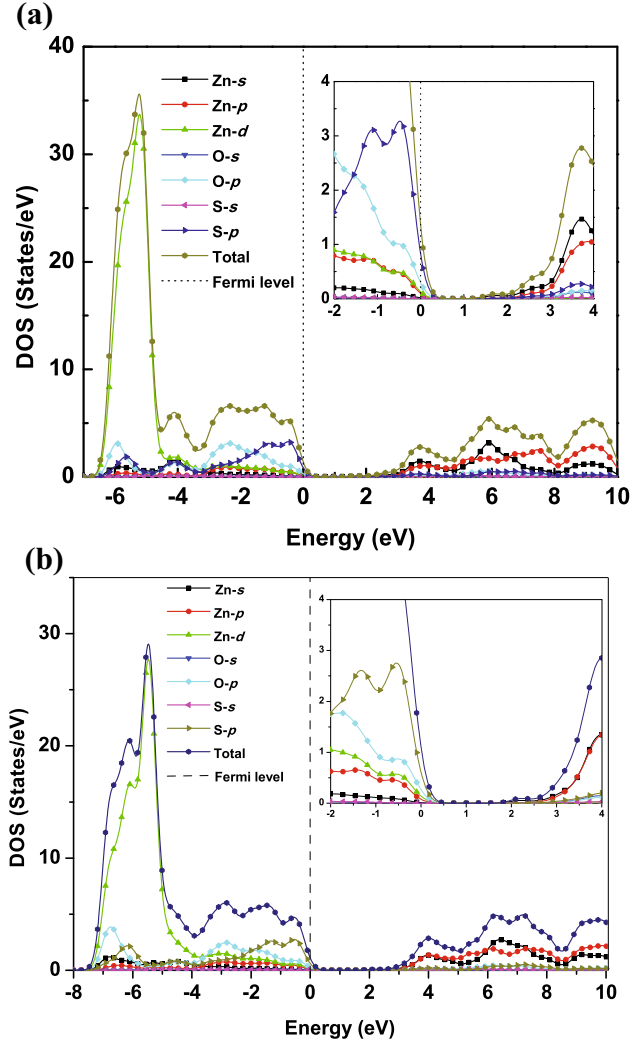


Fig. 6. The DOS of the chalcopyrite structure of $\text{ZnO}_{0.5}\text{S}_{0.5}$ at (a) 0 GPa and (b) 30 GPa. The color representations of the atomic orbitals are as following fashion: red for the Zn atomic orbital, blue for the O atomic orbital, yellow for S atomic orbital. The s orbitals are represented by the solid line, p by the dotted line, d by the dashed line, and total DOS by the darker dashed line (Color figure online).

(PDOS) for both $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$. The results are shown in Fig. 6. From Fig. 6a, the DOS and PDOS of $\text{ZnO}_{0.5}\text{S}_{0.5}$ show that, in the case of $\text{ZnO}_{0.5}\text{S}_{0.5}$, the top of the valence band (VB) is occupied by S-3p and p-d hybridization (Zn-3d, Zn-4p, S-3p, and O-2p), while the conduction band (CB) is dominated by Zn-pd hybridization. At 30 GPa (Fig. 6b), the bottom of CB slightly shifts away above the Fermi level which corresponds to the wider band gap at higher pressure. Moreover, the applied pressure causes VB broadening and S-3p PDOS lowering at around -1 eV below the Fermi level (see Fig. 6a and b). For $\text{ZnO}_{0.5}\text{Se}_{0.5}$, the DOS and PDOS (not shown) near the band edge are almost identical to those of $\text{ZnO}_{0.5}\text{S}_{0.5}$. The difference is just that the contribution is coming from Se-4p instead of S-3p. In addition, we also computed

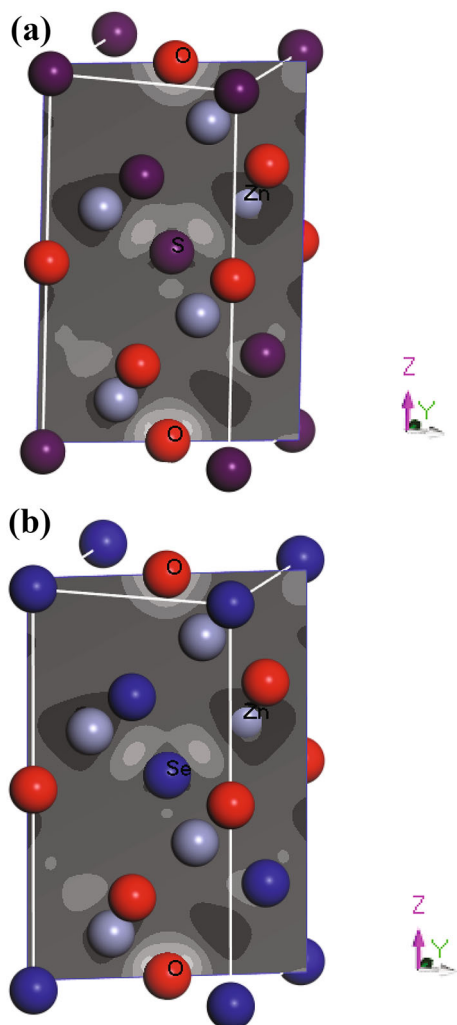


Fig. 7. The light (dark) color indicates the increasing (decreasing) of electron density relative to an isolated atom of Zn (gray), O (red), Se (blue) and S (purple) for (a) $\text{ZnO}_{0.5}\text{S}_{0.5}$ (b) $\text{ZnO}_{0.5}\text{Se}_{0.5}$ at 0 GPa (Color figure online).

the DOS of the chalcopyrite structure at 0 GPa using a spin-polarized scheme by giving an initial spin to the system. The optimized total spin calculation result reveals that the total spin of the chalcopyrite structure become zero, so the DOS of both spin-up and spin-down are the same (see Fig. SII in the supporting information).

We also analyzed the electron density difference of both chalcopyrite alloys at 0 GPa, as shown in Fig. 7. This indicates that bonding between Zn–O and Zn–S (Se) have ionic characters. The dark zone near the Zn cation indicates that the electrons transfer from the Zn cation to the O and S (Se) anions. Electron densities slightly increase nearer to O than S (Se) compared to the isolated O and S atoms due to the higher electronegativity of the O atoms. In addition, at high pressure up to 30 GPa, we found that the nature of the bonding between Zn, O, and S (Se) is still ionic.

CONCLUSION

The structural stability of five phases of $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$ has been examined at ambient pressure and high pressure up to 40 GPa within the GGA approximation density functional theory. The total enthalpy, phonon dispersions and MD calculations have been used for structural stability verification at both ambient and high pressure. From our results, it turns out that chalcopyrite is a stable structure up to 30 GPa for both alloys. On the other hand, even though the CuAu-I has the lowest enthalpy at 32 GPa and 33 GPa for $\text{ZnO}_{0.5}\text{S}_{0.5}$ and $\text{ZnO}_{0.5}\text{Se}_{0.5}$, respectively, it is an unstable structure. Moreover, their 30 GPa and room temperature MD results do not converge within 5 ps simulation time and there is no sign of convergence from our calculation. This implies that the CuAu-I structure is an unstable structure under those conditions. Moreover, in this work, we report the equilibrium lattice parameters, bulk modulus under ambient pressure and electronic structures at both ambient and high pressures. The electronic structures show that they are direct band gap at gamma point semiconductors and that their energy band gaps vary in the same fashion with the increasing pressure: the higher the pressure, the wider the band gap. For both alloys, the PDOS analysis shows that, up to 30 GPa, the applied pressure does not change the atomic state characters of the electronic states near the top of the valence and the bottom of the conduction bands, but mainly modifies the dominant Zn-3d atomic state of the deep Bloch state at -1 eV below Fermi level.

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ELECTRONIC SUPPLEMENTARY MATERIAL

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The High-Pressure Superconducting Phase of Arsenic

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Ab initio random structure searching (AIRSS) technique is predicted a stable structure of arsenic (As). We find that the body-centered tetragonal (bct) structure with spacegroup $I4_1/acd$ to be the stable structure at high pressure. Our calculation suggests transition sequence from the simple cubic (sc) structure transforms into the host-guest (HG) structure at 41 GPa and then into the bct structure at 81 GPa. The bct structure has been calculated using *ab initio* lattice dynamics with finite displacement method confirm the stability at high pressure. The spectral function α^2F of the bct structure is higher than those of the body-centered cubic (bcc) structure. It is worth noting that both bct and bcc structures share the remarkable similarity of structural and property. Here we have reported the prediction of temperature superconductivity of the bct structure, with a T_c of 4.2 K at 150 GPa.

The group-V element is one of central interest in a discipline in high-pressure physics and continues to attract a lot of attention as it has an incommensurate host-guest (HG) structure. The existence of a HG structure in the group-V elements is observed in As-III, Sb-IV, and Bi-III¹. They are a common high-pressure structure among the elemental metals. With increasing pressure, for As, a HG structure transforms into a body-centered cubic (bcc) structure at pressure 97 GPa. For Sb, a HG structure transforms into a bcc structure at pressure 28 GPa. For Bi, a HG structure transforms into a bcc structure at pressure 8 GPa. It is worth noting that the bcc crystal structure of them is the most stable structure at the highest pressure.

Arsenic (As) maintains the bcc crystal structure up to at least 122 GPa², the structural phase transition under high pressure is influenced by *s-d* hybridization from lower pressure to higher pressure phases³. At ambient pressure, As possesses a rhombohedral As-type (As-I) structure and transforms into a simple-cubic (As-II) structure at 25 GPa. At higher pressure, it transforms into a body-centered monoclinic host-guest (As-III) structure at 48 GPa, and then into a body-centered cubic (As-IV) at 97 GPa. Moreover, As is also presented by experimental study with superconducting transition temperature (T_c) of 2.5 K and 32 GPa⁴.

Several metals are superconducting at high pressure^{5–10}, with increasing pressure, it indicates that the superconducting transition temperature (T_c) is also increasing. A striking example of the group-II elements, Ca has been reported highest T_c among elemental metals, with a T_c of 29 K at 216 GPa⁵. Sr and Ba have been reported to possess a T_c of 8 K at 58 GPa⁶, and a T_c of 5 K at 18 GPa⁷, respectively. Moreover, the group-III elements, the T_c of Y has reached of 20 K at 115 GPa^{8,9} and Sc has also observed to possess a T_c of 19.8 K at 107 GPa⁹. Furthermore, the group-V element, As has reached a maximum T_c of 2.7 K at 24 GPa¹⁰, Sb has reported to possess a T_c of 3.6 K at 3.5 GPa¹⁰, and Bi has reported to possess the highest T_c among the group-V element, with the T_c of 8.7 K at 9 GPa¹⁰. Recently, Chan *et al.*¹¹ predicted the T_c of the simple cubic (sc) structure in the pressure range 30–50 GPa with the T_c as high as 2.99 K at 30 GPa. They also reported that the T_c of the sc structure decreases monotonically with increasing pressure T_c at 0.58 K and 50 GPa.

An important and a fundamental question remains to predict a new phase of As in the pressure range 100–300 GPa because there is no high-pressure phase beyond the bcc structure². Thus, the searching technique leads to the discovery of high-pressure As structure. In addition, there is no reported the T_c for the predicted structure in As. It would be interesting to investigate the role of electron-phonon coupling (EPC) in order to predict T_c at high pressure.

In this work, in order to understand the predicted structure at high pressures, it is important to obtain as much information as possible about the structure. Hence, there have also been opened questions for As under

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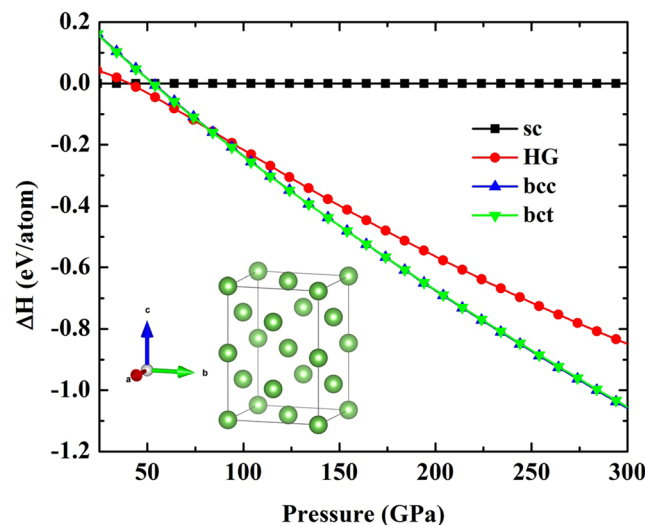


Figure 1. Comparison of the enthalpies of As phases up to 300 GPa. As structures relative to the sc structure at 0 K.

extreme compression: (i) what is a new structure beyond the bcc structure at high pressure? (ii) Is the metallic high-pressure phase a superconductor? In order to address these problems, we report a theoretical investigation of the theoretical prediction which presents a new lowest enthalpy phase of As.

Results and Discussion

Our calculation has searched at pressures above 100 GPa, we find the lowest enthalpy structure of As which is the body-centered tetragonal (bct) structure with spacegroup $I4_1/acd$. We also show that the simulated crystal structure of the bct structure is obtained as implemented in VESTA¹² (Fig. 1). The optimized structural parameters for the bct structure are $a = 4.072 \text{ \AA}$ and $c = 5.802 \text{ \AA}$ with As atoms located at 8 a symmetry site (0, 0.5, 0.25). In Fig. 1, we present the enthalpies of different As phases with respect to the sc structure which are plotted as a function of pressure. Crossing points of curve from each structure represent the sc structure transforms into the HG structure at 41 GPa and into the bct structure at 81 GPa as shown in Fig. 1.

With increasing pressure, the transition sequence is successfully observed by the experimental study¹. The low-pressure sc structure of As transforms into the monoclinic host-guest (HG) structure at pressure 48 GPa, and then into the body-centered cubic (bcc) structure at pressure 97 GPa¹. On the contrary, our calculation proposes that transition sequence should be from the sc structure transforms into the HG structure at pressure 41 GPa and then into the bct structure at 81 GPa. Moreover, we show that the bcc and bct structures of As are very close in enthalpy which the bct structure has only slightly lower enthalpy than the bcc structure by 1 meV/atom.

Interesting, the bcc structure is the super-spacegroup ($Im\bar{3}m$) and the bct structure is sub-spacegroup ($I4_1/acd$) of the bcc structure which suggests that the bct structure is a possible coexistence phase with the bcc structure. Our enthalpy calculation reveal that both the bcc and bct structures are remarkably closed overpressure range 100 to 300 GPa.

In fact, the bcc and bct structures have very similar crystal structures. In order to determine difference between the bcc and bct structures, Fig. 2 shows a comparison of crystal structures by simulating powder diffraction patterns at 100 GPa. The peak 200, 211, 220, and 310 of the bct structure are distorted from the bcc structure because the bct index peaks split into two peaks with respect the bcc structure. The bct has been confirmed with slightly distorted parameter a/c lowered by 1% with respect to the bcc structure.

This calculation leads to a new stable structure, we identify the dynamic stability of the bct structure by the phonon dispersion relation. The lack of imaginary frequencies provides a confirmation that the bct structure is stable at pressure 300 GPa (Fig. 3).

In the whole pressure interval of 150–300 GPa, we use a fixed value for the effective Coulomb interaction parameter. It is worth noting that the value of effective Coulomb interaction parameter also used $\mu^* = 0.10$, which is assumed for all metals by Allen and Dynes¹³. In fact, the μ^* plays an important role to give the T_c at high pressure. Especially, the nature of As is observed that the T_c is decreased with increasing pressure through the evolution of μ^* ¹¹. We also explored the effects on T_c of changing μ^* from 0.10 to 0.18^{13–15} at 150 GPa as shown in Table 1. Thus, we did consider the effect of $\mu^* = 0.10$ on the predicted T_c because it gives the highest T_c among the evolution of μ^* . Our prediction concerning the superconducting phase of As at high pressures would be experimentally confirmed. At 150 GPa, the spectral function α^2F of the bct structure is higher than those of the bcc structure around frequency region 6–13 THz. Likewise, the integrated λ of the bct structure is also higher than the bcc structure (Fig. 4). Moreover, it exhibits the metallization and it predicts to give temperature superconductivity in the bct structure, with the T_c of 4.2 K at 150 GPa as can be seen Fig. 5.

At high pressure, pressure-induced superconductivity shown in Fig. 5. We also explore the effects on T_c of increasing pressure. Our calculations reveal T_c both the bcc and bct structures with increasing pressure, which

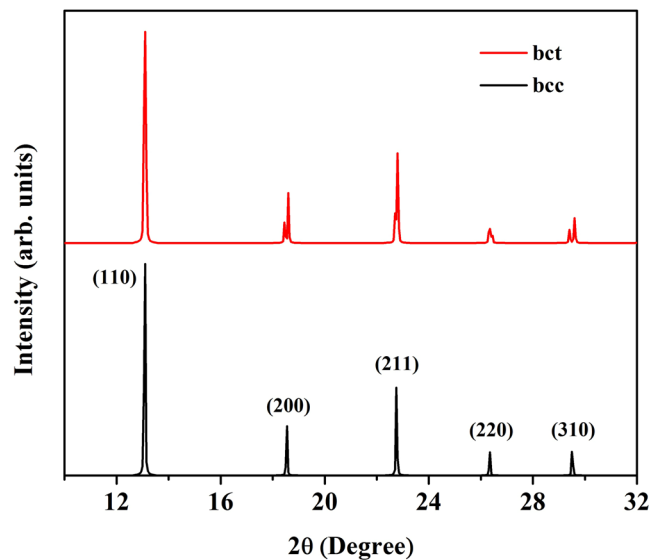


Figure 2. Simulated x-ray powder diffraction patterns of the bcc structure (black) and the bct structure (red).

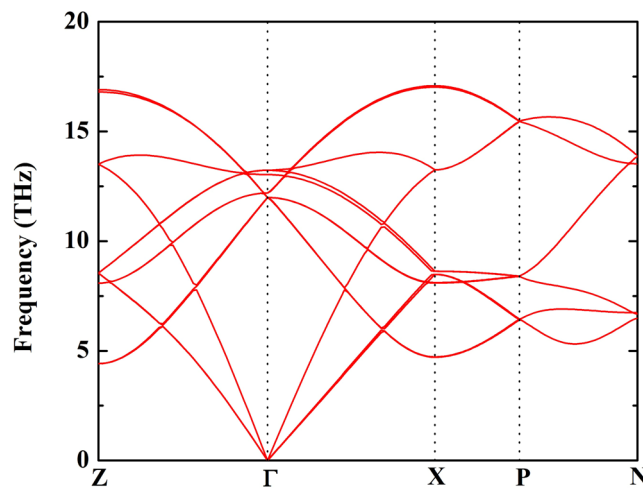


Figure 3. The dynamical harmonic stabilization of the bct structure at pressure 300 GPa.

Structures	T _c (K)			
	$\mu^* = 0.10$	$\mu^* = 0.13$	$\mu^* = 0.15$	$\mu^* = 0.18$
bct	4.2	2.5	1.6	0.7
bcc	3.4	2.0	1.3	0.5

Table 1. Calculated effective Coulomb interaction parameter μ^* , and superconducting transition temperature T_c for As at 150 GPa.

generally shows monotonic decreasing behaviours. Especially, the λ of the bct structure is higher than the bcc structure at 150 GPa which has led to suggestions for possible the highest T_c of the bct structure. It indicates that the T_c of the bct structure is higher than the bcc structure, where it possesses the highest T_c of 4.2 K.

Above 150 GPa, we find that the T_c of the bct structure is lower than the bcc structure as well as T_c gradually decreases with pressure. We calculate λ and the averaged phonon frequency (ω_{log}) as a function of pressure of the bcc and bct structures. The λ of the bcc and bct structures decrease monotonically between 150 GPa and 300 GPa, respectively. The ω_{log} of the bcc and bct structures increase monotonically between 150 GPa and 300 GPa, respectively as can be seen the inset in Fig. 5.

Moreover, we strongly suggested that the bct structure is not superconducting phase above 300 GPa. This is due to the fact that the bct structure remains in the metallic state at 300 GPa, we propose that it becomes a normal metallic state since the λ of the bct structure is poorly characterized, with increasing pressure. It should be noted that the λ is weakly coupling for calculation the T_c . Here again, the μ^* plays a key role, in the sense that the

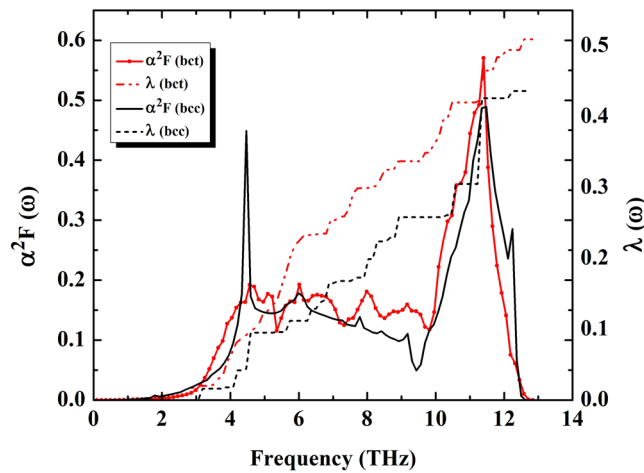


Figure 4. Spectral function $\alpha^2F(\omega)$ and integrated λ as a function of frequency of As at pressure 150 GPa.

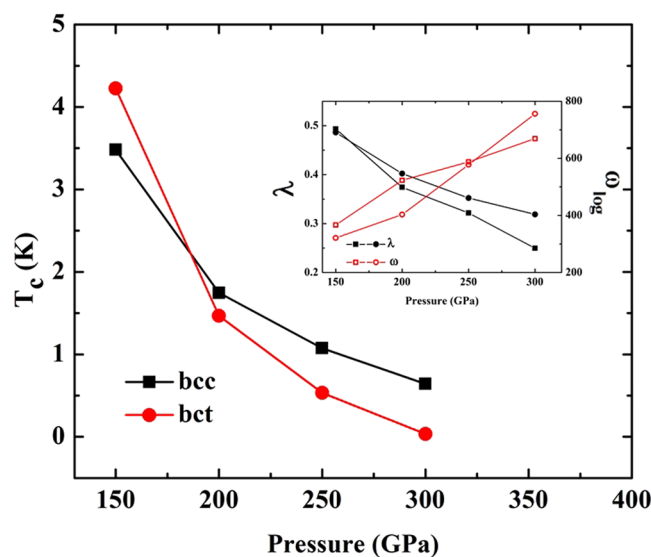


Figure 5. Superconducting T_c of As as a function of pressure. The square and the circle symbols represent calculations for the bcc and bct structures, respectively. The inset shows calculated electron-phonon coupling for the bcc structure (filled square) and the bct structure (filled circle) and averaged phonon frequency as a function of pressure for the bcc structure (hollow circle) and the bct structure (hollow square).

increasing pressure induces the T_c of the bct structure decreasing. This might lead to new interpretation of the experimental data above 150 GPa.

Conclusion

In conclusion, the AIRSS technique reveals the new stable bct structure with spacegroup $I4_1/acd$ of As at high pressure. We show that structural phase transformation of As from sc to HG to bct at 41, and 81 GPa, respectively. We confirm that bct is thermodynamically stable above 81 GPa and our result show that it is also dynamically stable at 300 GPa. Therefore, we suggest the transitions sequence from the sc structure transforms into the HG structure at 41 GPa and then into the bct structure at 81 GPa. We find that the T_c of the bct structure is the maximum around 4.2 K at 150 GPa. It is worth noting that from our calculation both bct and bcc structures share remarkable similarity in structural and property. Thus, both structures may be observed by experimental at low temperature and high pressure.

Methods

We used *ab initio* random structure searching (AIRSS) technique^{16,17} and *ab initio* calculation of the Cambridge Serial Total Energy Package (CASTEP)¹⁸ to predict the candidate crystal structures of As under pressure. The AIRSS technique is used to predict the crystal structures of materials^{16,17,19–22}. A plane-wave basis-set energy cut-off of 280 eV and an initial Brillouin-zone (BZ) sampling grid of spacing $2\pi \times 0.07 \text{ \AA}^{-1}$ were used for this calculation. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parametrization²³

for the exchange-correlation functional was used for the structure searching. The AIRSS technique generated unit cells of random shapes with reasonable volumes.

We studied simulation cells containing 2, 4, 6, 8, 10, and 12 atoms of As at pressure 100, 150, 200, 250, and 300 GPa. The cell shapes and atomic positions are then relaxed to the ground state structure at each pressures. The AIRSS technique calculated the enthalpies of the phases at any pressure by using the simple linear approximation¹⁷.

$$H(p) \simeq H(p_s) + V_s(p - p_s), \quad (1)$$

Where p is any pressure and V_s is the volume of the phase at p_s . The quantities $H(p_s)$, p_s and V_s are calculated for each relaxed into higher-symmetry space groups obtained in a search.

We are here presented electronic structure by using the GGA-PBE²³ for the exchange-correlation functional to density functional theory. We employed the projector augmented wave (PAW) method²⁴, as implemented in the Vienna ab initio simulation package (VASP)²⁵. The PAW potential with a 15-electron ($3d^{10}4s^24p^3$) for As has been employed with plane waves basis set up to a cutoff energy of 500 eV and the initial BZ sampling grid of spacing $2\pi \times 0.02 \text{ \AA}$.

All structures were relaxed and their equations of state were obtained by fitting to the calculated energy-volume data with the third-order Birch-Murnaghan equation. We then calculated the enthalpy-pressure relationship and the high pressure phase from the experimental information¹.

The phonon dispersion of candidate structure was calculated by *ab initio* lattice dynamics with finite displacement method, as implemented in VASP code and the phonopy package²⁶.

We calculated the EPC with density functional perturbation theory²⁷. The plan waves basis set was expanded with a kinetic energy cutoff of 60 Ry. The calculation studies presented here are based on the GGA-PBE. We employed PAW method as implemented in Quantum Espresso²⁸. The BZ integrations in the electronic and phonon calculations were performed using MP meshes. Both the meshes of k-points for electronic states and the meshes of phonons were used in these calculation. For As-IV, individual phonon calculations were performed on the first BZ on $4 \times 4 \times 4$ q-meshes with a $12 \times 12 \times 12$ k-points mesh. For high-pressure candidate structure, individual phonon calculations were performed on the first BZ on $4 \times 4 \times 4$ q-meshes with a $8 \times 8 \times 8$ k-points mesh. For As-IV, The EPC matrix elements were computed in the first BZ on $4 \times 4 \times 4$ q-meshes using individual EPC matrices obtained with a $24 \times 24 \times 24$ k-points mesh. For the bct structure, The EPC matrix elements were computed in the first BZ on $4 \times 4 \times 4$ q-meshes using individual EPC matrices obtained with a $16 \times 16 \times 16$ k-points mesh. We calculated T_c using the Allen-Dynes equation¹³, which is corresponded for $\lambda < 1.4$,

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right], \quad (2)$$

where $\omega_{\log}$ is the averaged phonon frequency. We used effective Coulomb interaction parameter $\mu^* = 0.10$. It is assumed by the original Allen-Dynes formula¹³.

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Author Contributions

Author contributions: P.T., R.A., and T.B. designed research; P.T. and W.L. performed research; P.T., W.L., R.A., and T.B. analyzed data; and P.T., W.L., R.A., and T.B. wrote the paper.

Additional Information

Competing Interests: The authors declare no competing interests.

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Structural prediction of host-guest structure in lithium at high pressure

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Ab initio random structure searching (AIRSS) technique is used to identify the high-pressure phases of lithium (Li). We proposed the transition mechanism from the fcc to host-guest (HG) structures at finite temperature and high pressure. This complex structural phase transformation has been calculated using *ab initio* lattice dynamics with finite displacement method which confirms the dynamical harmonic stabilization of the HG structure. The electron distribution between the host-host atoms has also been investigated by electron localization function (ELF). The strongly localized electron of p bond has led to the stability of the HG structure. This remarkable result put the HG structure to be a common high-pressure structure among alkali metals.

Lithium (Li) is one of the most fascinating element in the periodic table and continues to attract a lot of attention due to the outstanding properties suitable for several applications, for example, battery technology¹, hydrogen storage², high electrical resistance³, high superconducting transition temperature⁴. Moreover, Li is one of central interest in many disciplines, especially in high pressure physics. It is the huge interest in the theoretical study⁵ and the experimental observation⁶ as there is the stability of some of the complex structure. While the high-pressure phase of alkali metals, namely, sodium, potassium, and rubidium, have also been found to be the complex structure. The complex structure of alkali metals were reported to have the host-guest (HG) structure^{7–9}. Interestingly, one important question that remains unresolved is the HG structure in Li at high pressure. Recently, T. Matsuoka *et al.*¹⁰, reported structural phase transitions in lithium (Li) using experimental apparatus. The reported transition sequence is $Im\bar{3}m$ (0–8 GPa) $\rightarrow$ $Fm\bar{3}m$ (8–39 GPa) $\rightarrow$ $R\bar{3}m$ (39–44 GPa) $\rightarrow$ $I\bar{4}3d$ (44–73 GPa) $\rightarrow$ $C2mb$ (73–80 GPa) $\rightarrow$ $C2cb$ (80–120 GPa) $\rightarrow$ $Cmca$ (>120 GPa)^{6,11–13}. However, it does not have the HG structure at any pressure among such sequence.

Goncharov *et al.*¹⁴ have suggested that Li can be an incommensurate HG structure since crystal structure at the pressure above 50 GPa has never been unveiled. They suggested the distances between metal atoms in the incommensurate guest chains may be substantially shorter than expected, causing an increase of the phonon frequency because the host modulates the guest atom positions. However, a clear explanation based on the theoretical aspect has not yet been achieved. Among structural prediction in the crystal structures of materials, Li is one of the most from interested structural predictions at high pressure^{5,15–17}. The theoretical study revealed novel structures in Li^{15–17} at high pressure but they have not found the HG structure. Hence, the question regarding the stability of HG structure can be related to the broader issue, namely, the importance of the accuracy of *ab initio* calculation used in the prediction.

In a recent theoretical study by Pickard and Needs¹⁸, the low-pressure close-packed structures were reported to be able to transform into the HG structure at terapascal pressures. They have shown that the formation of *s-p* hybridized bonds described by a two-component model consisting of positive ions and interstitial electron blobs at very high pressures. Interest in the formation of *s-p* hybridized bonds began to point out that it can be an incommensurate HG structure¹⁴. At this point, the observed accumulations of electrons on the interstitial sites can determine the stable structure.

In this study, we explore an existence of HG in Li metal by performing *ab initio* random structure searching (AIRSS) method¹⁹. This approach is predicted the structure which is confirmed the previously proposed

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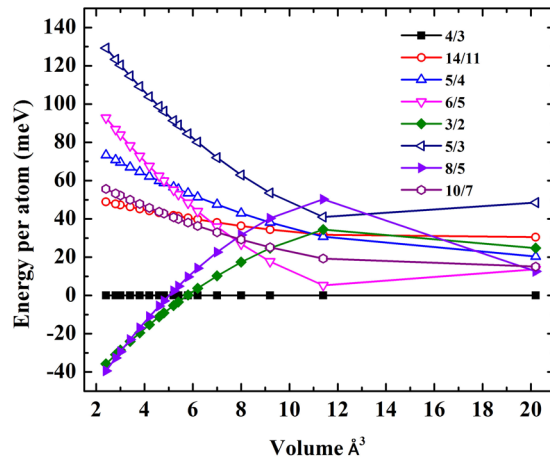


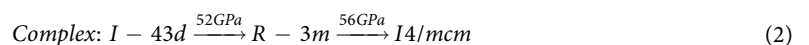
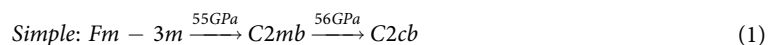
Figure 1. Total energies of various commensurate analogues with respect to the energy of the commensurate supercell with commensurate value $c_H/c_G = 4/3$ as a function of volume/atom.

experimental observation¹⁴. Moreover, we present that the discoveries of the transitions sequence can lead to the new interpretation of Li. We report the stable structure through the observation of the formation of *s-p* hybridized bonds in Li. The importance of this result is that it clearly shows the formation mechanisms of the HG structure at high pressure. Our findings provide a significant advance in the understanding of the behavior of solid Li at high pressure.

Results and Discussion

We find the experimentally observed unknown phase to be stable in a range of pressure above 50 GPa¹⁴. Based on structural predictions using AIRSS technique, we have obtained the lowest-enthalpy crystal structure with space group *I4/mcm*. We refer the predicted stable structure that the *I4/mcm* is the periodic approximations to the incommensurate host-guest structure as the new structure of high-pressure Li of *I4/mcm* symmetry is composed of two structures. In fact, it is well known that each of the host-guest structures has the same host framework consisting of eight-atom units, and the number of guest atoms varies. The HG structure is described by approximating with a commensurate supercell along the *c* axis. Thus, based on this structural model, the definition of approximating with a commensurate supercell along the *c* axis can be written as c_H/c_G where c_H is the host lattice along the *c* axis and c_G is the guest lattice along the *c* axis. To treat the parameter of c_H/c_G , the HG structure has kept the value of c_H/c_G channels in along the *c* axis of the host structure. The lowest total energy of the HG structure is calculated by approximating with a commensurate supercell along the *c* axis. This is due to the fact that the HG structure is the aperiodic structure along the *c* axis of the host structure as the component of the guest structure made up of chains that lie in this channel. Therefore, it is well known that the guest structure is an incommensurate with the host structure. In order to accurately calculate the dependence of c_H/c_G of the HG on applied pressure, we present the stability of the HG structure through various commensurate analogues with respect to the $c_H/c_G = 4/3$. By approximating the complex HG structure, $c_H/c_G = 4/3$, a commensurate supercell of the host structure is generated $3c_H$ and also the guest structure with $4c_G$. We choose the following sets of the parameter for c_H/c_G : 4/3, 14/11, 5/4, 6/5, 3/2, 5/3, 8/5, and 10/7, which yield two kinds of structures as far as symmetry is involved. Our calculations determine a stable structure by calculating total energies of various commensurate analogues with respect to the energy of $c_H/c_G = 4/3$ commensurate supercell as a function of volume per atom, which can be seen in Fig. 1. Our calculations indicate a dramatic increase in the energy difference of the HG structure. The $c_H/c_G = 4/3$ is the most energetically stable over a wide range of volumes. At the maximum pressure, it shows the compressibility transformation of the HG structure. With increasing pressure, our calculation propose an incommensurate-to-incommensurate phase transition by examining the c_H/c_G . In the case of the HG structure, we have predicted that the 4/3 (1.333) transforms into the 3/2 (1.5) and transforms into the 8/5 (1.6), respectively.

From full details of the total energies of various commensurate procedures, we use the commensurate value of 4/3 for describing the stable structure. Enthalpies of different phases are shown with respect to the enthalpy of the *I43d* as can be seen in Fig. 2. We have precisely indicated that it is the thermodynamically stable structure over a wide range of pressures. We find that the crystal structure of Li exhibits different origins in two-phase transition sequences at the pressure around 50 GPa as shown below:



The first transition sequence is associated with the simple structural phase transformation in which the fcc structure transforms into the *C2mb* structure and then the *C2cb* structure, respectively. While the *C2mb* is stable in a very narrow pressure range, the *C2cb* structure is revealed to be the most enthalpy favourable. The second

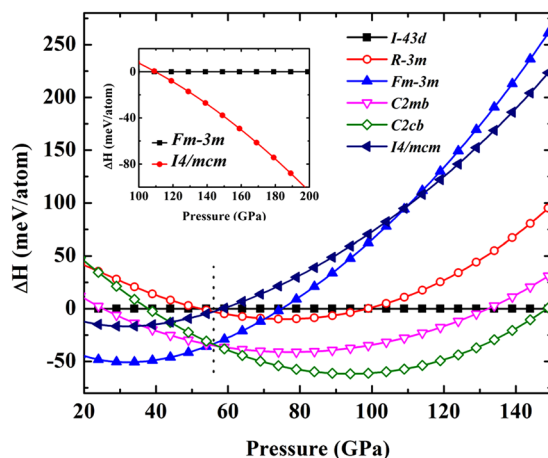


Figure 2. Comparison of the enthalpies of Li phases up to 150 GPa. Li structures relative to the $I\bar{4}3d$ structure at 0 K. The inset shows the enthalpy of the fcc structure with the $I4/mcm$.

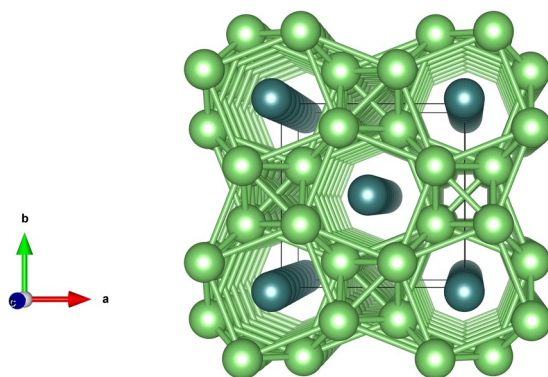


Figure 3. The crystal structure of the host-guest structure of Li. The host structure (dark green atoms) with guest chains (light green atoms) is shown in a c -axis projection.

transition sequence is relevant to the complex structural phase transformation at finite temperature by determining enthalpy-pressure (Fig. 2), in which the $I\bar{4}3d$ structure transforms into the $R\bar{3}m$ structure and then the $I4/mcm$ analogue. This result opens up the possibility that different origins in two-phase transition sequences may allow the $I4/mcm$ structure to be energetically stabilized even for pressures above 56 GPa for the complex structural phase transformations. Specifically, we propose that the Li metal is likely to crystallize in the $I4/mcm$ structure at high temperature.

Furthermore, the $I4/mcm$ structure is predicted to be the thermodynamically stable structure at high pressure. As displayed in the inset in Fig. 2, the $I4/mcm$ structure become more favorable than the fcc structure above 110 GPa. This is due to the fact that the enthalpy of fcc structure is lower than that of the $I4/mcm$ structure at low pressure but higher at high pressure. Interestingly, our calculations indicate the pressure-induced phase transitions in the fcc structure can transform into the complex structures ($C2mb$, $C2cb$, and $I4/mcm$).

Figure 3 displays a schematic of the HG structure at 150 GPa. We have described in greater detail, the HG structure is a commensurate supercell in along the c axis by approximating $c_H/c_G = 4/3$ and component of the guest structure made up of chains that lie in channels in along the c axis of the host structure. The optimized lattice parameters for the host structure are $a = 4.525$ Å and $c = 2.856$ Å with Li atoms located at $8h$ symmetry sites of space group $I4/mcm$ at $(0.166, 0.666, 0)$ and Li atoms are placed at $(0, 0, 0)$ and $(0.5, 0.5, 0)$ in the guest structure.

By analogy, s and p -state electrons of Li^{20,21} represent to the orbital quantum numbers which refer to σ and π states. However, the different characteristics of σ and π bond have presented in an electron localization function (ELF)^{22,23}. The distances between the first (host-guest) and second (host-host) nearest neighbors (NN) are 2.927 Å and 4.140 Å at pressure 0 GPa, 2.252 Å and 3.185 Å at pressure 30 GPa, and 1.687 Å and 2.385 Å, at pressure 150 GPa, respectively. Displays a schematic of the HG structure combined with the ELF as can be seen Fig. 4). We have compared the ELF of the HG structure in the (001) atomic planes reveals the bonding network at pressures 0, 30, and 150 GPa, respectively. At ambient pressure, the electrons with the $\sigma(s)$ - $\pi(p)$ bonding is regularly distributed between the host-guest atoms and the host-host atoms. With increasing pressure, 30 GPa, the ELF display a slight decrease in distribution of electrons between the host-guest atoms and it displays the σ bond led

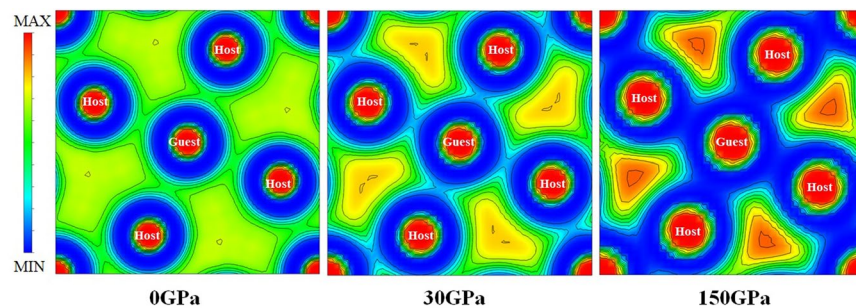


Figure 4. The electron localization function (ELF) in the (001) atomic plane of the host-guest structure of Li under pressures of 0, 30, and 150 GPa.

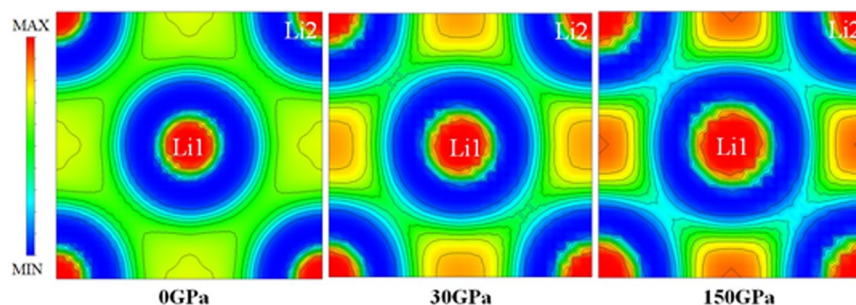


Figure 5. The electron localization function (ELF) in the (001) atomic plane of the fcc structure of Li under pressures of 0, 30, and 150 GPa.

to the weakly bonding²¹. While distribution of electrons is increased between the host-host atoms in this region, it is a strong localization electron of π bond. Obviously, the distribution of electrons becomes more rough at pressure 150 GPa. The accumulation of electrons between the host-host atoms shows that the bonds are the strongly formed in $\pi(p)$ state. The bonding is favored in the π bond when the interatomic distance is shorter than 1.687 Å, which therefore contributes to the stability of the HG structure at high pressure²⁴. According to the calculation of Neaton and Ashcroft²⁵, they reported the localization of electron density interstitial regions with “pair” of electrons. The core region, which is the s - $p\pi$ hybridization state²⁵, has led to the localization of electron density. Our calculation point out that the host-host atoms within the pair has a large core consisting of 1s electrons. With increasing pressure, the outer 2s electrons are pushed out of the s - $p\pi$ hybridization state. This remarkable result is unusual in the understanding that there is truly no the s - $p\pi$ hybridization state between the host-guest atoms but there is the s - $p\pi$ hybridization state between the host-host atoms. Also, it is useful to point out that it can be an incommensurate HG structure. In addition, our study gives the excellent account of the experimental observation¹⁴. The interpretation of the bonding nature is examined by analyzing the ELF. First, we observe that the pairing of electrons in the HG structure is a covalent bond²⁶. Second, we see that the calculation of ELF shows the electron localization of π bonding between the host-host atoms, which would tend to favour superconductivity at higher pressure. Therefore, we strongly suggest that there are the strongly localized electrons between the host-host atoms, which is form π bonding, and it leads to superconducting phase. Hence, the question of whether metallic HG structure is a superconductor can only be answered by the experimental observation.

Moreover, the transition mechanism from the fcc to HG structures is proposed by describing the crystallographic groups. It shows that the HG structure is the thermodynamically stable structure. At this point, we can examine the transition mechanism by the analysis of local changes of coordination in the (001) atomic plane. Notably, the ELF reveals the influences of pressure on the chemical bonding that it is given to clarify the electronic origins of the stability of the HG. This is because the electron localization tends to accumulate between the host-host bonds in Li framework. It is obvious that electrons tend to move away from the host-guest bonds (ambient pressure) to the host-host bonds (high pressure), which has been observed by the local changes of coordination in the (001) atomic plane. This is due to the fact that the accumulation of the electron localization increases according to the increasing pressure. Especially, the accumulation of the electrons could be delivered through the high-density between the host-host bonds at 150 GPa as can be seen in Fig. 4. Likewise, the fcc structure, the analysis of local changes of coordination in the (001) atomic plane is compared at 0, 30, 150 GPa as shown in Fig. 5, the influences of pressure on the chemical bonding of the fcc structure shows that the electrons are regularly distributed between the Li1-Li1 bonds and Li1-Li2 bonds at 0 GPa. With increasing pressure, the distribution of electrons is slightly increased between the Li1-Li1 bonds and decreased between the Li1-Li1 bonds at 30 GPa. In addition, at 150 GPa, the distribution of electrons between Li1-Li1 bonds is more accumulated, while a slight decrease in the distribution of electrons between Li1-Li2 bonds is observed. Certainly, the electrons move away from the Li1-Li2 bonds (ambient pressure) to Li1-Li1 bonds (high pressure) as well as the Li1-Li1

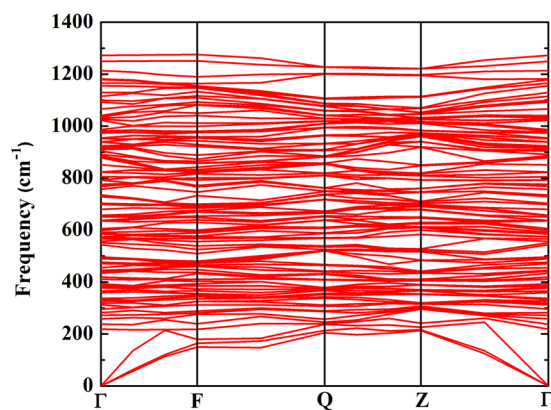


Figure 6. The dynamical harmonic stabilization of the HG structure at pressure 180 GPa.

bonds shows the appearance of the metallic bonds. In fact, the accumulation of the electron localization increases according to the increasing pressure, therefore the accumulations of electrons to the interstitial sites of the lattices of the HG and fcc structures may account for their transitions mechanism at high pressure. The interpretation of the bonding nature indicated that the covalent bonds in the HG structure can be characterized as a metallic bonding. Moreover, a remarkable property of the fcc structure is the metallic phase as well, thus giving rise to a metal-metal transition, which can be explained by the fcc-HG transformation.

To investigate the stability of Li, we have found that the commensurate value of $4/3$ is the most stable above pressure 110 GPa (see in Fig. 2). Here we calculate the dynamical harmonic stabilization of the commensurate value of $4/3$ of the HG structure. The dynamical stability as obtained from the phonon dispersion relation is analyzed as a function of pressure (Fig. 6). At pressure 180 GPa, the lack of imaginary frequencies ensures a dynamical stability of Li metal in HG structure. We also observe high-frequency band from our calculation which we believe that it gives a significant contribution to the strongly localized electron of π bond. Moreover, the distances between the host-host atoms indicate the hardening phonon and it has also led to the stabilization of the HG structure.

Conclusion

In summary, the AIRSS calculation is performed to predict a new stable the HG structure of Li above 110 GPa. We propose the complex structural phase transformations at finite temperature and high pressure in which the HG structure is the ground state structure and stable beyond the pressure of above 110 GPa. It should be noted that the fcc structure can generate the HG structure at a finite temperature and high pressure. The dynamical harmonic stabilization unveils the dynamically stable structure of Li metal at 180 GPa. The distribution of electrons between the host-host atoms is strongly localized electron of π bond which has led to the stability of the HG structure. This remarkable result confirms that Li can form the HG structure under high pressure and high temperature which put the HG structure to be a common high-pressure structure among alkali metals.

Methods

We have used the AIRSS technique¹⁹ and *ab initio* calculation of the Cambridge Serial Total Energy Package (CASTEP)²⁷ to predict the HG crystal structure of Li under high pressure. The AIRSS technique is the high potential for the prediction of the materials. For example, it has been used to predict the crystal structures in material science such as hydrogen^{28,29}, helium³⁰, lithium¹⁷, carbon³¹, nitrogen^{32–34}, oxygen³⁵, aluminium¹⁸, strontium³⁶, metal hydrides^{19,37–39}, and molecular crystals^{40–42}.

We have performed the AIRSS calculation to aid purify the high-pressure phase of Li. Regarding the first type, we place Li atom randomly within the cells and relax cell by shaking. In the second type, we place atoms within the cells using preliminary experimental study⁴³ with constraints on the crystal symmetry^{29,31}. The cell shapes and atomic positions are then relaxed to the ground state structure at each pressure. We consider simulation cells containing 2, 4, 6, 8, 10, 11, 12, 14, 15 and 24 atoms of Li at pressures 20, 30, 40, 60, 80, 100, and 200 GPa. These findings help to space out the atoms suitably while retaining a high degree of randomness. A plane-wave basis-set energy cutoff of 270 eV and an initial Brillouin-zone (BZ) sampling grid of spacing $2\pi \times 0.07 \text{ \AA}^{-1}$ were found to be sufficient for the initial search over structures^{19,29,32,37}. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parametrization⁴⁴ for the exchange-correlation functional to density functional theory is used for the structure searches.

We have here presented the structures at low and high pressures using the GGA-PBE⁴⁴ for the exchange-correlation functional to density functional theory. We employ the projector augmented wave (PAW) method⁴⁵, as implemented in the Vienna *ab initio* simulation package (VASP)⁴⁶. The PAW potential with a 3-electron (1s2s) for Li has been employed with plane waves basis set up to a cutoff energy of 600 eV and the initial BZ sampling grid of spacing $2\pi \times 0.02 \text{ \AA}^{-1}$. The structures are relaxed using the conjugate gradient scheme. All considered structure are relaxed at each pressure until the Hellman-Feynman forces became less than $10^{-3} \text{ eV/\AA}$.

The structures are relaxed and their equations of state are obtained by fitting with the calculated energy-volume data to the third-order Birch-Murnaghan equation. We then calculate the enthalpy-pressure relationship and the high-pressure phase of the experimental information¹⁰.

The existence of the HG structure presented here is based on the GGA-PBE using *ab initio* lattice dynamics with finite displacement method as well as supercell scheme by CASTEP²⁷.

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Author Contributions

Author contributions: T.B., R.A. and P.T. designed the research, all authors performed research, analyzed the results and wrote the manuscript.

Additional Information

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Prediction of Superstructure and Superconducting State in Calcium under High Pressure

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ABSTRACT

We use *ab initio* molecular dynamics (AIMD) to predict the crystal structure of Ca at a temperature of 50 K and a pressure of 60 GPa. We use *ab initio* random structure searching (AIRSS) and Universal Structure Predictor: Evolutionary Xtallography (USPEX) to confirm crystal structure of Ca. At high pressure, we present that the β -tin structure transforms into the Sr-IV type (Cc) structure at a pressure of 75 GPa and transforms into the host-guest structure at a pressure of 202 GPa. Here we reported the metallic behavior which it led to the discovery of the strong coupling and the high- T_c superconductivity. The Cc structure has been calculated using *ab initio* lattice dynamics wherein finite displacement method confirms the stable structure at pressure 160 GPa. Specifically, we find that the Cc structure of Ca exhibits superconductivity, with a T_c of 25.2 K at 160 GPa. The calculated superconducting transition temperature is in good agreement with experiment.

Introduction

Calcium (Ca) is one of the most fascinating alkaline-earth metals, where the structural phase transition under high pressure is influenced by *s-d* hybridization from lower pressure to higher pressure phases.¹⁻³ At ambient pressure, the face-centered cubic (fcc) structure transforms into the body-centered cubic (bcc) structure at a pressure of 20 GPa and then transforms into the simple cubic (sc) structure at a pressure of 32 GPa.^{4,5} At pressure above 113 GPa, Ca-III possesses the sc structure and transforms into the P4₁2₁2 structure at pressure 119 GPa,⁶⁻⁸ and then to the Cmca structure at a pressure corresponding to 143 GPa^{7,8}, and the Pnma structure at a pressure of 158 GPa.^{8,9} At pressure above 122 GPa, Ca is predicted to exhibit an incommensurate host-guest (HG) structure with space group of I4/mcm (0,0, γ), which has commensurate value 4/3, inferred from *ab initio* calculations.¹⁰ The HG of Ca is found to be isostructural with the incommensurate host-guest structure of Sr-V and Ba-IV.^{11,12} Understanding the crystal structures of the HG structure is now very well established.^{13,14} The HG structure consisting of 128 atoms in a 2×2 supercell in the tetragonal *ab* plane with a commensurate value 4/3 has been determined by Angle Dispersive X-ray Diffraction (AXRD).

In the ongoing strong efforts^{4-6,15-18} to provide experimental observation and theoretical study for the sc structure, very significant attention has been directed towards the fact that the sc structure is distorted as the rhombohedral structure with a space group of $R\bar{3}m$.⁵ However, Yao *et al.*¹⁶ suggested that the sc structure is the stable structure at a temperature of 300 K and at a pressure of 60 GPa. In addition, the stable of the sc structure is confirmed by phonon calculation at a temperature of 300 K.^{17,18}

Finding the metallization pressure of Ca is one of the greatest challenges within the framework of high-pressure physics. Because, for the crystal structure of Ca-IV it is observed that it has the highest maximum superconducting transition temperature (T_c) of 25 K at a pressure 161 GPa.¹⁹ Recently, the crystal structure of Ca is studied in the high-pressure phase of Ca-VII and superconductivity by powder x-ray diffraction and electrical resistance measurements.¹³ They found that Ca-VII possesses the

highest T_c of 29 K at pressure of 216 GPa.

A striking stabilization of sc structure is confirmed by molecular dynamics¹⁶ and phonon calculation^{17,18} at a temperature of 300 K. This led to the important question of new high-pressure phase at low temperature.

In the present work, we intend to address few open questions related to Ca under extreme compression such as: (i) What is a new structure beyond the sc structure at low the temperature and high pressure? (ii) Is the metallic high-pressure phase a superconductor? In order to address these questions, knowledge of the structural phase transformation is the first step toward understanding the physical properties of Ca. We propose a procedure enabling one to obtain the crystal structure of Ca using *ab initio* techniques. We use *ab initio* molecular dynamics (AIMD) in order to determine the crystal structure of Ca as well as used *ab initio* random structure searching (AIRSS)^{20,21} and Universal Structure Predictor: Evolutionary Xtallography (USPEX)^{22,23} to confirm crystal structure of Ca which is obtained by AIMD calculation. Moreover, our study also computational reveal the superconducting transition temperature of the predicted structure at pressures above 120 GPa. Our study could be greatly helpful for future experiments at low temperature.

Results and Discussion

Our predictions of the high-pressure phases are based on AIMD calculations, where we have obtained three particularly low-enthalpy structures of Ca with sc, Cc , and P1 symmetry at a pressure of 60 GPa and at the temperatures of 300, 50, and 5 K, respectively as shown in Fig. 1. We found that the sc structure is the most stable at the temperature of 300 K in agreement with the theoretical study^{15,16} and the experimental observation.^{4,6} Interestingly, the sc structure transforms into the monoclinic structure with space group Cc at 50 K and 60 GPa, this monoclinic complex structure Cc is isostructural with Sr-IV.^{24,25} The Cc structure of Ca is utilized in this calculation, because of the remarkable structural phase transformation emerged from the sc structure. The lowest-enthalpy of the Cc structure is found to rapidly decrease at the beginning (1 ps) and found to slightly decrease overtime up to 5 ps showing the thermodynamic stability. We suggested that the enthalpy of Cc is lower and thermodynamically favorable than the sc structure. Moreover, two different powerful tools for predicting the crystal structures of Ca, AIRSS and USPEX methods have only led to the stable structure. We found that the Cc structure has shown fair agreement with the AIMD calculations.

Enthalpy difference (ΔH) - Pressure relations of fcc, bcc, β -tin, Sr-IV type (Cc) and HG structures are shown in Fig. 2. Crossing points of the curve from each structure represent the structural transformation, it is found that the fcc transforms into bcc structures at a pressure of 8 GPa and then transforms into the β -tin structure at a pressure of 32 GPa, where the transition sequences totally agree with theoretical study¹⁵ and experimental observation.²⁶ At higher pressure, it is found further that the β -tin transforms into the Sr-IV type (Cc) structures at a pressure of 75 GPa and to the host-guest structures at a pressure of 202 GPa. This is a remarkable result putting the Cc structure to be a common high-pressure structure in Sr.

Moreover, our results of the structural transformation is a similar with earlier theoretical study.²⁷ It is worth noting that our crystal structure of Sr-IV type, is monoclinic structure with a space group of Cc . Structural optimization of Cc yields $a = 6.08050$ Å, $b = 5.93290$ Å, $c = 4.60520$ Å, $\beta = 135.075^\circ$ with Ca atom located at $4a$ symmetry sites Ca_1 (0.890313, 0.334935, 0.168998), Ca_2 (0.611264, 0.160219, 0.332086), Ca_3 (0.502043, 0.462576, 0.497116) at a pressure of 160 GPa. It is a similar structure as for the $C2/c$ (Sr-IV type) structure.²⁷ Both the Cc structure and the $C2/c$ structure is a monoclinic distortion of the tetragonal β -tin structure of Sr-III.^{24,25} We take the agreement in the present case as the justification to rely on the Cc structure in the investigation by examining enthalpy. Our calculation found that the $C2/c$ structure is higher in enthalpy than the Cc structure about 0.11 eV. At this point, we would like to that the Cc structure is geometrically very close to the $C2/c$ structure. Hence, it may be possible that experimentally both the Cc and $C2/c$ structures may be found. In this result, we focus on the Cc structure because the Cc structure is energetically more favorable than the $C2/c$ structure, thus the Cc structure is chosen in this calculation. Moreover, it is the most stable in the pressure range of 75-202 GPa, which is suitable for finding the superconducting transition temperature T_c ; that we will come back to later.

Therefore, in order to analyze the reasons for the onset of the stable of Cc structure, we established from the calculations of its phonon dispersion. The dynamical stability of the Cc structure confirms that it is stable at a pressure of 160 GPa. This is due to the fact that there is lack of imaginary frequency, indicating the stable of the Cc structure (Fig. 3). We can now consider the metallic and superconductivity properties. The effect of pressure on the electronic properties of the Cc structure is investigated through the densities of states (DOS). Our calculation presents projected densities of states (PDOS) to the s , p , and d states of the Cc structure at a pressure of 160 GPa. The difference in energy characteristics of the s , p , and d states result in a quite pronounced change in the DOS under high pressure. It is well known that the shape of the DOS also depends on the crystal structure, it is found to be dominated by d -orbital near Fermi level which suggested the metallic behavior²⁸ as can be seen in Fig. 4. A striking feature of d -state, is a steep band which led to the discovery of the strong coupling and the high- T_c superconductivity.

This superconducting state can be understood through the T_c which is described by electron-phonon coupling λ , the averaged phonon frequency ω_{log} , and effective Coulomb interaction μ^* . Effective coulomb interaction, μ^* , is a free parameter

dependent on the metal type, e.g., $\mu^* = 0.13$ is suggested to be used for T_c calculation of transition metals²⁹, and $\mu^* = 0.10$ was used for metals³⁰. Moreover, variation of μ^* values was found to satisfy computational and experimental results, e.g., $\mu^* = 0.10$ for *bcc* and *Cmcm* structure in Sr³¹, $\mu^* = 0.15$ for *fcc* structure in Y³², $\mu^* = 0.16$ for *bcc* structure in H₃S³³ and $\mu^* = 0.18$ for *fcc* structure in Y³⁴.

T_c is generally fitted from a designated μ^* which will be applied in Allen Dynes equation (Equation 1)³⁰ where it was widely accepted to have λ to be less than 1.4³⁰.

$$T_c = \frac{\omega_{log}}{1.2} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right], \quad (1)$$

Since T_c from elemental metals mentioned above agreed in both computational study and experimental observation using Allen Dynes equation (EQ1)³⁰, the accuracy of analysis method was, therefore, evaluated. As the T_c of Sr was successfully analyzed using Allen Dynes approach and Sr is also the isoelectronic element of Ca. As a result, T_c of Ca could be successfully determined using the same method as Sr. In our estimation for T_c , we have tested five different values of Effective coulomb interaction μ^* : 0.10, 0.13, 0.15, 0.16, and 0.18 at pressures from 120 to 160 GPa using Allen Dynes equation (Equation 1)³⁰. Here we investigated superconductivity in Ca and evaluated the pressure-dependence of the superconducting transition temperature T_c . In Fig. 5a, the value of effective coulomb interaction parameter, μ^* , of 0.10 illustrates the T_c of 25.2 K at 160 GPa which are in good agreement with the reported value of 25 K at 161 GPa by Yabuuchi et al.⁶ This is also understood from the fact that μ^* of 0.10 gives excellent results for the simple metals.

The phonon characteristic of the *Cc* structure reveals the significance of the electron-phonon coupling (EPC), from the inset of Fig. 5b, λ increases with pressure from 120-160 GPa, the *Cc* structure has the strong electron-phonon coupling due to $\lambda > 2$ at pressures above 140 GPa. Similar structural stabilities driven by the strong electron-phonon coupling have been studied: for *fcc*-Y under pressure, it is found enhanced the EPC $\lambda > 2$ ³⁴ at a pressure of 31 GPa. For *I* $\bar{4}$ 3*m*-Ca, it is also found that the EPC $\lambda > 2$ at a pressure of 97 GPa.³⁵ In addition, the strong EPC is studied on the *P6*/*mmm*-SnH₄ at pressure 120 GPa which it is explained by Kohn anomalies.³⁶ Thus, we would like to elucidate that strong electron-phonon coupling of the *Cc* structure is due to Kohn anomalies. The most striking feature of this phonon branch is indicated from the soft mode in the phonon branch induced by Kohn anomalies. This is due to the fact that the phonon branch of the *Cc* structure has a softening phonon in along the $Y \rightarrow A$ and $A \rightarrow B$ directions. These observation of the strong electron-phonon coupling and resemblances with other similar structures leads us to predict that the *Cc* structure should ultimately be the high-temperature superconducting state.

Conclusion

In conclusion, by means of *ab initio* techniques, we have reproduced most of the studied perspective of the structural phase transitions in Ca. Our AIMD calculation finds that the *sc* structure is the most stable structure at a temperature of 300 K and a pressure of 60 GPa. With the decrease of temperature, we find that the *sc* structure transforms into the *Cc* structure at a temperature of 50 K and a pressure of 60 GPa. The structure of Ca is confirmed by AIRSS and USPEX. The existence of *Cc* structure in Ca demonstrates that the structural phase transitions under high pressure are quite similar corresponding to the structure sequence of Sr^{11,24,25,27,37,38} i.e., *fcc* $\rightarrow$ *bcc* $\rightarrow$ β -tin $\rightarrow$ Sr-IV type (*Cc*) $\rightarrow$ host-guest structure. The *Cc* structure is stable at a pressure of 160 GPa as confirmed from *ab initio* lattice dynamics with finite displacement method. Hence, it is possible that experimentally the *Cc* structure can be found at low temperatures. Specifically, we find that the Sr-IV type structure of Ca exhibits superconductivity, with a T_c of 25.2K at 160 GPa. Our calculated result of superconducting transition temperature is in remarkably good agreement with experiments.

Methods

We used AIMD calculation to find a new structure, the *sc* structure is the most stable structure at a temperature of 300 K and it is used as the initial structure for this calculation. The *sc* structure is simulated using supercell consisting of 27 Ca atoms. The irreducible Brillouin Zone (BZ) consisted of Monkhorst-Pack (MP) k-point sampling³⁹ of Γ -points for *sc* structure. In our AIMD calculations, we have used the generalized-gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)⁴⁰ exchange-correlation functional. The ultrasoft pseudopotentials⁴¹ (USPP) calculation was utilized to treat 3*s*, 3*p*, and 4*s* states as valence states. We used energy cutoff at 310 eV via NPT⁴² ensemble at 5, 50, and 300 K and 60 GPa which was carried out using 10 fs of integration time step resulting in 5 ps of integrated total time of simulation.

We calculated two different methodologies for structure prediction of Ca. We used AIRSS technique^{20,21} with CASTEP code^{43,44} and USPEX^{22,23} in combination with the VASP code.⁴⁵ We performed unconstrained searches with 2, 4, 6, 8, and 10 atoms per cell at pressures 40, 60, 80, and 100 GPa. The efficiency of AIRSS and USPEX methods have been successfully tested to confirm the crystal structures of Ca.

We find the structural phase transition of Ca using CASTEP code. The computational studies presented here are based on the GGA-PBE⁴⁰ exchange-correlation potential functional. USPP was also employed to treat 3s, 3p, and 4s states as valence states. A plane-wave basis set energy cutoff of 600 eV found to be sufficient for finding the ground state energy. The irreducible BZ consisted of MP k-point sampling³⁹ of $10 \times 10 \times 10$ k-points for fcc, bcc and β -tin structure. The host-guest and candidate structures used $2 \times 2 \times 1$ and $4 \times 4 \times 4$ k-point mesh, respectively. The calculations were based on primitive cell for the candidate structure and based on the conventional cell for other structures. The enthalpy-pressure curve was fitted by the third order Birch-Murnaghan equation of state (EOS).⁴⁶ The stability of high-pressure phases and phase transition were determined using enthalpy-pressure relation. In order to investigate the stability of the candidate structure, lattice dynamics calculation^{43,44} with finite displacement method has been performed using CASTEP.^{43,44}

The electron-phonon coupling (EPC) was calculated by density functional perturbation theory⁴⁷ with linear response using Quantum Espresso.⁴⁸ The plane-wave basis set energy cutoff of 40 Ry was used in both calculations. To investigate EPC, BZ integrations were done with MP k-point meshes. EPC matrix elements were computed in the first BZ on $2 \times 2 \times 2$ q-meshes using individual EPC matrices obtained with a $16 \times 16 \times 16$ k-points mesh for the high-pressure phase of the candidate structure.

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Author contributions statement

Author contributions: P.T. and T.B. designed research; P.T., W.C., and K.K. performed research; P.T., U.P., R.A., and T.B. analyzed data; and P.T., R.A., and T.B. wrote the paper.

Additional information

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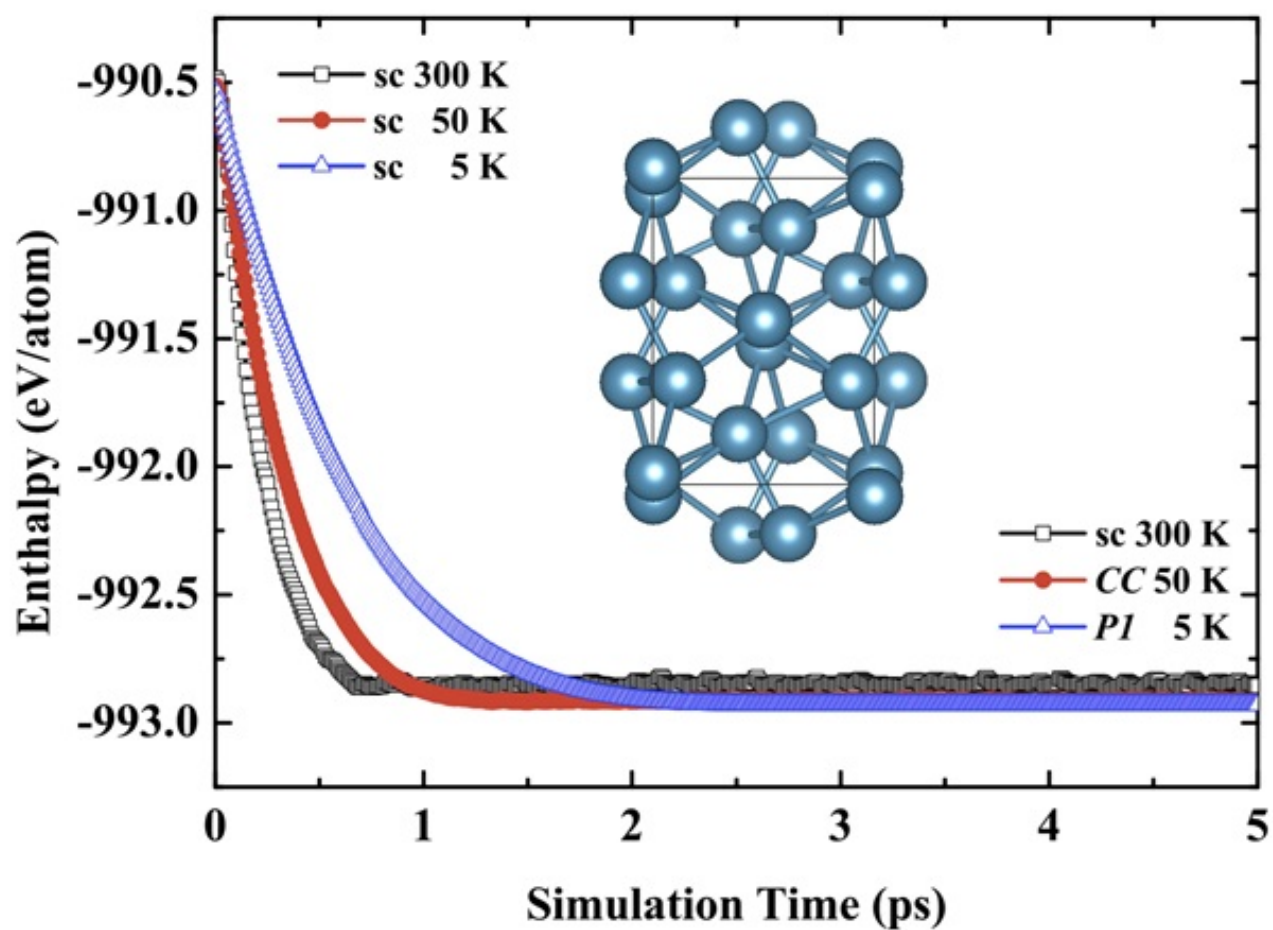


Figure 1. Simple-cubic (sc) super cells structure was calculated using MD simulation at 60 GPa and at temperatures 300, 50, and 5 K. Crystal superstructure is illustrated on the centre of graph.

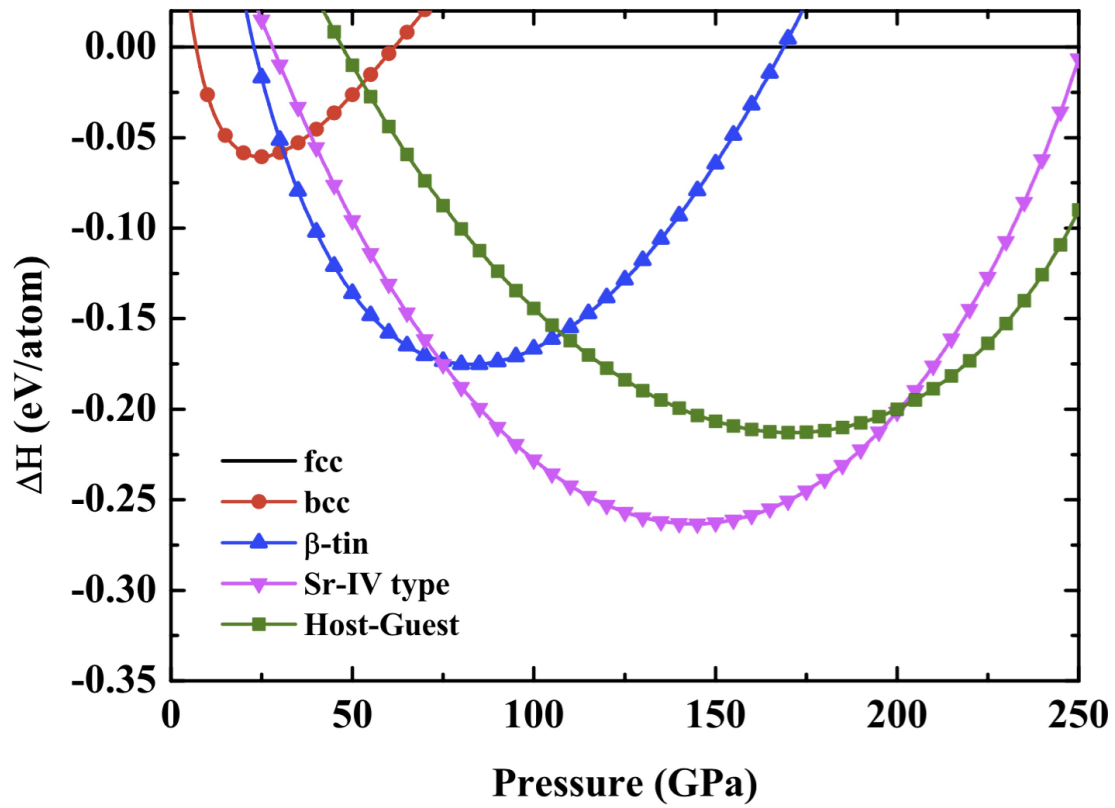


Figure 2. The enthalpy difference of bcc, β -tin, Sr-IV type, and host-guest structure related with the fcc structure at ambient pressure. The cross-section point of each line represents the occurring of transition event. The graph suggests that the transition will go from fcc $\rightarrow$ bcc $\rightarrow$ β -tin $\rightarrow$ Sr-IV type $\rightarrow$ host-guest, respectively.

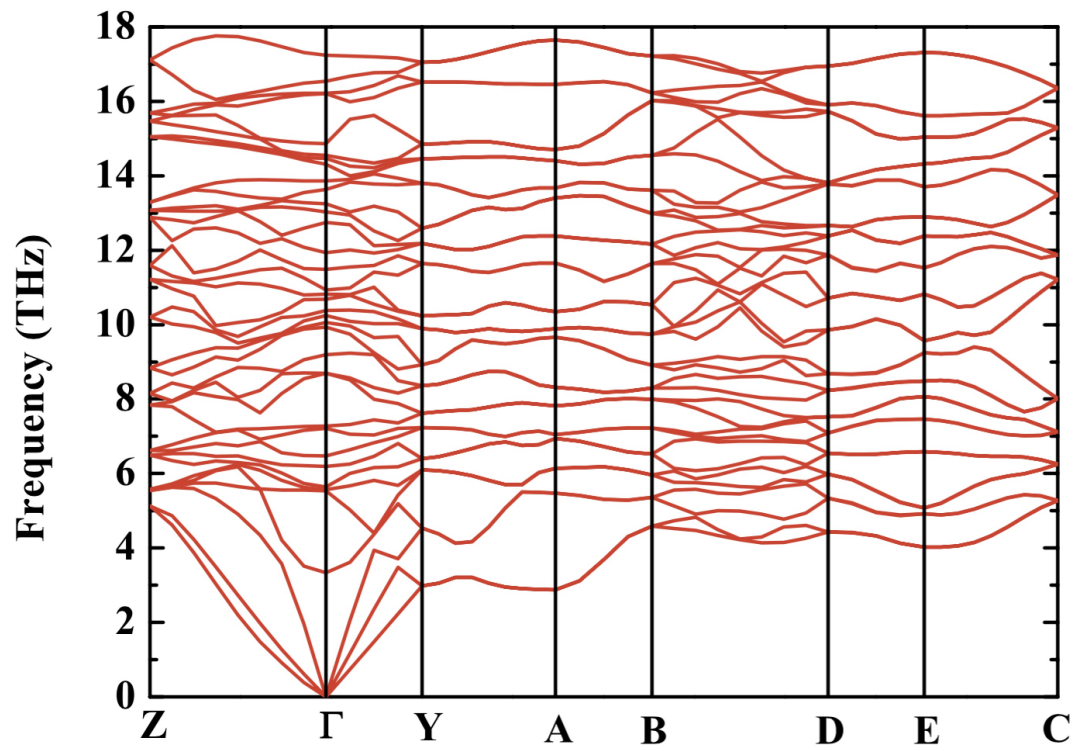


Figure 3. Phonon dispersion of the CC structure is indicated the Kohn anomalies at pressure 160 GPa. The phonon softening shows in branch along the $Y \rightarrow A$ and $A \rightarrow B$ directions.

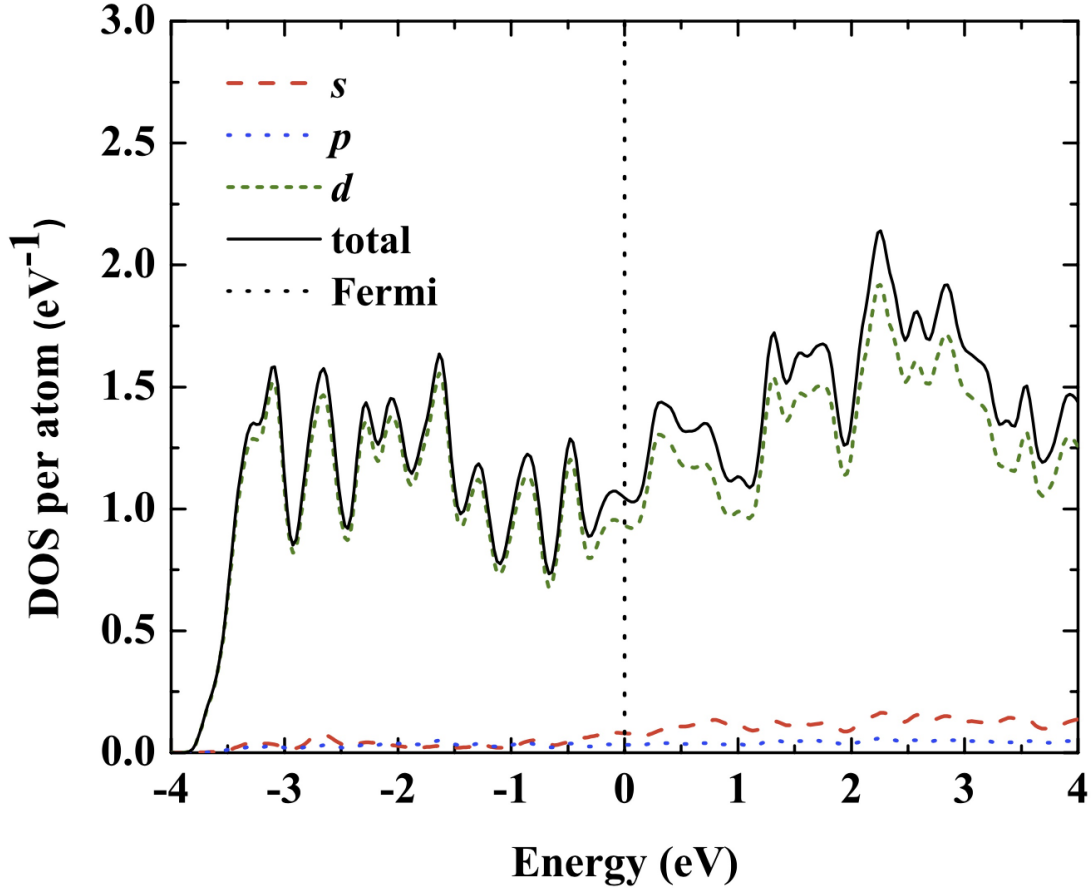


Figure 4. Total DOS, and projected DOS to s, p, and d orbitals of the CC structure near the Fermi level at 160 GPa.

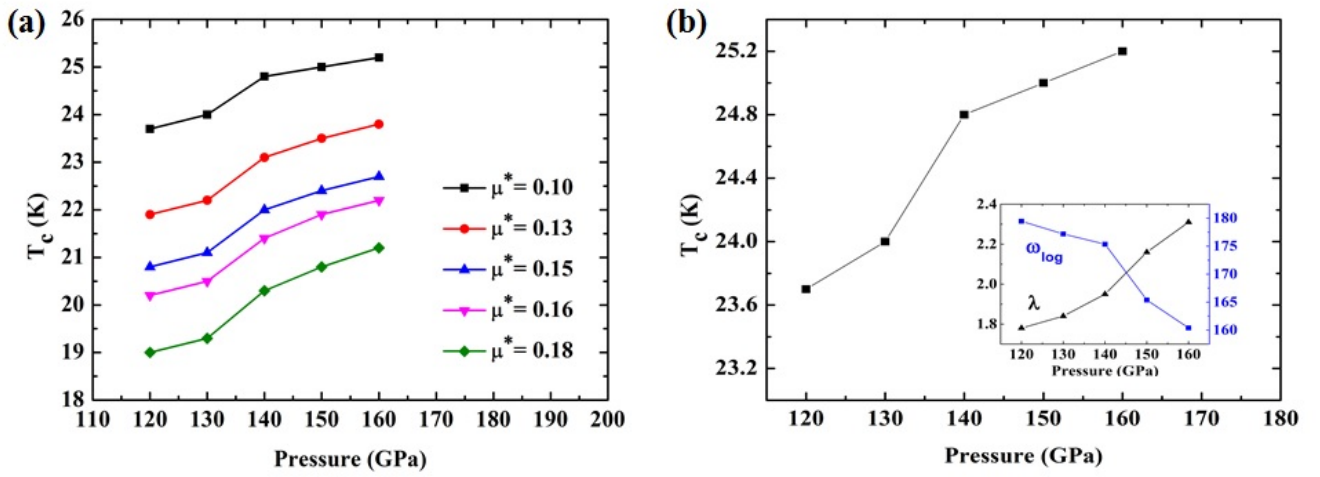


Figure 5. ((a) Our calculated T_c vs pressure for Ca using five effective Coulomb parameters. (b) The effective Coulomb $\mu=0.10$ shows the highest T_c and the inset shows calculated electron-phonon coupling (λ) and logarithmic phonon momentum (ω_{log}) as a function of pressure

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Keywords II-VI ternary alloys; ab-initio calculation; Phase stability; High Pressure; Density Functional Theory

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Effect of pressure on the structure stability, electronic structure and band gap engineering in $\text{Zn}_{16}\text{O}_1\text{S}_{15}$

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Abstract

Crystal structures and high pressure structural phase transitions of $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ have been investigated using density functional theory calculation. The two candidate high pressure structures namely Wurtzite and Zincblende were examined for their stability and properties up to 20 GPa. The co-exist phase of both structure which occurred during the difference film growth conditions was fully explained. Phonon dispersion and the Born criteria reveal that Zincblende is only stable up to 10 GPa. Besides, Wurtzite structure yield no imaginary phonon frequencies and also satisfy the elastic constants sufficiency condition up to 20 GPa which indicated that the co-exist phase would eventually become the single Wurtzite structure above 10 GPa. The electronic structure and PDOS were also fully investigated using HSE06. The multiple band gap energy and mid O-3 state between fundamental ZnS band gap was revealed for the first time. The pressure effect on their electronic structure has been investigated for possible applications in adjustable optoelectronic device.

Keyword: II-VI ternary alloys, ab-initio calculation, Phase Stability, High Pressure, Density Functional Theory

Introduction

The doping II-VI semiconductors, such as in ZnO and ZnS, are promising candidate for blue range optoelectronic and spintronic devices. II-VI wide band gap semiconductors have been used in blue range optoelectronic devices. By adding a portion of anion in II-VI host results in a large reduction of energy band gap. Recently, II-VI semiconductors also draw interest in solar cell devices due to their high bowing parameters which describe the change in energy band gap against doping concentration, so that lead to more adjustable electronic band gap than III-V group [1–3]. To describe the electronic band structure of mismatched alloys, the Band-anticrossing (BAC) model was used [4,5]. The authors found that common structures of ZnS at ambient are Zincblende (Cubic) and Wurtzite (Hexagonal) structures. Furthermore, for O doped ZnS, Pan *et al.* reported that structure of S rich $\text{ZnO}_{1-x}\text{S}_x$, i.e. $0.77 \leq x \leq 1$, grown by radio-frequency magnetron sputtering is Zincblende [2]. However, He *et al.* [3] reported another interesting result that doped $\text{ZnO}_{1-x}\text{S}_x$ ($0.94 \leq x \leq 1$) grown by pulsed laser deposition have Wurtzite structure. This inconsistency leads to naturally wonder that, in the theoretical point of view, how can both of them exist on S rich regime.

By means of first-principle calculations, Ishikawa and Nakayama [6] showed that in $\text{Zn}_{32}\text{O}_1\text{Te}_{31}$ there exist the local O-3s state taking place in the host forbidden band. On the other hand, for $\text{Zn}_{32}\text{O}_1\text{S}_{31}$ and $\text{Zn}_{32}\text{O}_1\text{Se}_{31}$, O-3s locates in the host conduction band and forms hybridizations with the host conduction states. However, the structure stability and the effects of pressure on their properties are still in doubt and need more advance research.

In this work, we examine the stability of Zincblende and Wurtzite $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ at ambient pressure and, then, investigate effects of pressure on their structural and electronic properties using *ab initio* calculation. To assert the mechanical stability of these structures and an additional Rocksalt structure which is a candidate for high pressure phase, the phonon dispersion and elastic constant calculations were performed along with the pressure-dependent energy band gap. Surprisingly, the results illustrate that this alloy is a multiple band gap semiconductor with the O – induced subband. These results would benefit to design of electronic and/or optoelectronic devices and, also, synthesizing conditions.

Calculation detail

Two dilute O-doped ZnS – i.e. $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ – systems are modeled by substituting an S atom of $2 \times 2 \times 1$ Zincblende and $2 \times 2 \times 2$ Wurtzite supercells, which compose of 16 Zn and 16 S atoms, with an O atom. First-principle calculations were performed using self-consistent field (SCF) method as implemented in Cambridge Serial Total Energy Package (CASTEP) code [7,8]. The generalized gradient approximation (GGA-PBE) is employed as the exchange correlation functional [9,10] for ground state property calculations. The HSE06 hybrid functional was used to perform electronic structure calculations [11]. The ultra-soft pseudopotentials are used for representation of the core ions [12]. The cell parameters of both supercells were obtained by structural optimization at given pressure and 0 K by mean of the Brodyden-Fletcher-Goldfarb-Shanno (BFGS) [13] with no any constraint on each atom. The k-point separation is set to $\Delta k_i = 0.035$, $i = x, y, z$, for Monkhorst-Pack grid [14] mesh in all calculations. The maximum kinetic energy of plane wave basis set is 650 eV for both structures. The converged calculations were obtained within the following criteria: the

total energy difference less than 5×10^{-7} eV/atom, Hellman–Feynman forces less than 0.01 eV/Å, the maximum ionic displacement within 0.0005 Å, and all of the stress components within 0.02 GPa. The phonon dispersions were obtained by performing the calculation using finite displacement method [15] with $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells for Zincblende and Wurtzite structures, respectively. The elastic constants, the average isotropic bulk modulus (B) and shear modulus (G) were obtained by applying Voigt–Reuss–Hill (VRH) method [16,17].

Result and discussion

To figure out that which one is the most stable structure of $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ at a given pressure, we compare the enthalpy/formula of Wurtzite with that of Zincblende as a function of pressure. As mentioned, the coexistence of Zincblende and Wurtzite structures of S rich in $\text{ZnO}_{1-x}\text{S}_x$ films at ambient pressure was experimentally observed by Pan *et al.* [2] and He *et al.* [3], respectively. The first one was obtained through annealing process at 773–873 K whereas the second one was performed at 1023 K. The difference in annealing temperatures results in different crystal structures. The thermal energy differences between these two sample preparations are in a range of 0.207 – 0.345 eV/formula, assuming that each atom gained $\frac{1}{2}k_B T$ thermal energy. According to the result shown in Fig. 1, we obtain that the enthalpy of Wurtzite structure is 0.238 eV/formula higher than that of Zincblende, at ambient which is in good agreement with the experimental result. So we can use these models to study the structural and energetic properties of $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ under pressure. The enthalpy difference peaks at 10 GPa with the value of 0.311 eV/formula. Then, it slightly decreases at 20 GPa and 30 GPa and then sharply decreases at 40 GPa and 50 GPa.

However, only this energetically consideration is not good enough for structural stability justification. A crystalline structure is stable if it satisfies two following conditions: (i) all its phonon modes have real-valued frequencies (dynamical stability) and (ii) its elastic constants, C_{ij} 's, obey the Born criterion (elastic stability) which are [18]

$$C_{44} - P > 0 ; C_{66} - P > 0 ; C_{11} - C_{12} - 2P > 0 ; (C_{33} - P)(C_{11} + C_{12}) - 2(C_{13} - P)^2 > 0$$

for the tetragonal and hexagonal crystal structure classes under hydrostatic pressure. Fig. 2, 3 and Table 1 show the calculated phonon dispersions in the first Brillouin zone and elastic constants of both structures, respectively. For Zincblende structure, the phonon dispersion, $\omega^2(k)$, and elastic constants show that this structure is mechanically stable at 0 to 10 GPa and unstable at 20 GPa as the former reaches negative values and the latter violate the Born criteria, i.e. $C_{11} - C_{12} - 2P = -11 < 0$, [see Fig. 2 and Tab. 1]. In contrast, the Wurtzite structure obeys both mechanical stability conditions at a range of pressure from 0 to 20 GPa [see Fig. 3 and Tab. 1].

Furthermore, it is worth examining the structural stability of Rocksalt structure under pressure since it is the common high pressure phase of ZnS. Energetically, the examination turns out that Rocksalt is the most energetically preferable structure and the phase transition from Zincblende or Wurtzite to Rocksalt takes place at around 17.5 GPa, see Fig. 4. Even Rocksalt structure is the

lowest enthalpy/formula but the negative Rocksalt phonon frequencies appeared at 1.75 and 25 GPa as shown in Fig. 5a and 5b respectively. According to Fig. 5c, the partial phonon density of state reveals that the imaginary frequencies of acoustic phonon mainly attributes to an O-atom. That means the instability of the Rocksalt structure under high pressure is induced by the doped O-atom.

Besides identifying the stability of both crystal structures under pressure up to 20 GPa, we also calculate the electronic structures of $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ system at ambient and also high pressure conditions, 0 to 20 GPa, using HSE06 and GGA exchange correlation functionals. The results are shown in Fig. 6. As seen in the figure, Zincblende and Wurtzite structures are direct band gap semiconductors at Gamma point with deep O-3s state located in the fundamental band gap of ZnS. This is the local state as described by Ishikawa and Nakayama [6] that causes $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ becoming a multiple band gap semiconductor defined by the direct energy gaps E_1 and E_2 in Fig. 6. E_1 and E_2 respectively represent a primary and secondary direct band gaps. At ambient pressure, HSE06 and GGA functionals yield the same trend in electronic structures at the fundamental band edges and at the middle of the fundamental gap. Due to the time consuming nature of HSE calculation, so, we further qualitatively analyze the electronic states in both structures by performing total density of state (DOS) and partial density of state (PDOS) calculations. According to Fig. 7, for both structures, DOS and PDOS illustrate that the top of valence band (VB) is mainly occupied by S-3p with small contribution of Zn-4s and p-d hybridization (Zn-4p, Zn-3d, and O-2p). While the bottom of conduction band is dominated by Zn-s and 4p orbital with S-s and doped O-3s state. These are surprising results compared to Ref. [6] in which electronic structures of Zincblende $\text{Zn}_{32}\text{O}_1\text{S}_{31}$ and $\text{Zn}_{32}\text{O}_1\text{Se}_{31}$ were obtained by performing density functional based calculations allowing GGA-PBE96 as exchange – correlation functional. In this work, there exists no O-3s state in-between VB and CB. On the other hand, the hybridization state between O-3s and host ZnS locates in CB [6]. In contrast, our results reveal that the O-induced state exist in both Zincblende and Wurtzite structures. The DOS and PDOS of Wurtzite and those of Zincblende are fairly the same in shape but with the larger gap for the former [see Fig. 6]. Moreover, the density of intermediate O-3s state of Zincblende structure is higher than that of Wurtzite which correspond to higher optical transition rate of electrons from VB into the intermediate state and from the intermediate state into host CB.

To elucidate effects of pressure on the energy gaps, we calculate HSE06 pressure - dependent energy gaps of both structures at a number of pressures. The obtained energy gaps are listed in Tab. 2. Interestingly, E_1 increases while E_2 decreases with increasing in pressure for Zincblende structure. For Wurtzite structure, E_1 and E_2 increase as pressure increase with faster rate of E_2 in the low pressure range, $P \leq 10$ GPa, and faster rate of E_1 in the high pressure range, $P \geq 10$ GPa. This can be easily seen from the change of ΔE . Our results provide basic knowledge and enable the flexibility of band gap engineering in this class of material by varying pressure. Additionally, this knowledge on pressure – dependent of optical band gap may provide an alternative way for structure characterization by observing its optical transition as a function of pressure.

Table 1 pressure – dependent bulk modulus and elastic stiffness constants of $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ of Wurtzite and Zincblende structures

Zincblende							
Pressure (GPa)	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B (GPa)
0	99	58	58	99	48	48	72
10	137	101	101	137	45	46	113
20	171	142	142	170	40	40	152
Wurtzite							
0	118	52	40	138	28	32	71
10	157	94	80	188	25	31	112
20	188	134	122	228	20	27	150

Table 2 pressure – dependent multiple primary energy gap, E_1 , secondary energy gap, E_2 , and their difference, ΔE , of Zincblende and Wurtzite structures

Zincblende				Wurtzite		
Pressure (GPa)	E_1 (eV)	ΔE (eV)	E_2 (eV)	E_1 (eV)	ΔE (eV)	E_2 (eV)
0	2.94	1.48	4.42	2.61	1.39	4.00
10	3.31	0.87	4.18	2.79	1.51	4.30
20	3.46	0.53	3.99	2.92	1.49	4.41

Conclusion

We examine the mechanical stability of Zincblende and Wurtzite $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ at ambient and high pressure by considering structural enthalpies, phonon dispersion, and elastic constants. Both of Zincblende and Wurtzite structures are stable at ambient pressure with lower enthalpy of the former. This corresponds to the experimentally observed existence of both structures at different temperatures under ambient pressure. At high pressure, the Zincblende structure is no longer stable and a phase transition pressure is at in-between 10 – 20 GPa. Besides, the electronic energy band gaps are calculated using the high accuracy HSE06 exchange correlation functional. The obtained electronic structures show that $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ is a multiple band gaps semiconductor with an O – induced state located in the forbidden band of the host ZnS. This state defines the primary band gap, E_1 , as an amount of energy required for direct transition from top of valence band into this state. Also, the secondary band gap, E_2 , is defined by the top of valence band and the bottom of shifted host conduction band. By increasing pressure, E_1 increases while E_2 decreases for Zincblende structure, and both of E_1 and E_2 increase for Wurtzite structure. This pressure dependency of energy band gap would benefit the band gap engineering for optoelectronic and photovoltaic applications.

Acknowledgement

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

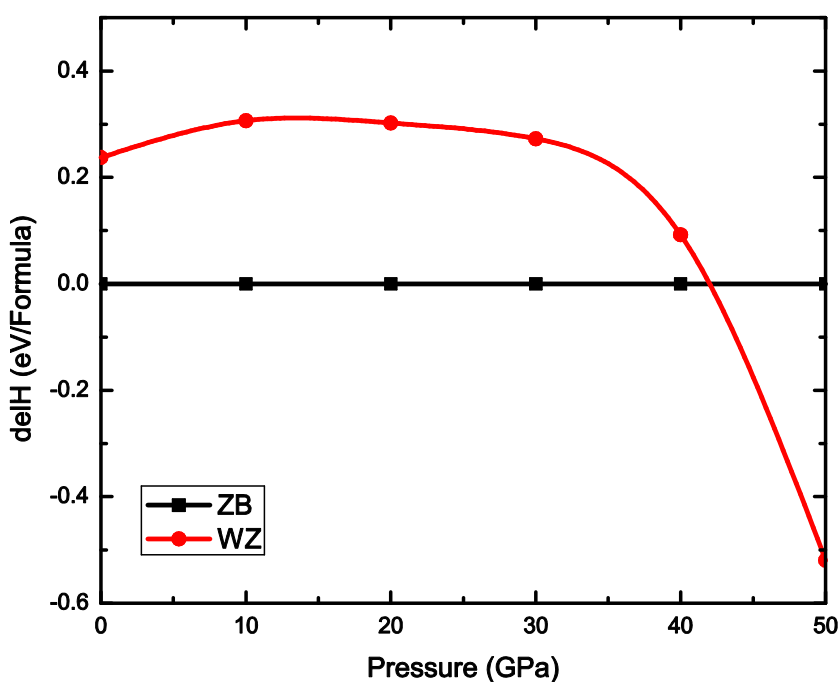


Figure 1. Enthalpy difference of Zincblende (black) and Wurtzite (red) $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ as a function of pressure compared with that of Zincblende structure.

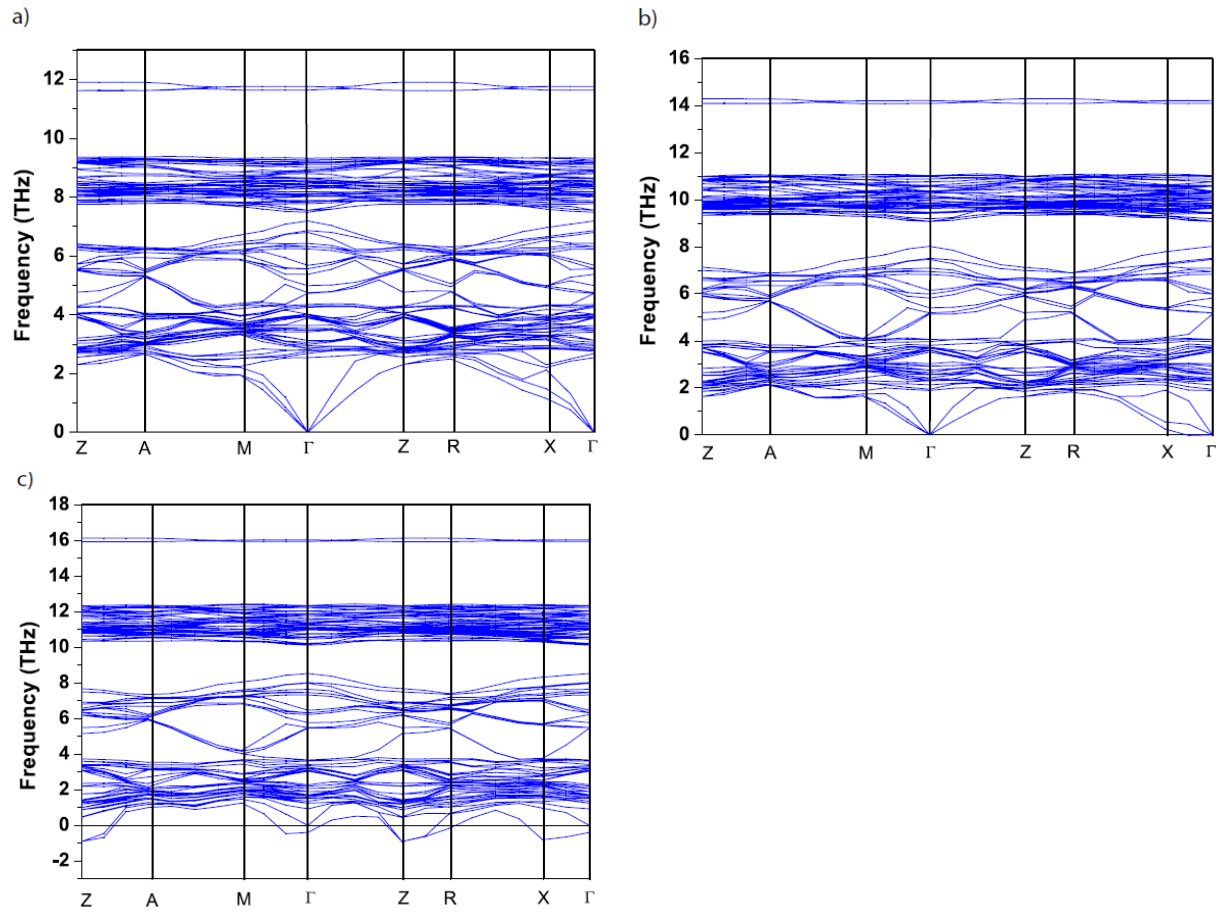


Figure 2. Phonon dispersions of Zincblende of $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ under a) 0 GPa b) 10 GPa and c) 20 GPa conditions.

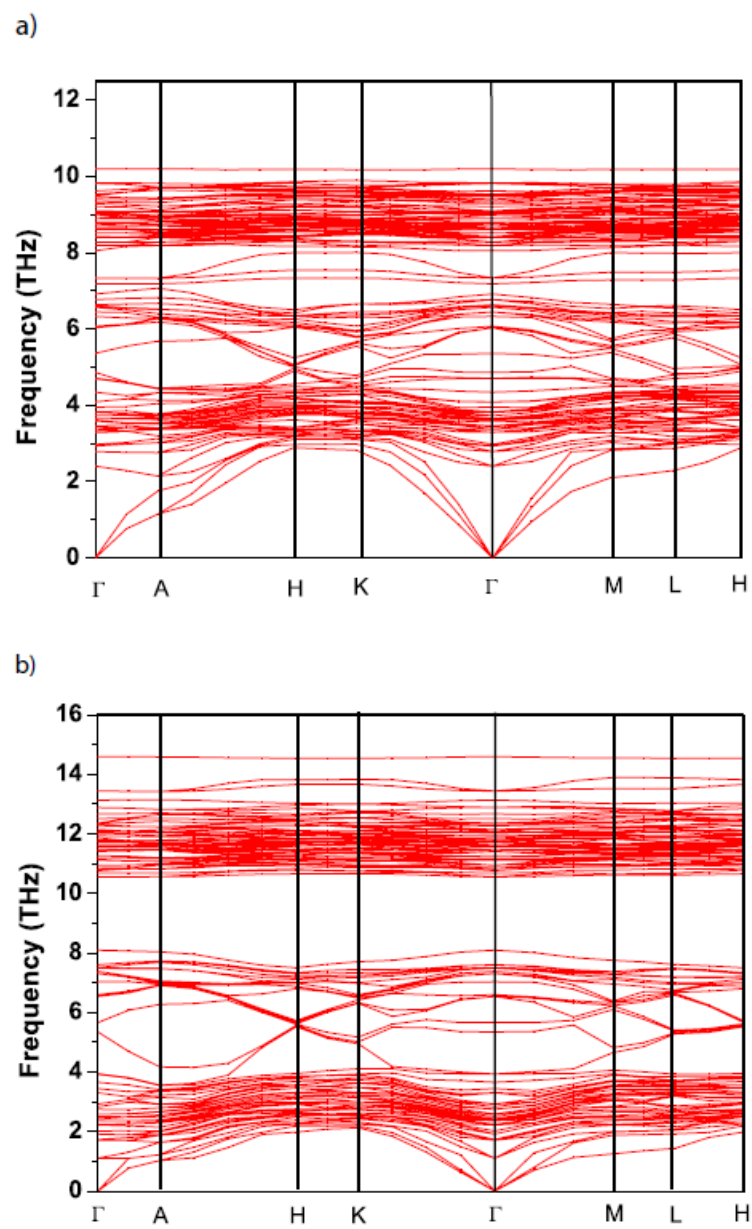


Figure 3. Phonon dispersions of Wurtzite of $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ under a) 0 GPa b) 20 GPa conditions.

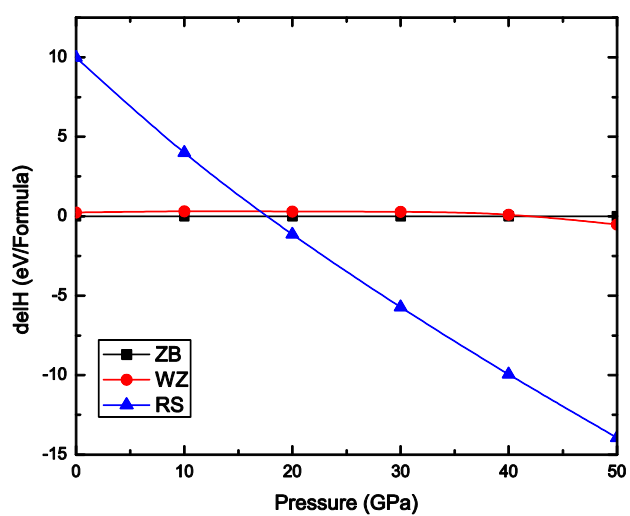


Figure 4. Enthalpy differences of Zinblende (black), Wurtzite (red), and Rocksalt (blue) $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ with respect to that of Zinblende structure as a function of pressure.

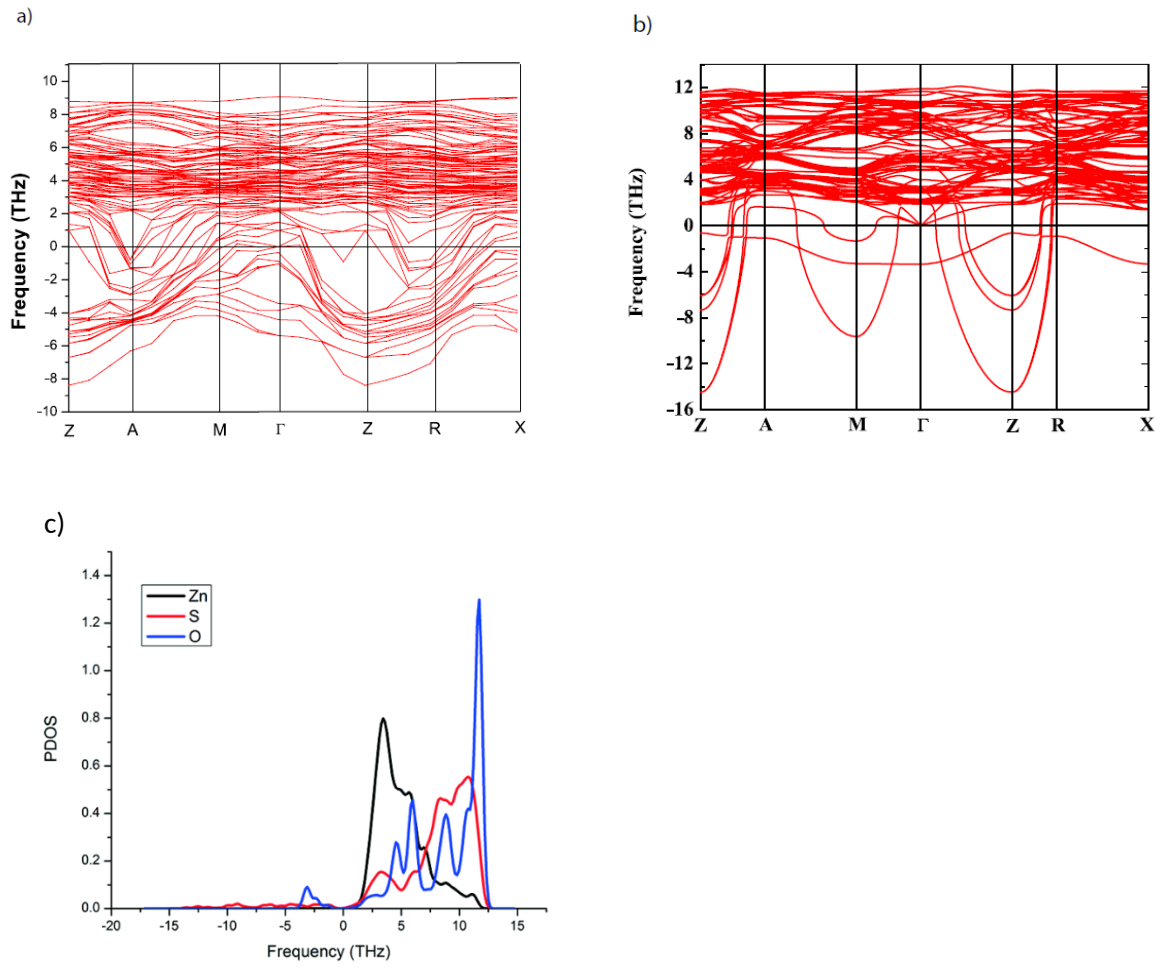


Figure 5. a) Phonon dispersion of Rocksalt $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ at a) 17.5 GPa b) 25 GPa conditions and c) The partial phonon density of states at 25 GPa conditions.

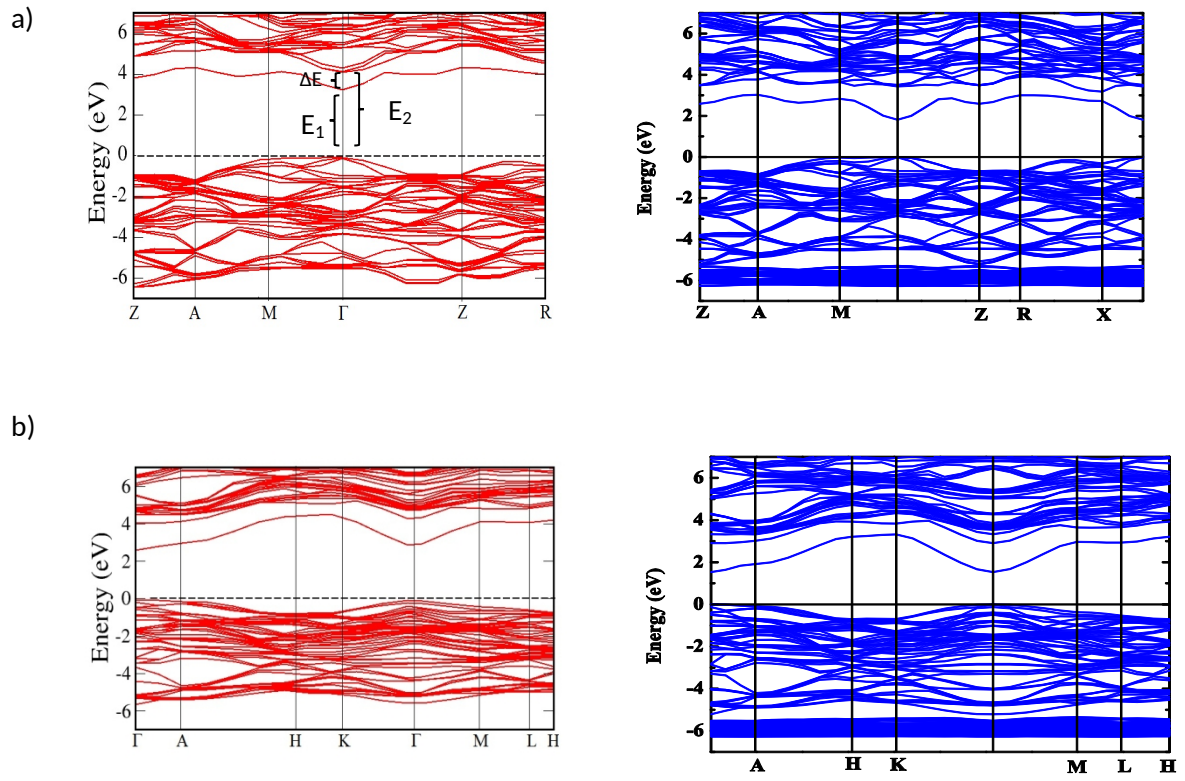


Figure 6. Electronic band structures at 0 GPa of a) Zincblende and b) Wurtzite $\text{Zn}_{16}\text{O}_1\text{S}_{15}$. The left and right panels respectively represent the results obtained by using HSE06 and GGA exchange - correlation functional.

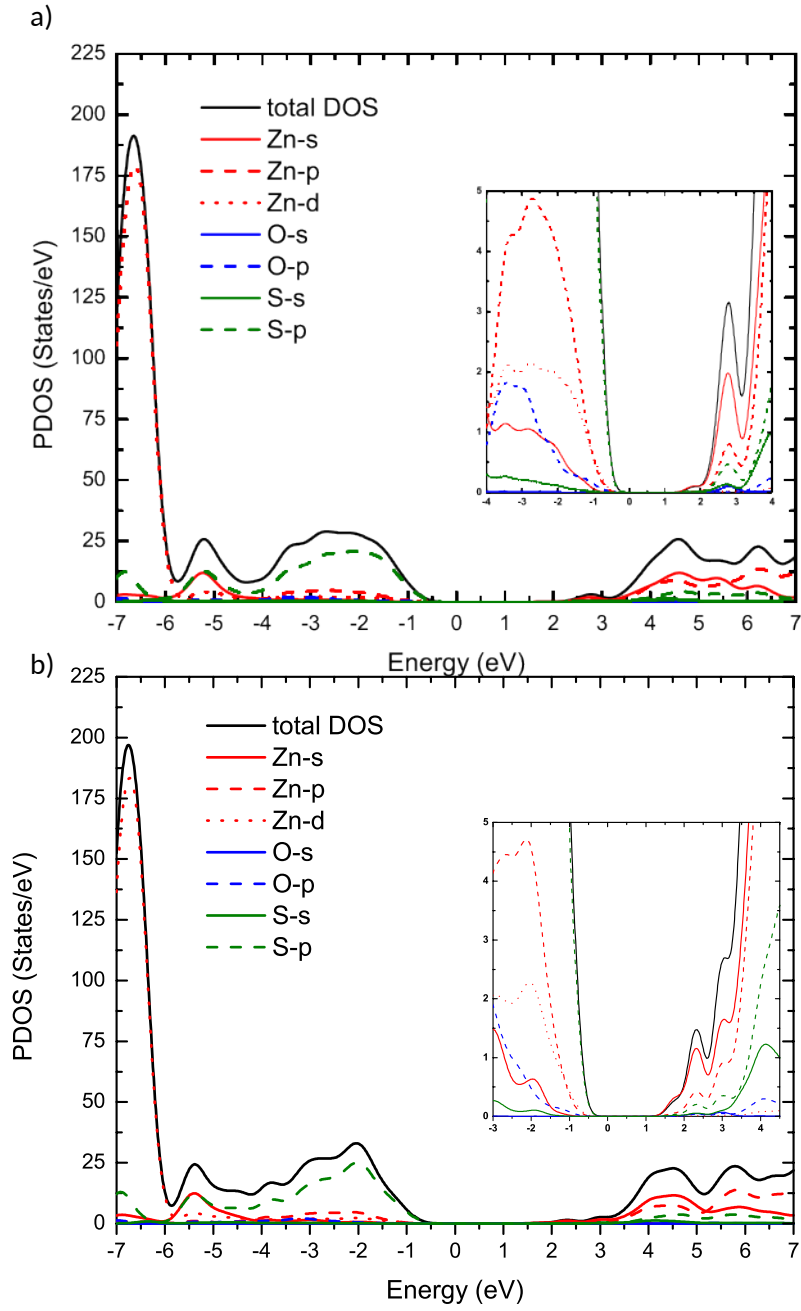


Figure 7. Total and partial DOS of a) Zincblende and b) Wurtzite $\text{Zn}_{16}\text{O}_1\text{S}_{15}$ at 0 GPa. The black solid line represents the total DOS whereas the red, blue, and green respectively represent atomic orbitals of Zn, O, and S. Colored solid and dashed lines represent s and p orbitals respectively while dotted lines represent the d orbital. The insets are details of DOS at the band edges. The top of valence band is set to be zero in the energy scale.

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Electronic Structure of High Pressure Phase IV and V of Methylammonium Lead Iodide Perovskite

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Abstract

We model the phase IV and phase V of Methylammonium lead iodide perovskite (MAPI) under high pressure between 0.3 – 4.0 GPa. As suggested by experiment, both phases share the $Im\bar{3}$ space group. However, physical properties, such as Pb-I bond length, Pb-I-Pb bond angle, and band gap, exhibit a discontinuity at the transition pressure around 2.5 GPa. We found that the orientation of the methylammonium (MA) molecules have large impact on the physical properties. In phase IV (0.3 - 2.5 GPa), the MA molecules in the simulation cell arrange themselves in such a way that the net dipole moment is finite and the simulation cell becomes non-centrosymmetric. Beyond the

phase transition pressure (> 2.5 GPa), the MA molecules rearrange themselves so that the net dipole moment vanishes and the simulation cell becomes fully centrosymmetric. We discovered that the van der Waals interaction plays a major role in the phase transition as it helps constraint the lattice shape and hence the space group.

Methylammonium lead iodide perovskite (MAPI) has attracted massive attention as it is a potential material for cheap and efficient solar cells.¹ Recently, MAPI solar cells have gained the efficiency up to more than 22%² and the stability of MAPI solar cells has been reported to be extended up to 1 year.³ However, many challenges are still waiting to be resolved before the commercialization of perovskite solar cell could take place.⁴ One major problem is that perovskites are highly unstable. They are sensitive to moisture, ultraviolet light and thermal stress.⁵⁻⁷ The lifespan of most perovskite solar cells are in the order of weeks to only several months.⁸ Even the most stable cell reported is guaranteed to last for one year under controlled conditions,³ whereas the well-established silicon solar cells would still be functioning for at least 25 years outdoors.

Aside from stability problem, there are researches that focus on improving band gap,^{9,10} i.e. the electronic property, in order to raise energy conversion efficiency, so that it approaches that of the theoretical QS limit. Doping metals not only have effect on structural property of perovskite, but also affect its electronic properties.⁸

The physical properties of MAPI have been investigated under high pressure as it possesses series of physically interesting phase transitions.¹¹ At $P = 0$ GPa and $T = 165$ K,¹² MAPI has a tetragonal $I4/mcm$ structure (Phase II) and undergoes a phase transition to an $Im\bar{3}$ structure (Phase IV) at $P = 0.3$ GPa. At $P = 2.5$ GPa, MAPI undergoes another phase transition into another $Im\bar{3}$ structure (Phase V). Experimental data showed that Phase IV and V are distinctive in terms of molecular volume, Pb-I bond length, Pb-I-Pb bond angle and the energy band gap. These properties exhibit a disruptive jump at the phase transition. Even though the analysis of the experimental data can determine the space group of Phase IV and V, the molecular orientations of Methylammonium (MA) molecules have not been

identified. In this work, we modeled the MA orientations in Phase IV and V, evaluated the structural and electronic properties, and compared these results to the available experimental data.

In this research, we have used the density functional theory as implemented in Quantum ESPRESSO code.¹³ We used ultrasoft pseudopotentials and a plane wave basis set.^{14,15} For 8-formula-unit simulation cells ($2 \times 2 \times 2$ supercell of cubic Phase I), the energy cutoff is set at 90 Ry (1224.5 eV). The k-point mesh is set to $6 \times 6 \times 6$. The total energy are converged within 2 meV (0.021 meV/atom). This enables us to examine the difference between each MA molecule orientation precisely.

For the exchange-correlation potential, we have used a generalized gradient approximation (GGA) functional.¹⁶ However, there are a number of physical phenomena that need special treatments, such as relativistic effects of Pb atoms and many-body van der Waals (vdW) interaction. The vdW interaction is incorporated in the vdW-DF-cx¹⁷ functionals. The relativistic effects are incorporated in the PBEsol functional,¹⁸ which we studied both scalar and full relativistic effects. In our work in manuscript, we tested van der Waals functional by calculating the lattice parameter and the molecular bond length of MAPI in the ambient-pressure cubic phase, also shown in the Supplementary Information.¹⁹ The vdW interaction is incorporated in the vdW-DF-cx¹⁷ functionals as it gives smallest mean error of tested parameters.

We took the high pressure structure $Im\bar{3}$ as suggested by the experiment for the majority of this study.¹¹ The space groups give a guide for the positions of Pb and I atoms. Szafrński and Katrusiak¹¹ have identified the voids inside the Pb-I mesh, which can be identified into 2 groups according to their shapes as *dumbbells* and *sphere*. Figure 1 shows procrystal electron density isosurfaces at $0.0004 e/\text{\AA}^3$, which are interpreted as crystal voids. The dumbbell has three possible orientations along [100], [010] and [001] of the simulation cell, referred to as x-dumbbell, y-dumbbell and z-dumbbell, respectively. The unknown is the way one can place the MA molecules into those voids. Neglecting the on-axis rotation of the MA molecule,

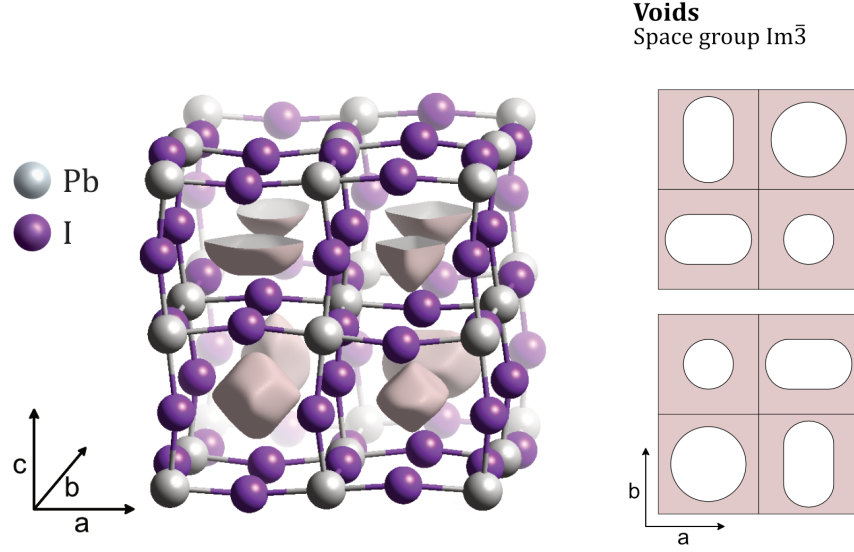


Figure 1: a) The high-pressure phase $Im\bar{3}$ of $MAPbI_3$, showing atomic structure and the shape of voided spaces in the cation sites. b) Simplified illustration of the structure and the void. The diagram plane is in ab -plane and the lower diagrams show the bottom layer of the cell. Larger circles are the spherical voids, and capsule shapes and smaller circles are the dumbbell voids in a -, b - and c -direction, respectively.

there are two possible C-N orientations in one dumbbell void, which are opposite to each other. For the spherical voids, the possibilities of MA orientation is not constrained. The simulation cell, which include 8 formula units of $MAPbI_3$, features two x-dumbbell, two y-dumbbell, two z-dumbbell and two sphere voids. Therefore, there are $2^6 \times (\text{possibility of MA spherical rotation})^2$ possible ways to place the MA. The exact position of C, N and H atoms cannot be directly observed due to experimental limitation.²⁰

In this work, MA molecules are depict by arrows. The arrow head is N and the tail is C. Among large number of possibilities, we chose to investigate a number of extreme cases where i) the MA orientation gives the maximum dipole moment (Scheme α) and ii) two other cases where the total dipole moment is zero (Scheme β and Scheme γ). The schematic model of each simulation cells are shown in Figure 2. Shown in Figure 2 is Scheme α in which the MA orientations give up the centrosymmetric property and the net dipole moment is maximum. Figure 2 and 2 show Scheme β and Scheme γ , respectively, in which the MA orientations give the perfect centrosymmetric property and the net dipole moment vanishes.

The difference between Scheme β and γ is the MA orientations in the spherical voids. The latter is not align along simulation cell basis vectors, but point along direction $[111]/[\bar{1}\bar{1}\bar{1}]$.

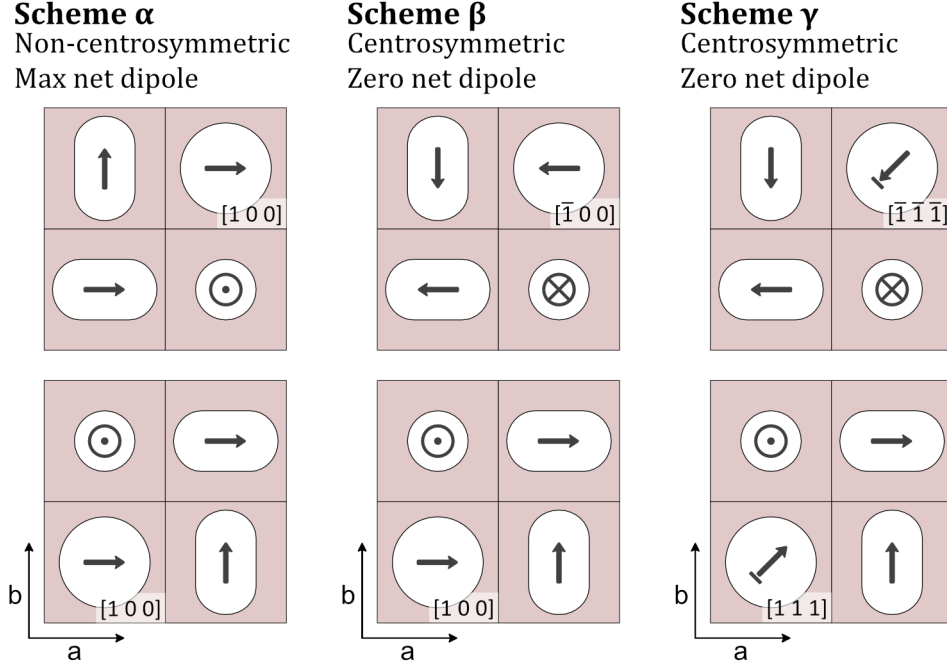


Figure 2: Schematic orientation of the MA, i.e. CH_3NH_3 , molecules. Arrows (and symbols) in the diagrams show the orientation of the CH_3NH_3 molecule inside each void. The arrow head is N and the tail is C. Circle means that the arrow is pointing outward from the paper and the cross (x) means that the arrow pointing into the paper. Scheme α has the maximum net dipole. Scheme β is centrosymmetric and has lowest energy. Scheme γ is another centrosymmetric configuration, but the MA orientations in the spherical voids point in $[111]/[\bar{1}\bar{1}\bar{1}]$ direction. In terms of energy, Scheme $\gamma < \beta < \alpha$.

We also considered an alternative experimental high-pressure structure *Imm2*, reported by Kong et al.²¹. Only Pb and I atoms position are identified. We analyzed the voids inside the cell using CrystalExplorer²² then, from the shape of the voids, we've placed the MA molecules as shown in Supplementary Information.

We found that MA configuration which gives zero dipole is energetically preferred in low pressure. However, while the structure with maximum dipole, or Scheme α is not energetically preferred in low pressure, it becomes the most energetically stable at higher pressure. This result is in agreement with experiment report for MAPbBr_3 perovskite, where

MA molecules become ordered at high pressure and are locked in place.²³

We have studied the pressure-enthalpy relation for MAPbI_3 primarily in the pressure between 0 and 40 kbar. In addition to the $Im\bar{3}$ structure with centro/non-centrosymmetric MA orientation, the well-studied, ambient-pressure phase, (t)etragonal- MAPbI_3 , and alternative high pressure structure $Imm2$, reported by Kong et al.²¹, were also included. The $Imm2$ structure's ground state enthalpy is higher than that of $Im\bar{3}$ structures for every point in this pressure range, i.e. the $Imm2$ symmetry structure is not energetically favorable. Thus, we have dropped it from the MA orientation study.

Results shows that MA configuration which gives zero dipole is energetically preferred in low pressure. However, while the opposite, i.e. structure with maximum dipole, or Scheme α , is not energetically preferred in low pressure, it becomes the most energetically stable at higher pressure. Fig.3 shows enthalpy for each MA orientation as function of pressure. At $P = 5.5$ kbar which correspond to Phase IV in,²⁴ $Im\bar{3}$ structure with MA orientation Scheme γ (downward-pointing, open triangles in Fig.3) energetically preferred. Whereas, at $P = 38.3$ kbar, Scheme α (upward-pointing, open triangles) becomes more favorable. At this pressure, MAPbI_3 has transformed into Phase V according to Szafrński and Katrusiak²⁴. The enthalpy difference between MA configurations lies within 0.003 eV/formula unit.

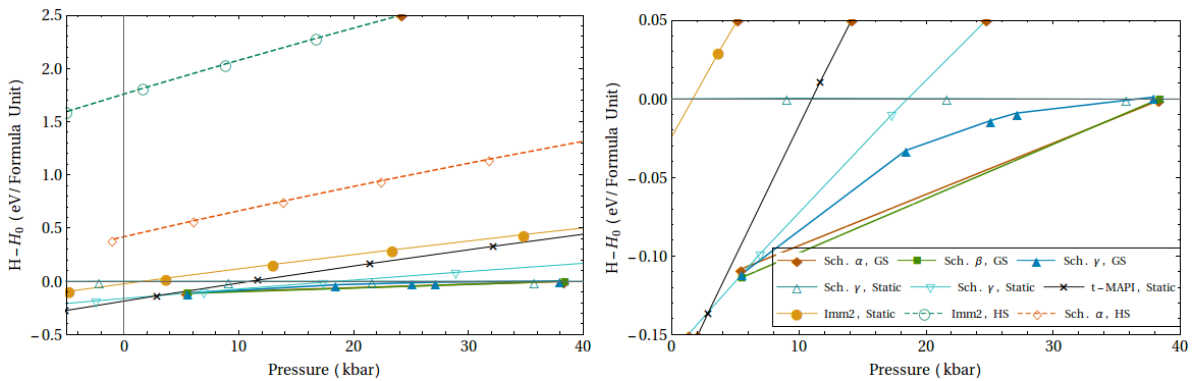


Figure 3: Enthalpy difference per formula unit w.r.t. Scheme α as a function of pressure of a) fully-relaxed ‘ground state’ (GS), b) ‘static’ phases which we take the atomic position of the respective GS then vary the cell volume. c) ‘High symmetry’ (HS) are the respective structures with symmetry as reported by other works, the atomic position are kept fixed to retain the symmetry.

It is worth noting that the vdW interaction plays a major role here. If the GGA with PBEsol functional were employed the the simulation cell will be greater distorted. The lattice parameters and Pb-I-Pb bond angle mean are reported in the Supplementary Information.

In detail, we performed structural optimization starting from Scheme γ . It is a good starting point because Scheme γ is not in a minimum energy state. It has a potential to evolve into a lower energy state. The structures of MAPbI₃ in Phase IV and V taken from experiment by Szafrński and Katrusiak¹¹ were relaxed under five pressure conditions: $P = 5.5, 18.4, 25.1, 27.1$ and 38.3 kbar. Additional structural data can be found in the Supplementary. At low pressure, 5.5 and 18.1 kbar, MA molecules in the spherical voids rearrange themselves into a new configuration that the net dipole is finite but less when compared with that of scheme α , which has maximum net dipole moment. At higher pressure, the relaxed structure resembles that of Scheme β where the net dipole vanishes and the MA molecules in spherical voids prefer aligning with a crystal plane. We note that, though we did not constrain the position of any atoms in the simulation cell, when the structure adjusts to the equilibrium configuration, the MA molecules in the dumbbell voids do not realign themselves at all. They remained parallel to the voids in the direction we initially place them. Thus, in MAPbI₃ crystals, the Pb-I inorganic network can impose partial constrain onto the organic cations.

We also performed structural optimization starting from Scheme α and β at $P = 5.5$ and 38.3 kbar and obtained the enthalpy for the ‘ground state’. MA reorientation in Scheme β resembles that of Scheme γ described in the previous section. This is to be expected, as both Schemes share the centrosymmetric MA orientation. For Scheme α at low pressure, the MA molecules in spherical voids deflect slightly from the original position. They tend to avoid aligning in the same direction as their neighboring molecule. This can be seen in the MA molecules in the spherical voids and their c-axis neighbors. At $P = 38.3$ kbar where the cell is subjected to higher pressure, the MA molecules in the spherical void and its c-axis neighbor deflect and form a scissoring pair. This is the only case which the MA molecules

in dumbbell voids deflected away from their original void shape and ultimately distort the PbI inorganic network, as shown in Fig.4. While the MA molecules in the spherical voids alter their position according to the shrinkage of the void, the MA in dumbbell void that experience enough repulsion from another MA also act against the Pb-I network, distorting the Pb-I octahedra network. The lattice parameter also shrinks by 0.5% compared to Scheme γ .

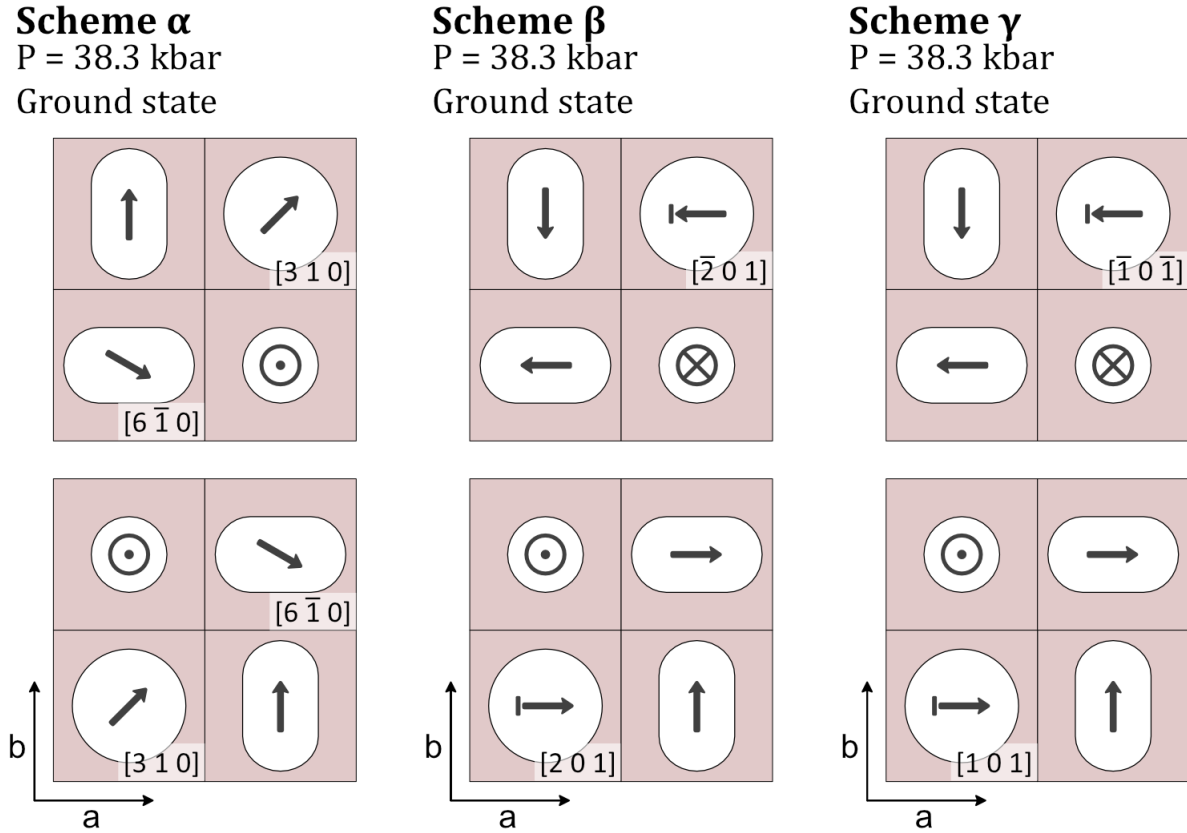


Figure 4: Schematic orientation of MA molecules. By structural optimization starting from Scheme a) γ , the MA evolved into b) at low pressure (0.55 - 2.5 GPa), and c) at higher pressure (2.7 - 3.83 GPa). Schematic orientation of MA molecules. By structural optimization starting from Scheme a) α , the MA evolved into b) at low pressure (0.55 GPa) and c) at higher pressure (3.83 GPa).

This result is in agreement with experiment report for MAPbBr₃ perovskite, where MA molecules become ordered at high pressure and are locked in place.²³

Previously, the locking of organic molecules in HOIPs have been speculated in both

experiment and in *ab initio* molecular dynamics study.^{23,25} Experimental studies have observed that HOIP with large organic cations (formamidinium (FA)) have longer lifetime when doped with smaller cations.²⁶ Doping with smaller cations distorts the inorganic Pb-I network. The distorted Pb-I network, then, constrains the movement of the larger organic cations. In case of FA molecule, the rotation become hindered due to the bent angle at the center of the molecule.²⁵ However, Ghosh et al.²⁵ have not report on the orientation of MA molecule. As MA molecules are smaller and has stick-like shape with no bent angles, their rotation would be less affected by the shrinkage of the void.

As pressure is applied to MAPbI₃, the molecular voids in the material contract, inadvertently leading to stronger vdW interaction between H atoms and I atoms. As MA is locked into its position and cannot spin freely at high pressure, it would slow down degradation, since Pb-I bond strength does scale up with pressure, while the vdW interaction between I and H in MA does.

At this stage, we calculated the structural properties, such as volume, Pb-I bond length, Pb-I-Pb bond angle, and the electronic band gap as a function of pressure, and compared with the available experimental data.

We found that MA configuration which gives zero dipole is energetically preferred in low pressure. However, while the structure with maximum dipole, or Scheme α is not energetically preferred in low pressure, it becomes the most energetically stable at $P = 3.83$ GPa. This result pave way to better utilization of organic-inorganic perovskite materials, as well as suggesting the experiment techniques to confirm our results.

Acknowledgement

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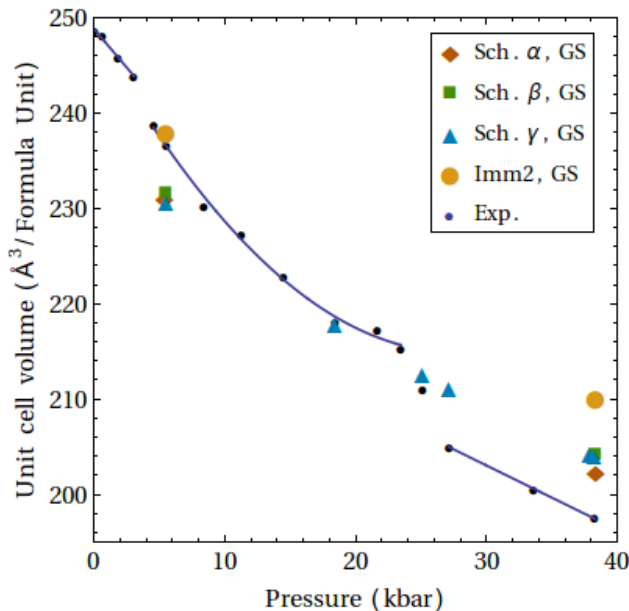


Figure 5: a) the atomic configuration for ground state of maximum dipole MA configuration (Scheme α) at high pressure and b) the pressure and volume relationship

at Large Scale Simulation Research Laboratory (LSR), National Science and Technology Development Agency (NSTDA), Thailand. This work has made use of results obtained with the Chalawan HPC cluster, operated and maintained by the National Astronomical Research Institute of Thailand (NARIT) under the Ministry of Science and Technology of Royal Thai government. Computing facilities have been partially supported by Super SCI-II research grant, Faculty of Science and Ratchadaphiseksomphot Endowment Fund of Chulalongkorn University (CU-59-046-EN).

Supporting Information Available

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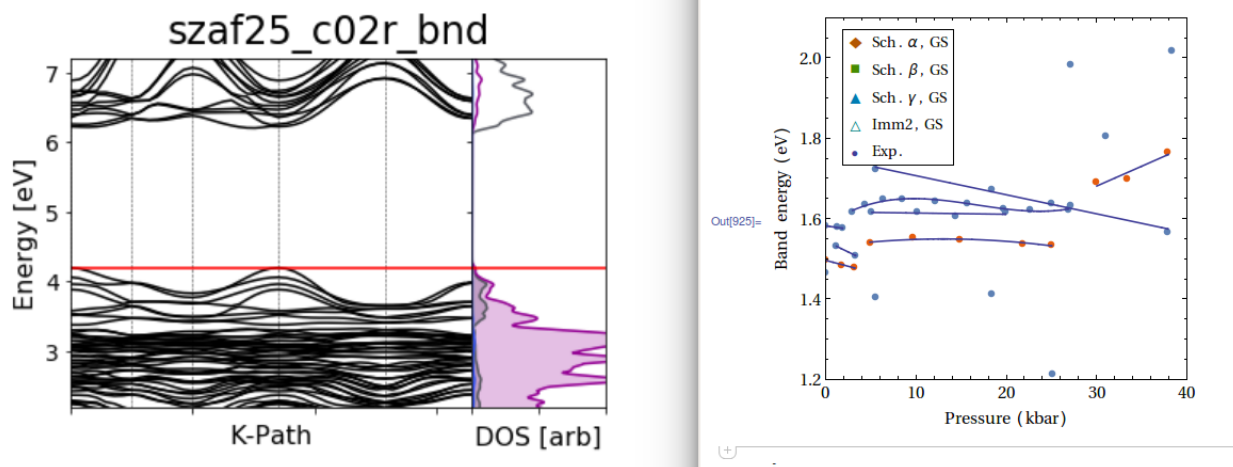


Figure 6: a) energy band structure for ground state of maximum dipole MA configuration (Scheme α) at high pressure and b) the pressure and band energy relationship

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The crucial role of density functional nonlocality and on-axis CH_3NH_3 rotation induced I_2 formation in hybrid organic-inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$ cubic perovskite

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Abstract

Effects of electronic nonlocality in density functional theory study of structural and energetic properties of a pseudocubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ are investigated by considering coherent rotation around C – N axis of a CH_3NH_3 cation. A number of truly non-local and semi-local exchange correlation density functionals are examined by comparing calculated structural parameters with experimental results. The vdW-DF-cx which takes into account the non-local van der Waals correlation and consistent exchange shows the best overall performance for density functional theory study of this system. Remarkable distinctions between results from vdW-DF-cx and those from PBEsol exchange correlation functionals are observed and indicate the need of including the non-local interaction in the study of this system, especially its dynamical properties. The obtained rotational barriers are 18.56 meV/formula and 27.71 meV/formula which correspond to rotational frequencies of 3.71 THz and 2.60 THz for vdW-DF-cx and PBEsol calculations, respectively. Interestingly, the maximally localised Wannier function analysis shows the hydrogen bonding assisted covalent character of two iodide anions at a moderate rotational angle which can lead to I_2 formation and then material degradation.

Introduction

In the last decade, there has been a booming interest in hybrid organic inorganic perovskites (HOIPs) originates from their potential applications in optoelectronic, thermoelectric, and photovoltaic technologies, owing to their favourable electronic, excitonic and optical properties¹⁻⁴. In only ten years' time, reported power conversion efficiencies of perovskite solar cells have been raised up from the first record of 2.2% in 2009, to 22.1% in 2016^{2,5,6}. Intensive researches have rendered perovskite solar cells into devices that are both easy to fabricate and have high cell power conversion efficiency, on par with those of silicon solar cells⁷. But commercial perovskite photovoltaic devices are still several years down the road, due to its stability issues⁸⁻¹¹.

HOIPs are in a class of material that has a perovskite crystal structure with an ABX_3 chemical composition, where A, B, and X represent an organic monovalent cation, an inorganic cation and a halogen, respectively. Methylammonium lead iodide (MAPbI_3) perovskite, which, as the name suggested, has methylammonium (MA) as the cation, is regarded as the archetype of HOIPs since it exhibits rich fundamental photovoltaic properties, and has recently been intensively studied and developed for solar cell devices. MAPbI_3 exists in three phases, namely orthorhombic (Pnma) at $0 \text{ K} < T < 165 \text{ K}$, tetragonal (I4/mcm) at $165 \text{ K} < T < 327 \text{ K}$, and cubic (Pm $\bar{3}$ m) at $T > 327 \text{ K}$ with ordered antiferroelectric MA cation arrangement for the first, and disordered arrangements for the latter two¹²⁻¹⁵. Orientation dynamics of the organic cations are associate with physical properties of MAPbI_3 . One is the ferroelectric effect which is related to an anomalous hysteresis in the HOIP solar cells¹⁶. Long migration length of electrons and holes¹⁷, structural evolution and stability also result from the said dynamics^{14, 15, 18 – 24}.

Recent experimental results suggest that there exist two kinds of dynamics associated with a MA cation in MAPbI_3 ²³. The first type is the reorientation of the C – N axis with estimated 3 – 14 ps time scale^{16, 17, 19, 23}. The second type is the much faster methyl and/or ammonium groups rotation about C-N axis with sub-picosecond time scale²⁵ that has recently been estimated at ~30 times faster²⁶. Such fast-rotation cannot be precisely probed by experiments²³. Moreover, the interplay between octahedron tilting and the MA dynamics still needs a clearer understanding, as it has recently been dubbed as the chicken-and-egg paradox by Li and Rinke²⁷.

Since the emergence of HOIPs as photovoltaic materials in 2009², density functional theory (DFT) based calculations have been adopted to study their properties and underlying physics. Most of the studies are based on the

standard semi-local generalised gradient approximation which cannot retain the non-local nature of electron correlation. However, many suggest the importance of including the non-local van der Waals (vdW) interaction in the calculations to recover such many-body effect^{24, 27–31}. Nevertheless, there are a number of methods for including the vdW-interaction implemented in the DFT based software packages. Each of them yields different levels of accuracy, especially, for molecular, sparse and hydrogen-bond materials. The detailed discussions on the methodology and accuracy of the vdW density functionals (vdW-DFs) can be found elsewhere^{32–34}.

In this work, we examine the application of various vdW-DFs and discuss in detail the equilibrium structural configurations corresponding to the on-axis MA rotation obtained by structural relaxations. As a result, vdW-DF-cx non-local exchange correlation (xc) functional shows the best overall performance for this system with some remarkable differences in the atomic configurations comparing with those of PBEsol semi-local xc-functional. By adding the non-local effect, lowering and broadening of the rotational energy barrier are observed. Furthermore, maximally localised Wannier function (MLWF) analysis illustrates the formation of hydrogen bond assisted I-I covalent bonding at a specific MA rotational angle which could lead to the formation of neutral I₂ defect and so the material degradation.

Results and Discussion

Structural parameters. First, we examine the xc-functionals by calculating structural parameters of the pseudocubic MAPbI₃ unit cell. Since the assigned Pm $\bar{3}$ m symmetry of MAPbI₃ was derived from the average structure of the material at high temperature. Therefore, the average values of such calculated parameters, i.e. average lattice constant ($\bar{a}$), average Pb-I bond length over three inequivalent I-atoms ($\overline{\text{PbI}}$), average C-H bond length ($\overline{\text{CH}}$), average N-H bond length ($\overline{\text{NH}}$), and C-N bond length (CN) obtained by performing full structural relaxation, there is no any constraint, where the C-N axis is at the lowest enthalpy arrangement¹⁴, are used for the comparison with Weller *et. al.*'s accurate powder neutron diffraction experimental results¹⁵.

The structural parameters are grouped into two subgroups according to magnitudes of their absolute errors, i.e. $\bar{a}$ and $\overline{\text{PbI}}$ as one subgroup and CN, $\overline{\text{CH}}$ and $\overline{\text{NH}}$ as the other. The mean absolute error (MAE) of each subgroup is given in TAB.1. The parameters $\bar{a}$ and $\overline{\text{PbI}}$ are in excellent agreement with experimental results (MAE(1) < 1%) for most of xc-functionals except for vdW-DF, vdW-DF2, and PBE. Notably, the vdW-DF-cx shows the best performance in predicting the lattice constant and the Pb-I distance, see MAE(1) in TAB.1. This is in good agreement with the vdW-DF testing performed by Berland and Hyldgaard. They examined the accuracy of a number of vdW-DFs in predicting the binding energy and equilibrium separation in H-bond and dispersive-force dominated systems and found that vdW-DF-cx shows the best overall performance³². However, MAE(2) in TAB. 1 shows that errors in CN, $\overline{\text{CH}}$, and $\overline{\text{NH}}$ are in approximately the same order for all xc-functionals, with an error of ~10% for CN and $\overline{\text{CH}}$, and ~5% for $\overline{\text{NH}}$. The disordered C-N axis orientation and the fast on-axis rotation of H-atoms could probably be responsible for the errors in structural parameters. The divergence from the experimental data might originate from the indistinguishability of the atomic position reported by the experiment. Since the position of C, N, H_C and H_N atoms cannot be experimentally captured due to the MA dynamics, their positions are approximately assigned to Wyckoff sites 4MM(100) and 1 of the Pm $\bar{3}$ m space group¹⁵. From the simulation viewpoint, by using only one pseudocubic primitive unit cell, the disordered nature of the organic cations is neglected, giving rise to the divergence from averaged value of the experimental data. Moreover, the effects of temperature which drive atoms from their zero-Kelvin equilibrium configurations are also not included. Although the simulations give large MAE(2), the lattice constant and the Pb-I bond length are in good agreement with those of the experimental results, thanks to their low dynamics. The latter validates the use of computational model for investigating the local structural and energetic responses to the rotation of H atoms about their C-N axis.

Structural	$\bar{a}$	$\overline{\text{PbI}}$	MAE(1)	CN	$\overline{\text{CH}}$	$\overline{\text{NH}}$	MAE(2)
PBE	6.471(0.2)	3.205(0.05)	0.1000	1.492(0.1)	1.094(0.1)	1.040(0.05)	0.097
PBEsol	6.299(0.02)	3.146(0.01)	0.0156	1.484(0.1)	1.100(0.1)	1.047(0.05)	0.098
rVV10	6.373(0.06)	3.183(0.02)	0.0404	1.503(0.2)	1.093(0.1)	1.040(0.05)	0.100
vdW-DF	6.554(0.2)	3.237(0.08)	0.1576	1.513(0.2)	1.090(0.1)	1.036(0.04)	0.101
vdW-DF2	6.562(0.3)	3.258(0.1)	0.1721	1.524(0.2)	1.087(0.1)	1.036(0.04)	0.104
vdW-DF2-b86r	6.357(0.04)	3.173(0.01)	0.0268	1.496(0.2)	1.097(0.1)	1.043(0.05)	0.100
vdW-DF-cx	6.320(0.003)	3.149(0.01)	0.0061	1.493(0.2)	1.098(0.1)	1.044(0.05)	0.100
vdW-DF-ob86	6.329(0.01)	3.153(0.006)	0.0083	1.497(0.2)	1.097(0.1)	1.043(0.05)	0.100
Exp.	6.317(0.0)	3.159(0.0)	-	1.348(0.0)	0.994(0.0)	0.994(0.0)	-

Table 1. Calculated average structural parameters using semi-local and non-local vdW-DFs compared with experimental results¹⁵. The numbers in parentheses stand for deviation of calculated values from experimental ones. MAE(1) and MAE(2) are mean absolute error of subgroups of parameters $\{\bar{a}, \bar{b}\}$ and $\{\text{CN}, \bar{\text{CH}}, \bar{\text{NH}}\}$, respectively.

Energy barriers, Equilibrium atomic configurations, and H-bonds. The rotational energy barriers are obtained by performing structural relaxation without any constraint after coherent H-atoms rotation (solid lines in FIG.2). The rotation of MA is discretised to 12 rotational steps with 10° step size owing to its C_{3v} symmetry, see FIG.1 for atomistic structural model. Hereafter, only the results from vdW-DF-cx and PBEsol xc-functionals are shown as they are the representatives of non-local and semi-local xc-functionals respectively, results from all xc-functionals are provided in supplementary information. According to FIG.1(c), the rotational potential energy, $\Delta E(\theta) = E(\theta) - E(0^\circ)$, illustrates that the vdW-DF-cx energy barrier ($\Delta E^{\text{vdW-DF-cx}}(50^\circ) \cong 18.56$ meV/formula) is 9.16 meV/formula lower than that of PBEsol ($\Delta E^{\text{PBEsol}}(60^\circ) \cong 27.71$ meV/formula) and the vdW-DF-cx rotational potential energy curve is broader than that of PBEsol.

Lowering of the vdW-DF-cx energy barrier attributes to the distinction of optimised structures and the nature of electronic interaction incorporated in the xc-functionals. To understand these, we calculate $\Delta E(\theta)$ of the vdW-DF-cx-structures for $\theta = 0^\circ$ to 60° , due to a symmetry of the energy curves (see FIG.1(c)), with applications of the following xc-functionals: vdW-DF-cx, PBEsol, vdW-DF-cx-ex (non-local correlation is turned off), and PBEsol-ex (PBEsol density gradient correlation is turned off). The structural contribution can be perceived by comparing ΔE^{PBEsol} with $\Delta E^{\text{PBEsol(vdW-Str)}}$. This contribution attributes to: *i.* unit cell deformation (FIG.3(a), (b)), *ii.* I-displacement (octahedron distortion) (FIG.3(c)-(e)), *iii.* MA arrangement and its internal distortion, and *iv.* hydrogen bonding (FIG.4 (b)). For instance, at $\theta = 60^\circ$, $\Delta E^{\text{PBEsol}} - \Delta E^{\text{PBEsol(vdW-Str)}} \cong 3.1$ meV (FIG. 2) is a consequence of: *i.* short PBE-optimised lattice vectors are comparing to those of vdW-DF-cx-optimised structure while a difference in unit cell shearing is negligible, *ii.* noticeably large PBE-optimised I₂ atomic displacement in opposite of [100] direction comparing to that of vdW-DF-cx-optimised structures. Moreover, at this angle, only Hn₁ - I₁^(bc), Hn₂ - I₁^(c), and Hn₃ - I₂^(a) hydrogen bonds play the role (FIG.4(b)), and those of PBEsol-optimised and vdW-DF-cx-optimised structures are almost the same. It is important to note here that the internal distortion of MA is negligible. Thus, $\Delta E^{\text{PBEsol}} > \Delta E^{\text{PBEsol(vdW-Str)}}$ mainly attributes to unit cell and octahedron deformations. The electronic interaction contribution can be observed by comparing $\Delta E^{\text{PBEsol(vdW-Str)}}$ with $\Delta E^{\text{vdW-DF-cx}}$. At $\theta = 60^\circ$, $\Delta E^{\text{PBEsol(vdW-Str)}}$ is ~ 7.0 meV higher than $\Delta E^{\text{vdW-DF-cx}}$ which reflects the fact that electronic non-local interaction lowers the rotational potential energy. $\Delta E^{\text{PBEsol-ex(vdW-Str)}}$ with $\Delta E^{\text{vdW-DF-cx}} - \Delta E^{\text{vdW-DF-cx-ex}}$. PBEsol correlation is positive at $\theta = 10^\circ, 20^\circ$ while vdW-DF-cx correlation is negative at all rotational angles. Moreover, at these beginning rotational angles, the exchange parts of both semi-local and non-local xc-functionals are almost the same. The non-local correlation becomes crucially important at the moderate rotational angles ($\theta = 40^\circ, 50^\circ, 60^\circ$). The lowering of rotational potential barrier is predominately noted by the non-local interaction keeping H-atoms and I-atoms further apart from each other.

The broadening of vdW-DF-cx rotational potential energy curve can be related to an abrupt change of H-atom positions, illustrated in FIG. 4(a), accompanying with I₁ and I₃ displacements in [001] and [100] directions, respectively. These differences in optimised structures reflect the noticeable distinction in force field calculated by semi-local and non-local xc-functionals. This is emphasised by the totally difference in changes of C-N axis altitudinal angle when the MA undergo on-axis rotation shown in FIG. 3(f). This indicates the need for theoretical revision of dynamical properties of this material in which the truly non-local interaction is included as its importance has recently been realised in spin-polarised system³⁵ and nonmagnetic transition metals³⁶.

Furthermore, we examine the rotational potential energy when there are constraints imposed in structural relaxation process. The results are shown in FIG. 1. The vdW-DF-cx and PBEsol rotational energy barriers are 37.7 meV and 50.7 meV, respectively when the cell parameters are kept at the lowest energy configuration (B), and 50.6 meV and 47.0 meV, respectively, when both cell parameters and I-atomic positions are kept at the lowest energy configuration (C). We also calculate the free on-axis rotational frequencies corresponding to such energy barriers. By obeying the transition-state theory³⁰, the frequency is given by: $\nu = \frac{k_B T}{h} e^{-\Delta E/k_B T}$ when ΔE is the rotational energy barrier. The obtained frequencies for the relaxation model A, B, and C are 3.71 (2.60) THz, 1.83 (1.16) THz, and 1.16 (1.32) THz, respectively, for vdW-DF-cx (PBEsol) calculation. These rotational frequencies may help one experimentally justifies which MA rotational mechanism it is, if the local rotational frequency could be experimentally probed.

As we have seen in FIG. 4(b), even in this high symmetry phase the complexity of hydrogen bonding takes place in this material. Especially when MA undergoes rotation, the hydrogen bonding associated with a specific H-atom can be turned on/off or switches to bond with the other I-atom depending on the rotational angle. For example, Hn₁ strongly bonds with I₃^(ab) at $\theta \in [0^\circ, 40^\circ]$ then switches to strongly bond with I₁^(bc), (a criterion used for strong H-bond is $\text{H} \cdots \text{I} \leq$

3 Å). To illustrate that, we perform the maximally localised Wannier function (MLWF) analysis by projecting the 25 bands Bloch manifold onto 12 atom-centred MLWFs manifold³⁷. The complete MLWFs calculated at $\theta = 0^\circ, 40^\circ, 60^\circ$ are given in supplementary information. Here, it is worth highlighting a MLWF that localised in vicinity of the $I_1^{(bc)}$ obtained at $\theta = 60^\circ$. This MLWF mainly has I-p lone pair atomic orbital character and, also, shows covalent bonding character with the $I_3^{(ac)}$ assisted by Hn_1 , see FIG. 5. This result is the first direct theoretical evidence supporting the recently experimental observation of interstitial iodide migration that lead to I_2 formation in tetragonal MAPbI₃ and then material degradation. Additionally, our result show that I – I covalent bonding is assisted by hydrogen bonding formed when the structure is at the top of rotational potential hill which mean that I_2 formation is induced by MA rotation.

Conclusions. We have performed density functional theory (DFT) based calculations to investigate the equilibrium atomic configurations of the pseudocubic MAPbI₃ hybrid perovskite with respect to on-axis coherent methylammonium rotation. First, we assess the accuracy of a number of semi-local and non-local van der Waals exchange correlation density functionals (xc-functional) by calculating the structural parameters and compare them to the experimental values. According to the results in TAB.1, vdW-DF-cx xc-functional shows the best overall performance for structural property DFT calculation of this material. Second, we report details of structural and energetic responses to the MA rotation obtained through the full structural relaxations. Comparison of results calculated with application of vdW-DF-cx with those of PBEsol xc-functionals shows noticeable lowering and broadening of vdW-DF-cx rotational potential energy curve. The non-local vdW correlation becomes crucial at the rotational angles (at $\theta = 40^\circ, 50^\circ, 60^\circ$) where the potential energy is much higher than the lowest energy (at $\theta = 0^\circ$). That manifest an inevitability of including truly non-local xc-functional in DFT study of this system. Also, the rotational potential barriers and corresponding rotational frequencies are calculated for the cases that the unit cell is fixed, and both unit cell and I-atom positions are fixed in the relaxation processes. Finally, a maximally localised Wannier function analysis reflects that the I – I covalent bonding can be formed at $\theta = 60^\circ$ with the assistance of hydrogen bonding. This can lead to I_2 formation and material degradation.

Methods. Static DFT calculation is performed with the pseudopotential and plane wave method implemented in Quantum-Espresso package³⁸. The core ions are represented by original scalar relativistic ultrasoft pseudopotentials taken from PSLibrary project³⁹. Spin-orbit coupling (SOC) effects are not included in this work, as previous study suggested that SOC does not significantly affect ground state properties of this material⁴⁰. The kinetic energy cut-off is set to 70 Ry. The unshifted k-point mesh is gridded into 6 x 6 x 6 by Monkhorst-Packs scheme⁴¹. This configuration yields convergence of total energy within 2 meV. The nonlocal vdW exchange correlation functionals considered in this work are as follows: rrv10⁴², vdW-DF^{43, 44}, vdW-DF2⁴⁵, vdW-DF-ob86⁴⁶ and vdW-DF-cx⁴⁷. The Perdew-Burke-Ernzerhof (PBE)⁴⁸ and PBEsol⁴⁹ functionals are also applied for comparison. The relaxation algorithm of atoms and lattice parameters used is Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm with a force/atom tolerance equal to 0.001 Hartree/Bohr. The initial structure is the lowest enthalpy configuration reported by Brivio *et al* study¹⁴ (available online⁵⁰) re-optimised with our settings. The calculations of exchange energies are achieved by setting of the Quantum-Espresso input variable, i.e. input_dft, as following: input_dft = 'sla+pw+cx13', and input_dft = 'sla+pw+psx+noge' for vdW-DF-cx and PBEsol exchange (with local correlation) density functionals respectively. For maximally localised Wannier function (MLWF) calculation, the k-space is meshed by 8 x 8 x 8 grid. Twenty-five Bloch wave functions are projected onto twelve atom-centred MLWFs with convergent criteria of the spread function equal to 10^{-10} Å².

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Author Contributions

T.B. designed the research; all authors performed research, analysed the results. T.B., R.K. and V.S. wrote the manuscript.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

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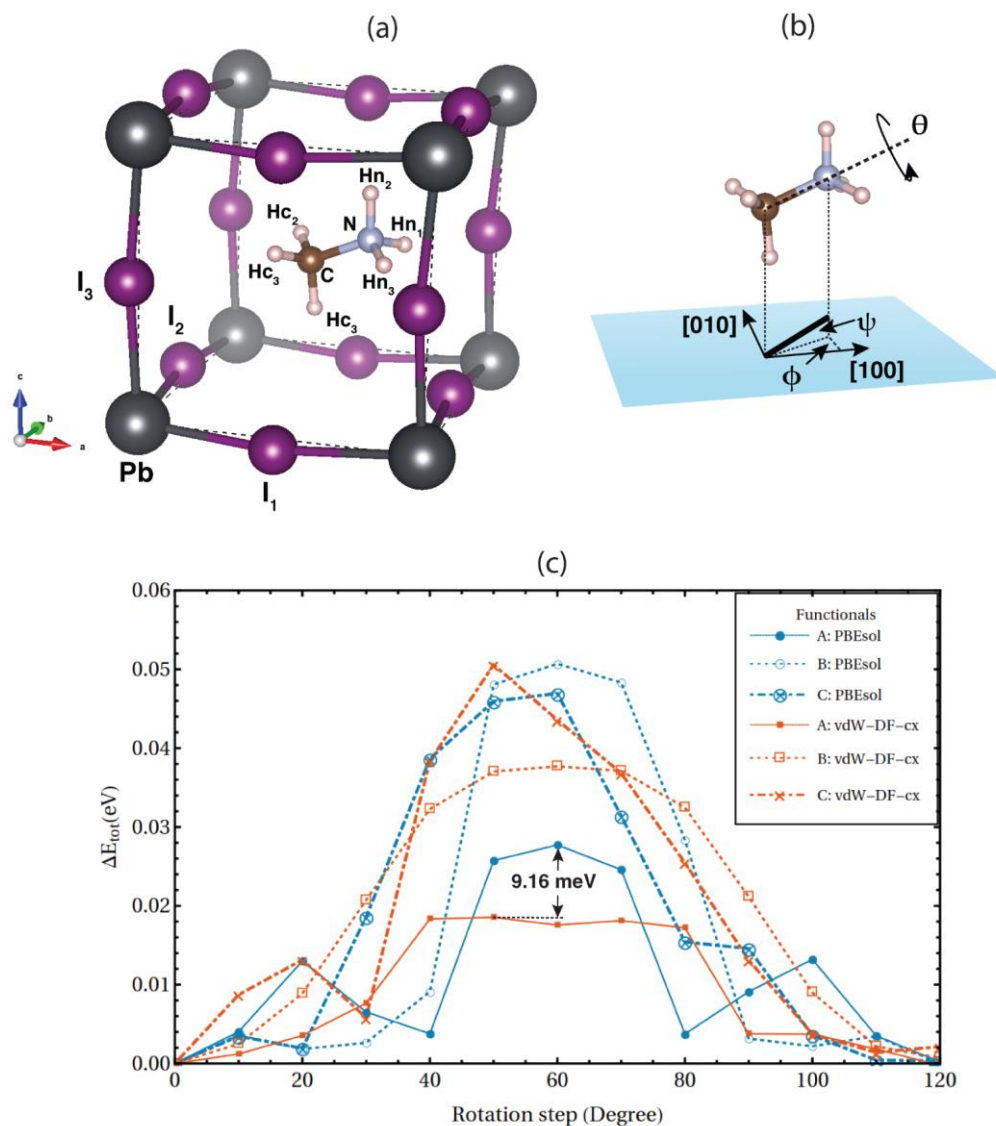


Figure 1. (a) atomistic model of a unit cell. (b) parameters that describe MA orientation (ϕ , ψ), and rotation (θ). (c) rotational barriers obtained by performing structural relaxation with: (A) no any constraint, (B) fixed cell parameters at initial structure, and (C) fixed cell parameters and I-atomic position at initial structure.

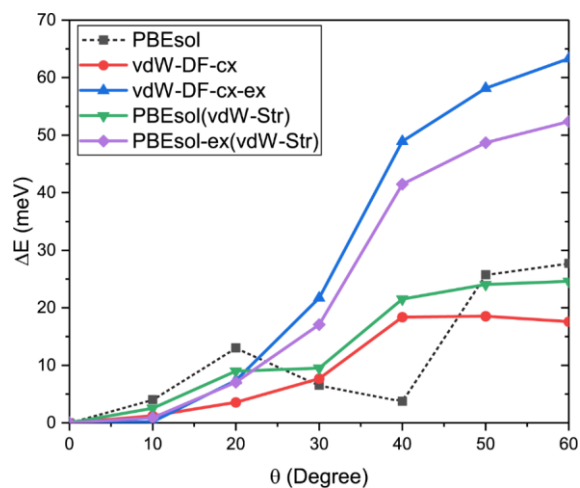


Figure 2. Rotational potential energy curves of the vdW-DF-cx-optimised structure calculated with vdW-DF-cx (red), PBEsol (green), PBEsol with gradient correction correlation off (purple), and vdW-DF-cx with nonlocal correlation off (blue). Dashed line is the rotational potential energy curve of the PBEsol-optimised structure.

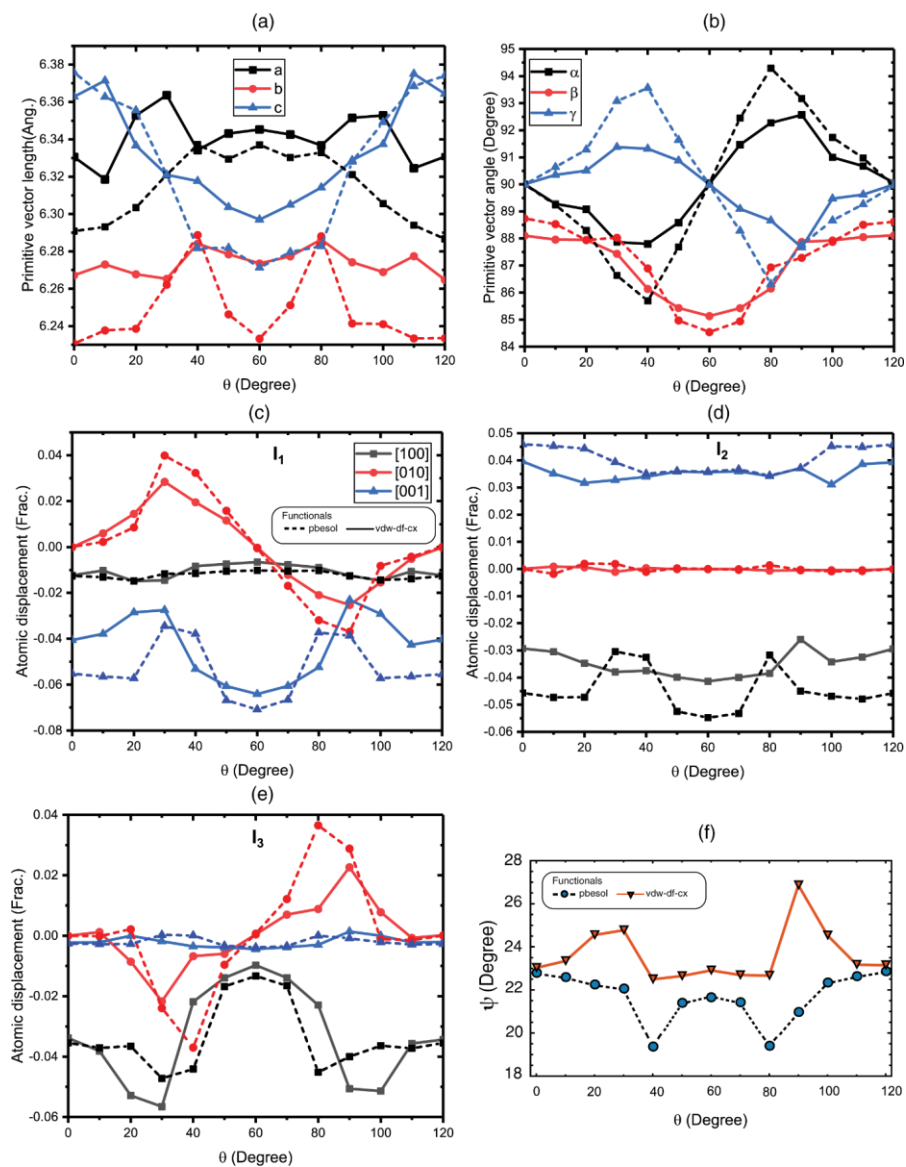


Figure 3.(a) Magnitudes of primitive vectors, (b) angles between them, and (c)-(e) atomic displacements (from Pb – I bond center) in crystallographic directions of three inequivalent I-atoms calculated by applying vdW-DF-cx (solid) and PBESol (dashed) xc-functionals. (f). Altitudinal angle of C – N axis

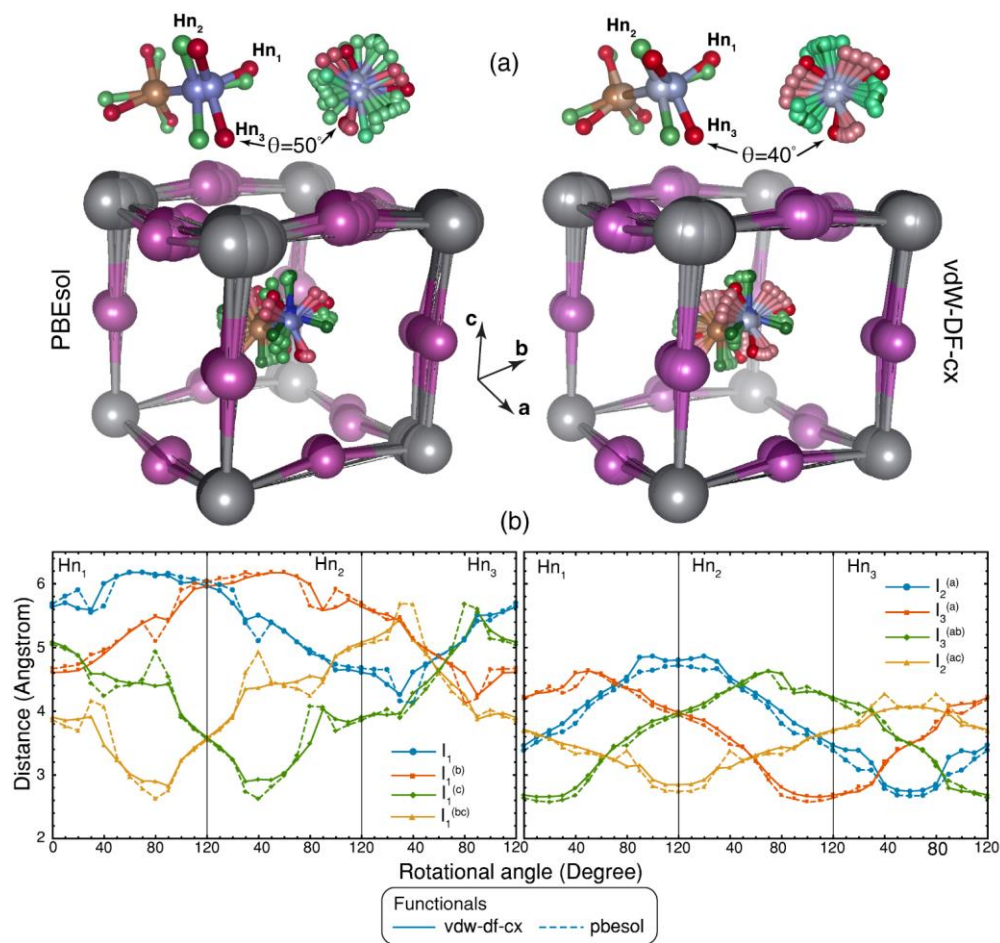


Figure 4.(a) Atomistic representations of optimised structures with PBEsol (left), and vdW-DF-cx (right) xc-functionals for $\theta = 10^\circ$ to 80° illustrate the abrupt changes in H-atom positions at $\theta = 50^\circ$ and $\theta = 40^\circ$ obtained by applying PBEsol and vdW-DF-cx xc-functionals, respectively. (b) H-I distances obtained by structural relaxation with application of vdW-DF-cx (solid) and PBEsol (dashed) xc-functionals where $I_i^{(xyz)}$ represent a replication of the I_i - atom obtained by performing translational symmetry operation with x, y, and z primitive vectors.

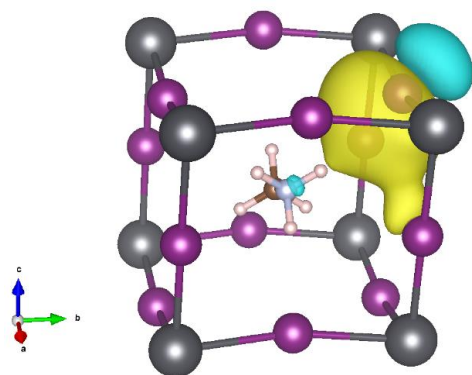


Figure 5. An isosurface of MLWF with the isosurface value $= \frac{\pm 1}{\sqrt{V}}$ calculated with vdW-DF-cx xc-functional at $\theta = 60^\circ$ where V is a unit cell volume in $\text{\AA}^3$. Yellow and turquoise represent positive and negative values, respectively.

Supplementary information

The crucial role of density functional nonlocality and on-axis CH_3NH_3 rotation induced I_2 formation in hybrid organic-inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$ cubic perovskite

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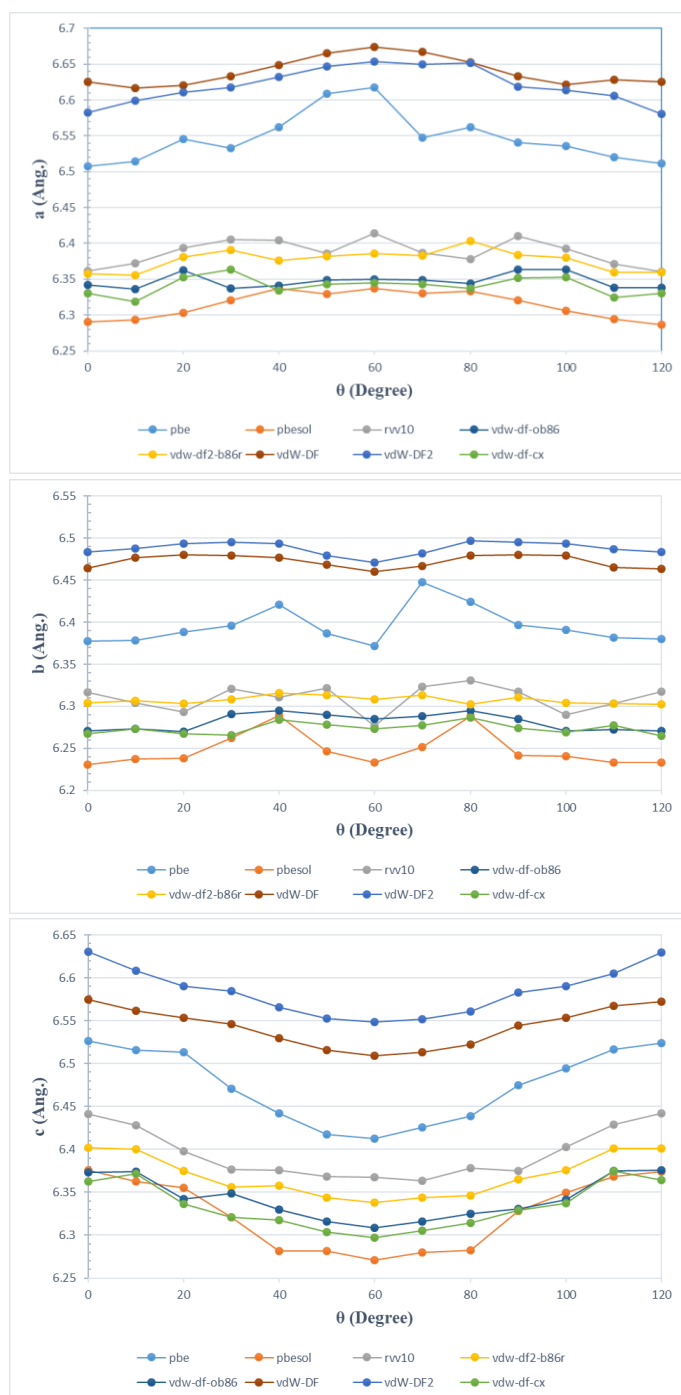


Figure S. 1 Magnitudes of three optimized primitive vectors obtained by performing full structural relaxation, which is there is no any constraint, with applications of a number of semi-local and non-local exchange correlation functionals as a function of rotation angle. The results show inconsistency of PBE, vdW-DF, vdW-DF2 exchange correlation functionals with the others.

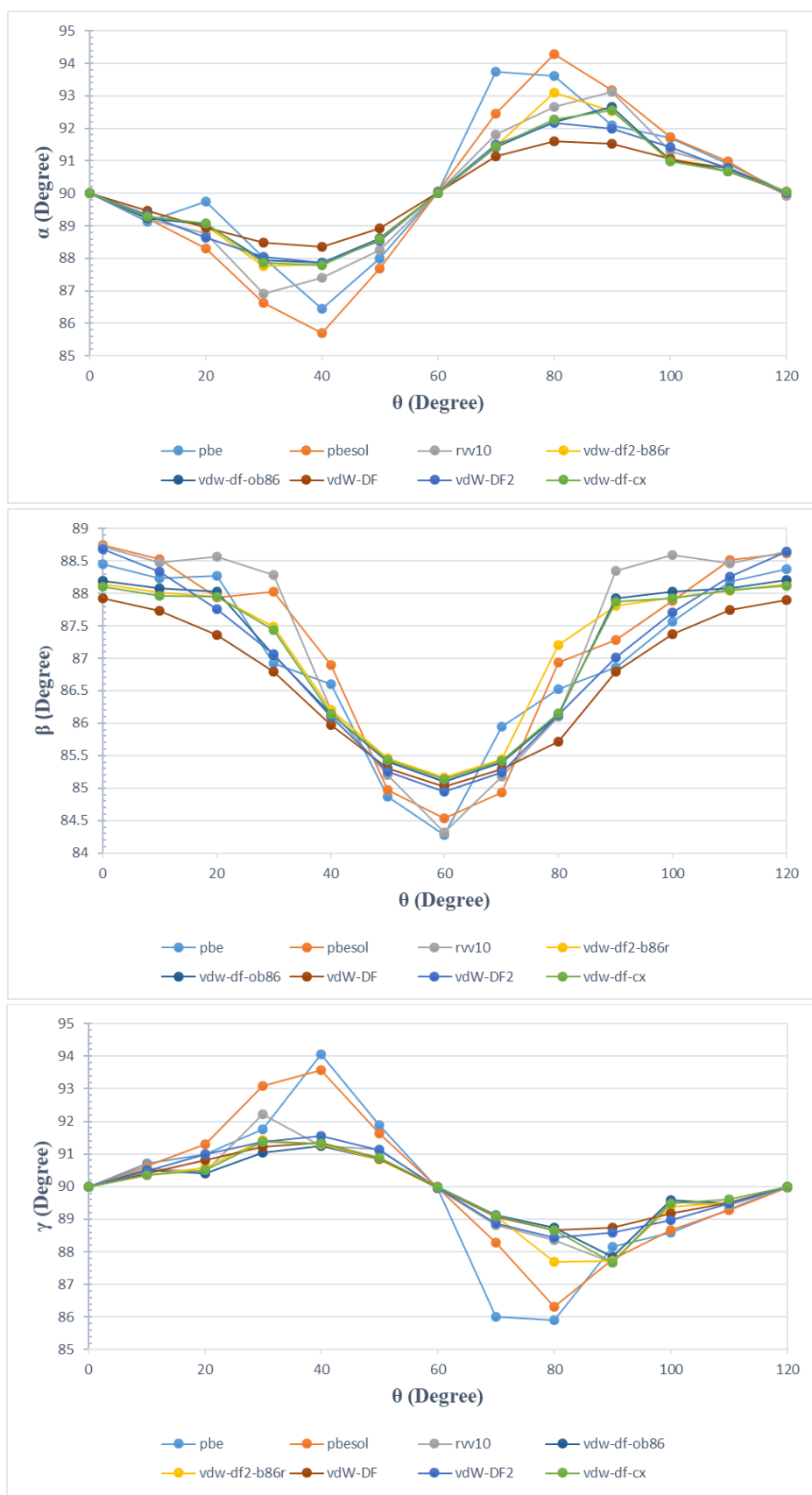


Figure S. 2 Magnitudes of three angles between the primitive vectors obtained by performing full structural relaxation, which is there is no any constraint, with applications of a number of semi-local and non-local exchange correlation functionals as a function of rotation angle.

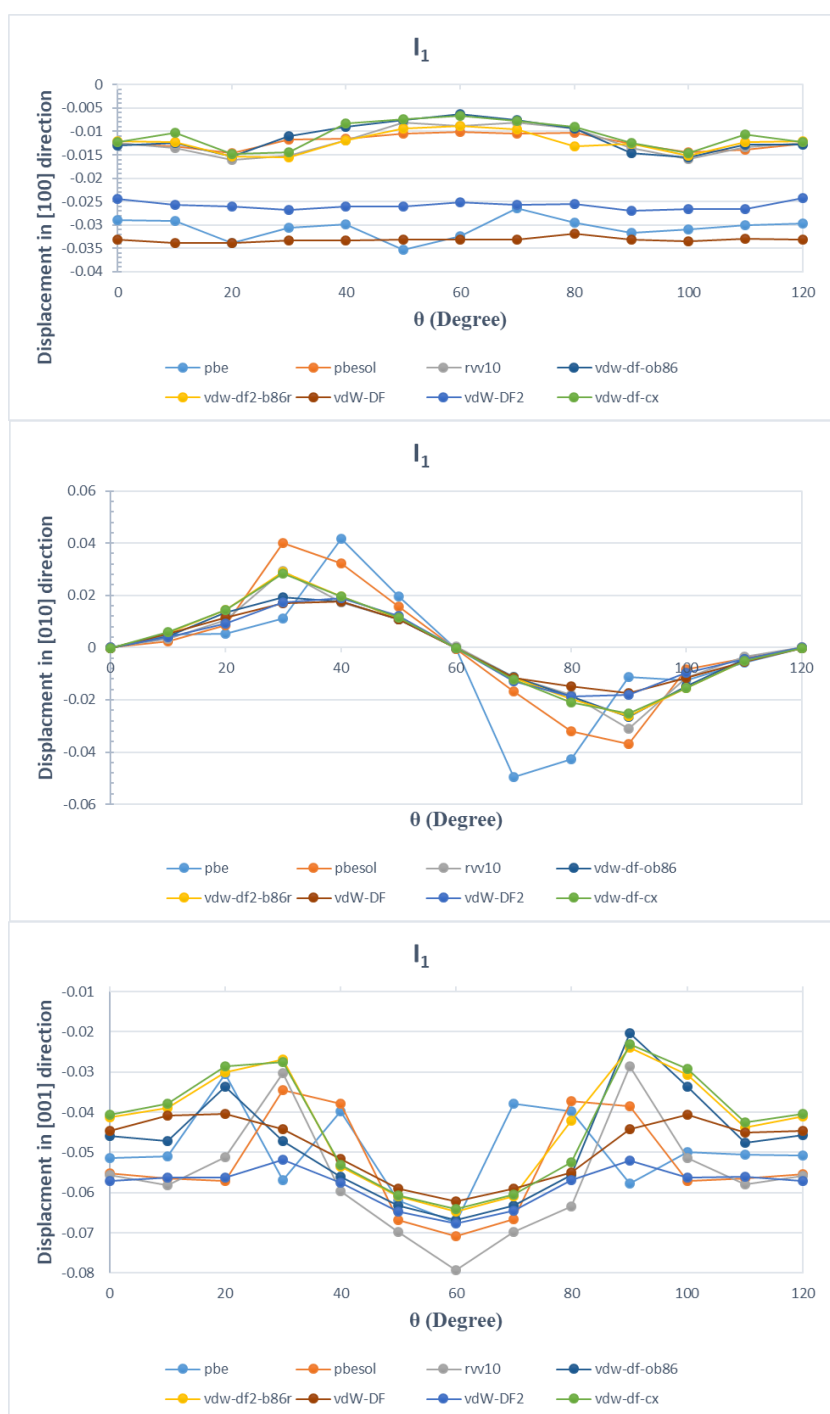


Figure S. 3 Displacements of I_1 -atom from the mid-point of a primitive vector “ $\mathbf{a}$ ” in three crystallographic directions obtained by performing full structural relaxation, which is there is no any constraint, with applications of a number of semi-local and non-local exchange correlation functionals as a function of rotation angle.

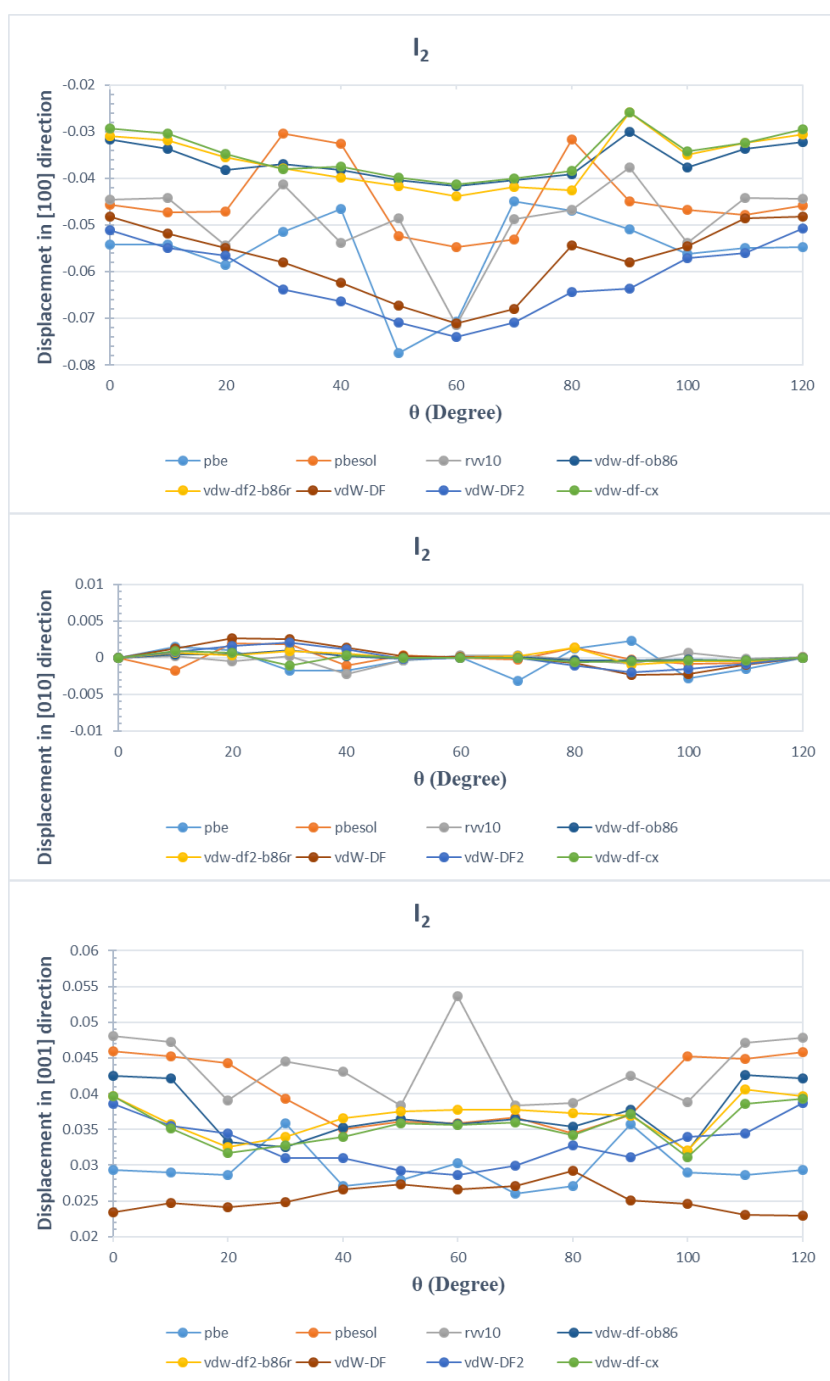


Figure S. 4 Displacements of I_2 -atom from the mid-point of a primitive vector "b" in three crystallographic directions obtained by performing full structural relaxation, which is there is no any constraint, with applications of a number of semi-local and non-local exchange correlation functionals as a function of rotation angle.

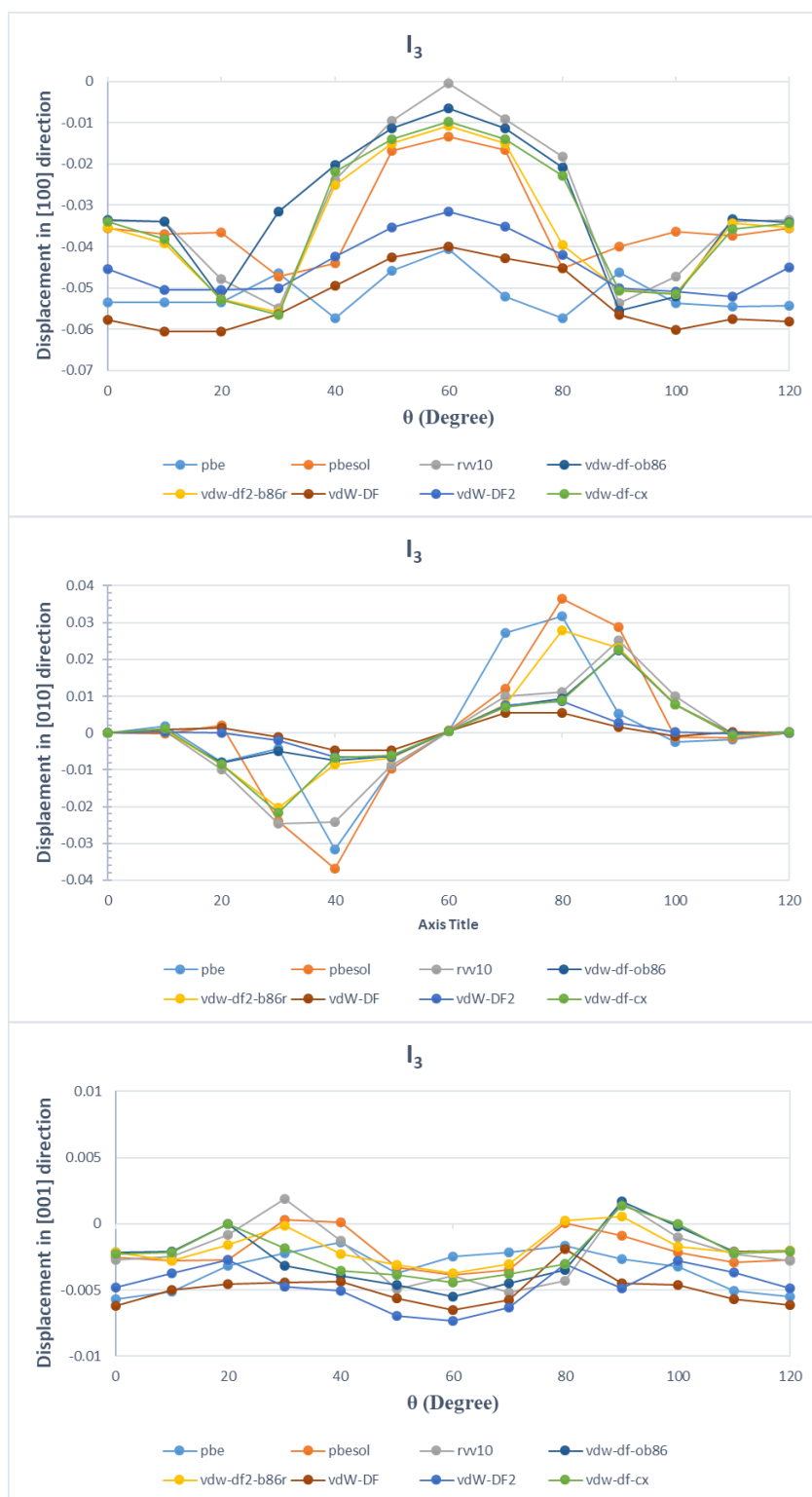


Figure S. 5 Displacements of I_3 -atom from the mid-point of a primitive vector “c” in three crystallographic directions obtained by performing full structural relaxation, which is there is no any constraint, with applications of a number of semi-local and non-local exchange correlation functionals as a function of rotation angle.

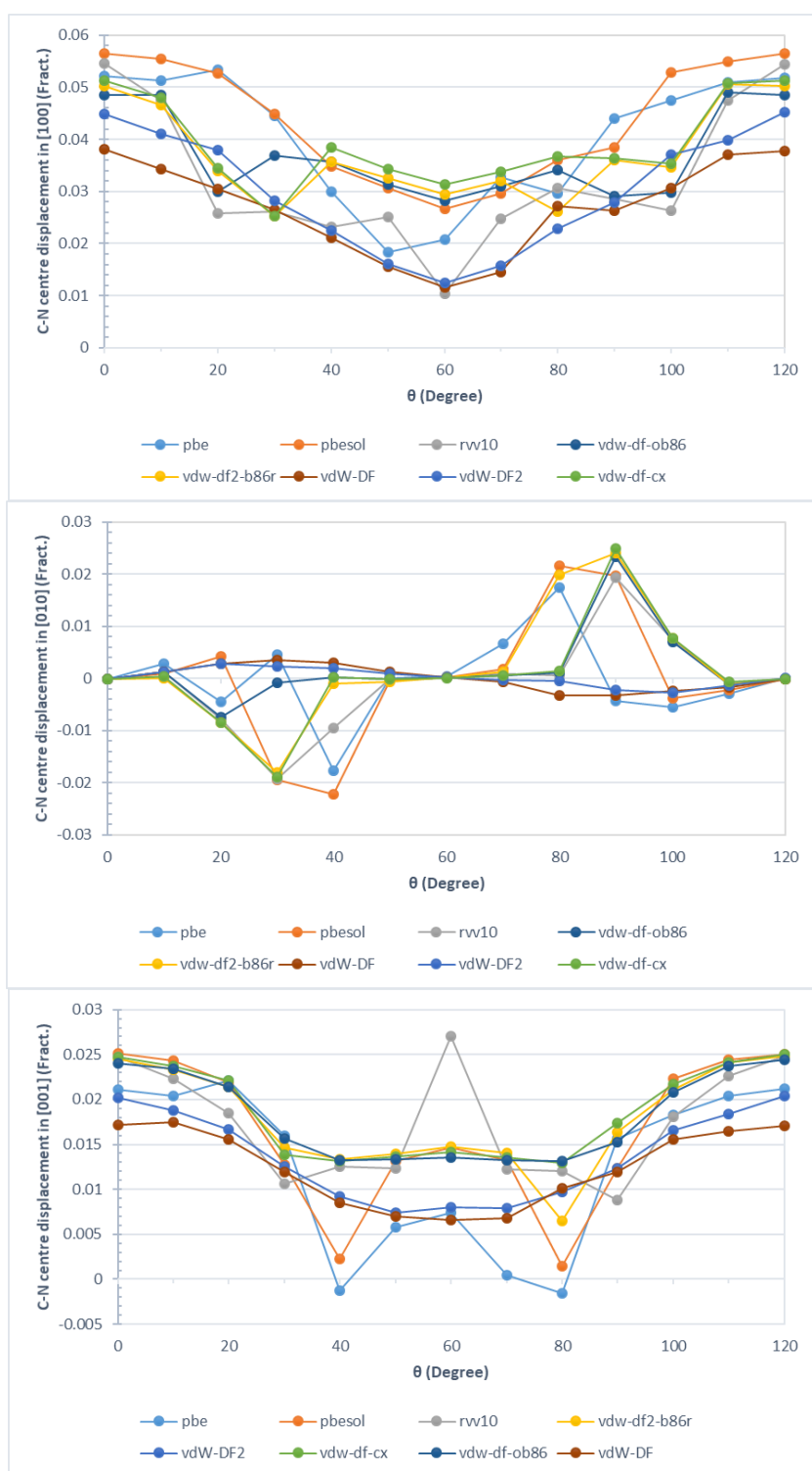


Figure S. 6 Deviation of C-N centre from [0.5, 0.5, 0.5] in three crystallographic directions obtained through full structural relaxations.

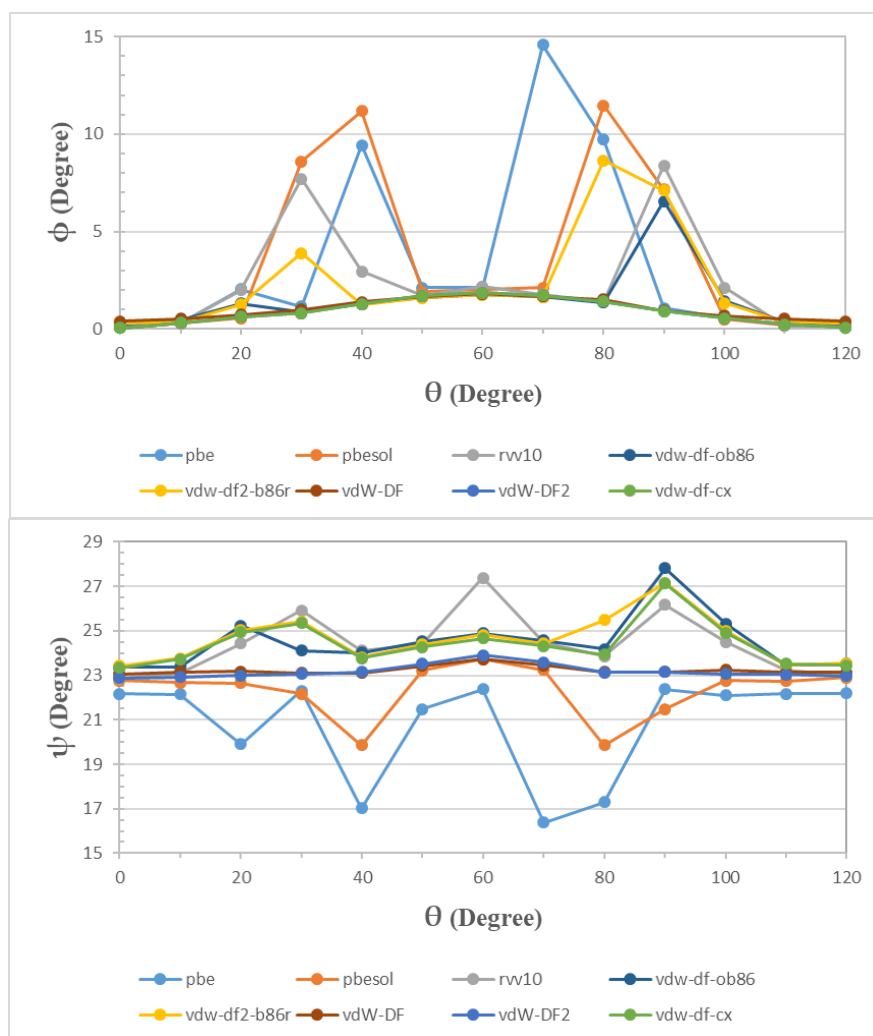
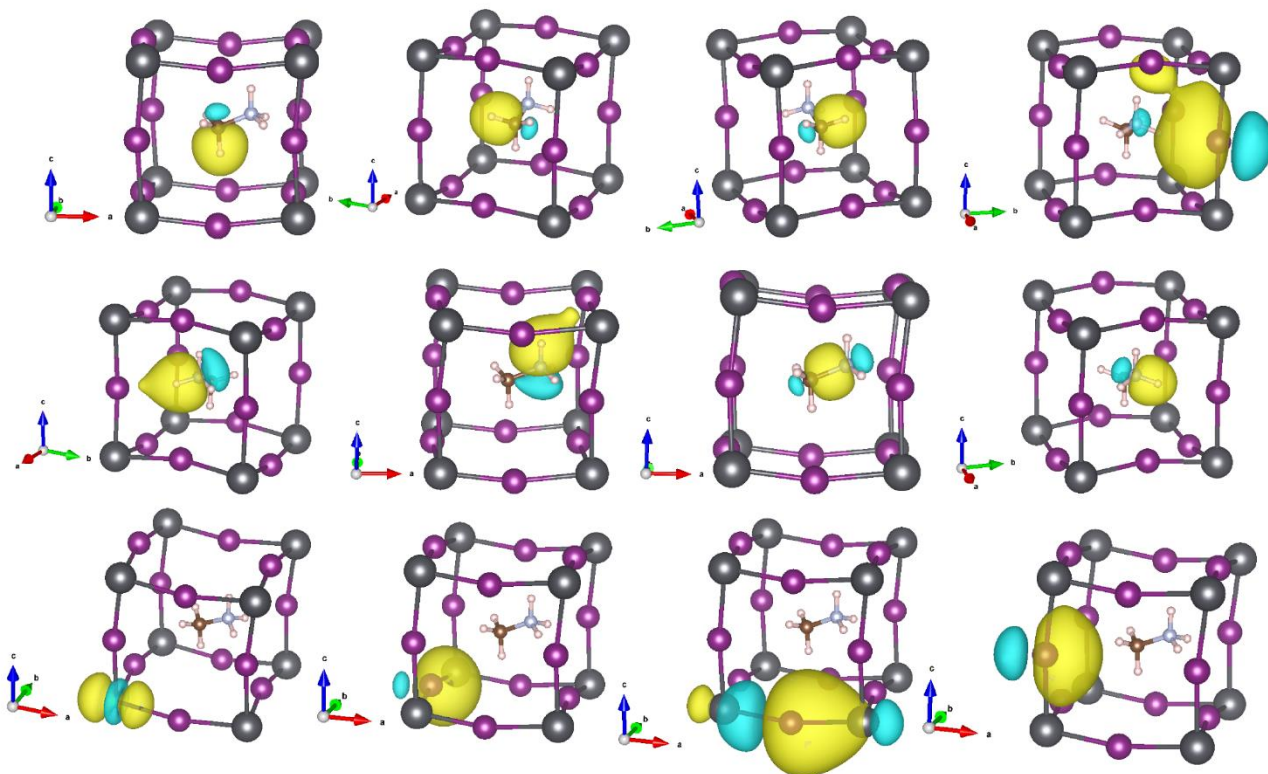
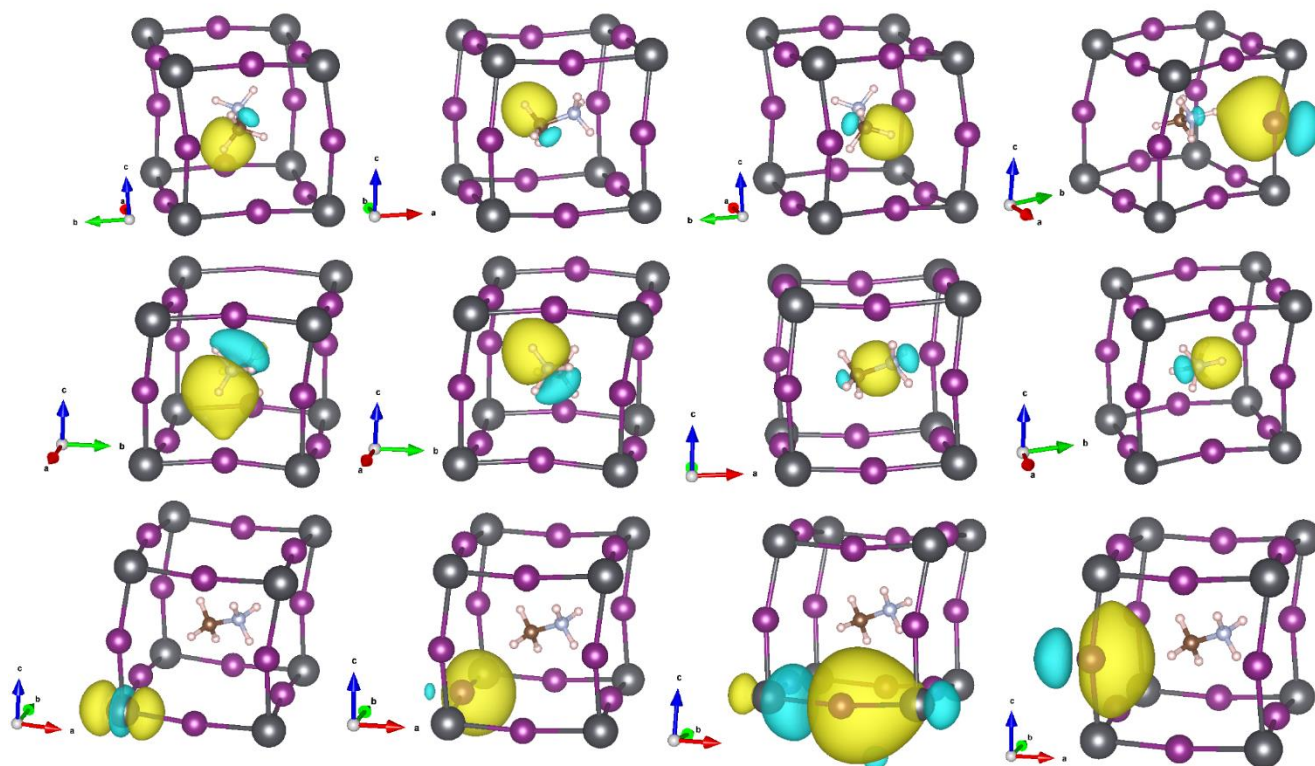


Figure S. 7 Arrangement of C-N axis obtained through full structural relaxations. Measures of ϕ and ψ are corresponding to Fig. 1(b) in the main text.

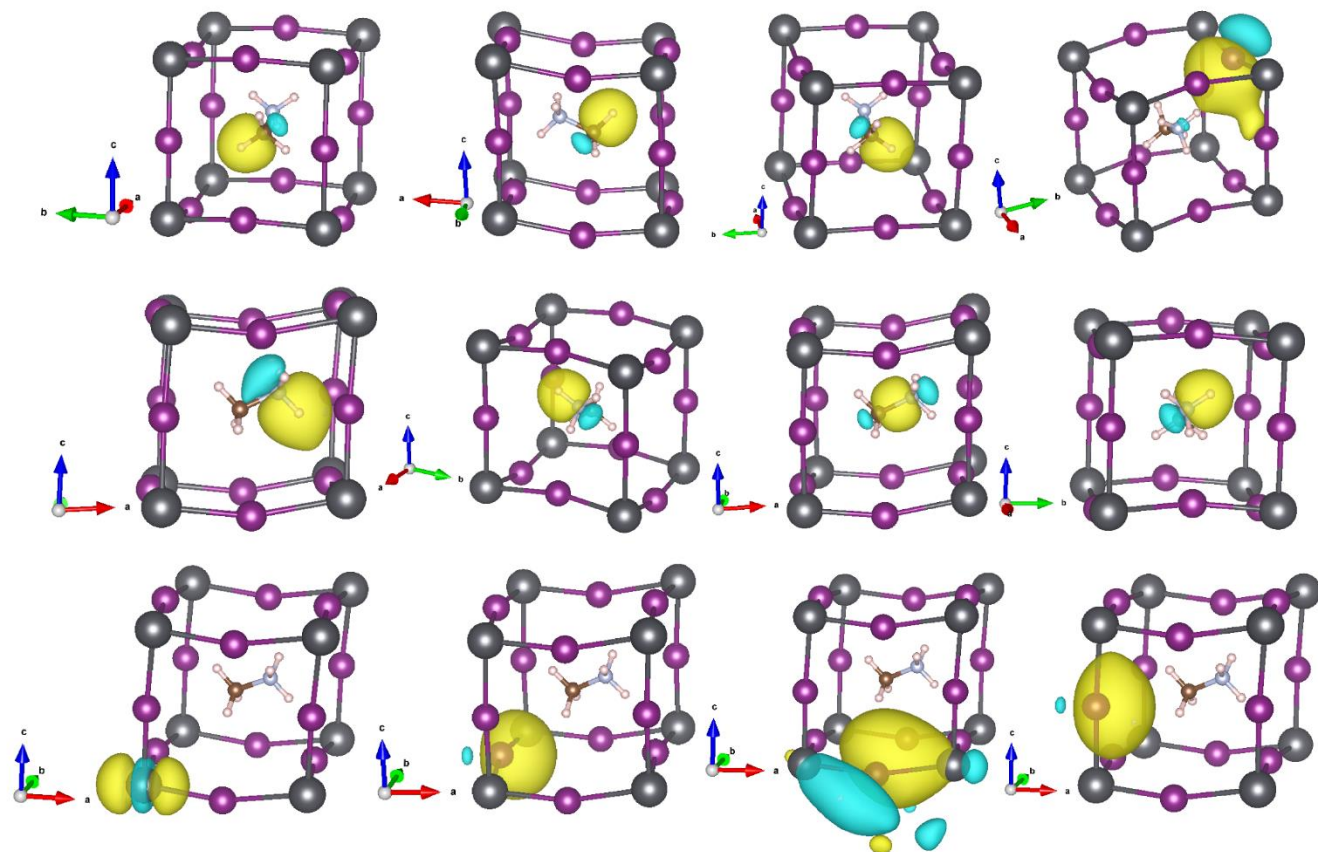
PBEsol: $\theta = 0^\circ$



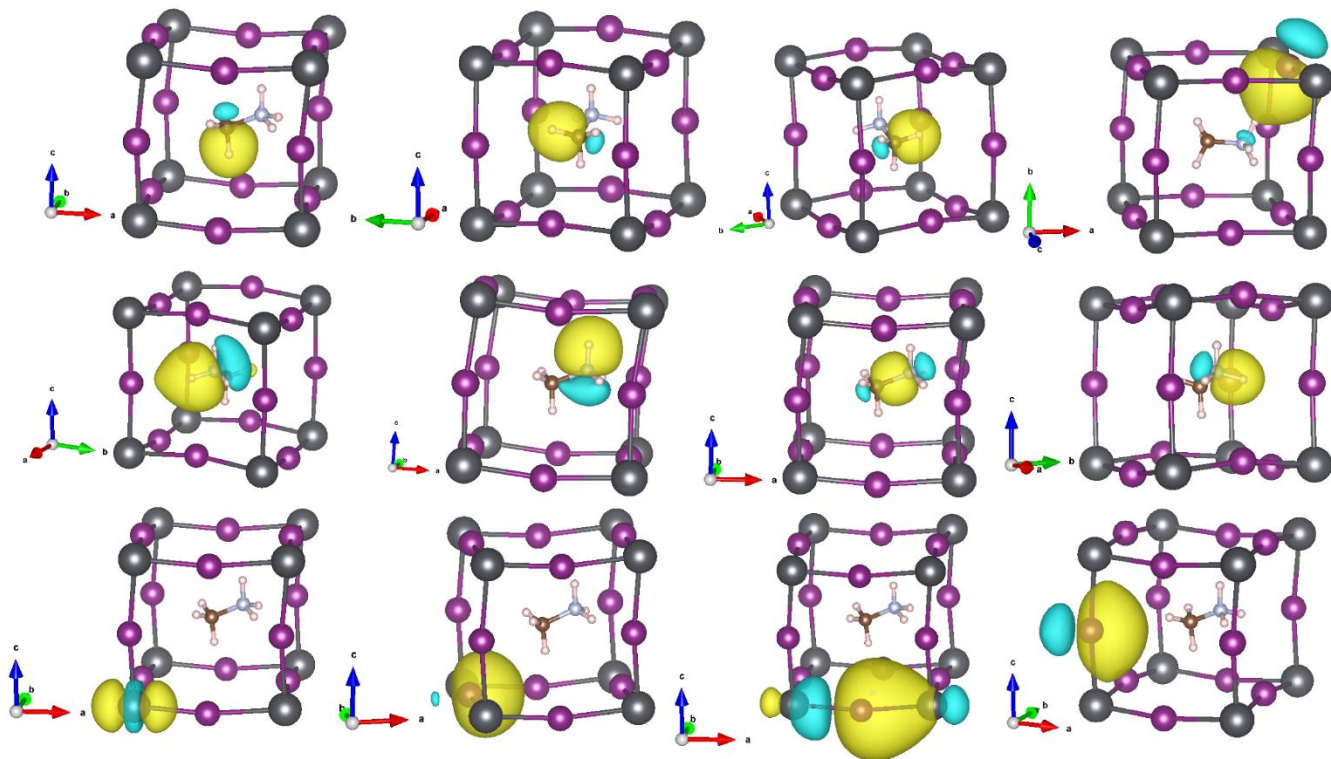
PBEsol: $\theta = 40^\circ$



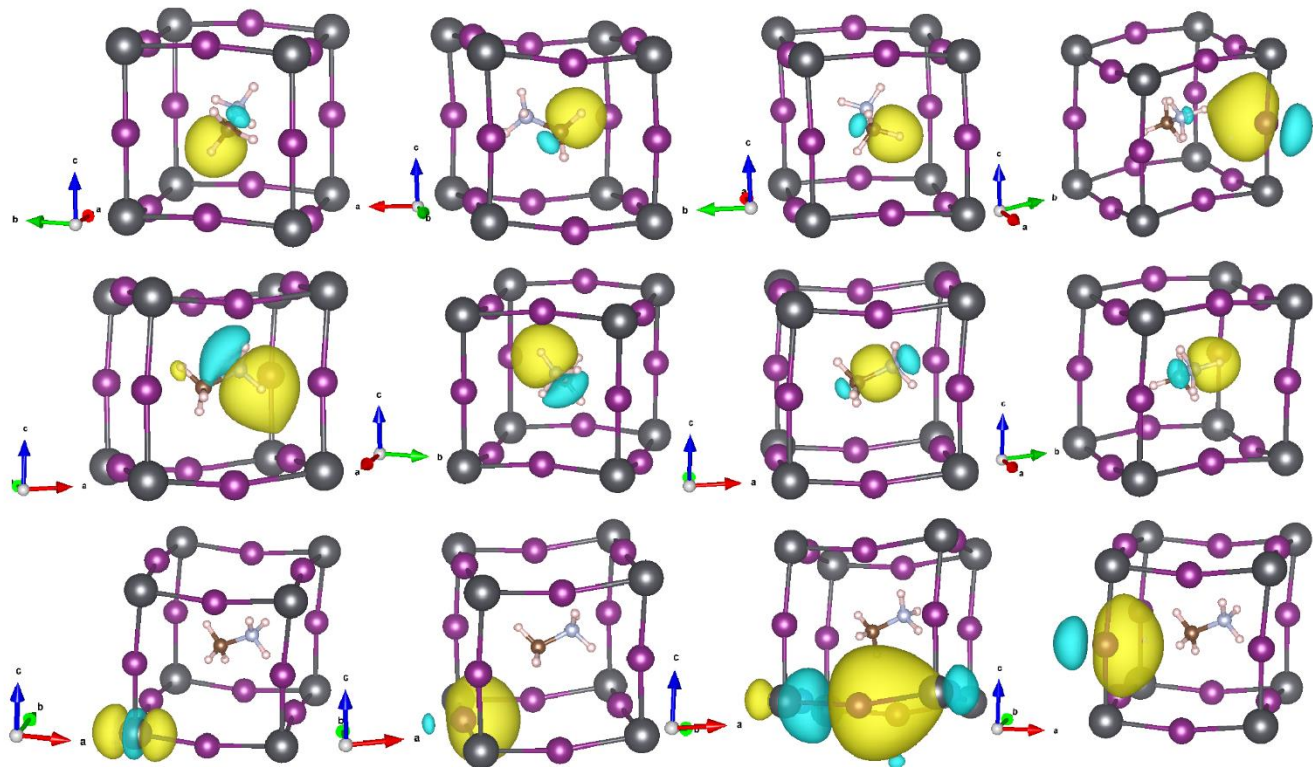
PBEsol: $\theta = 60^\circ$



vdW-DF-cx: $\theta = 0^\circ$



vdW-DF-cx: $\theta = 40^\circ$



vdW-DF-cx: $\theta = 60^\circ$

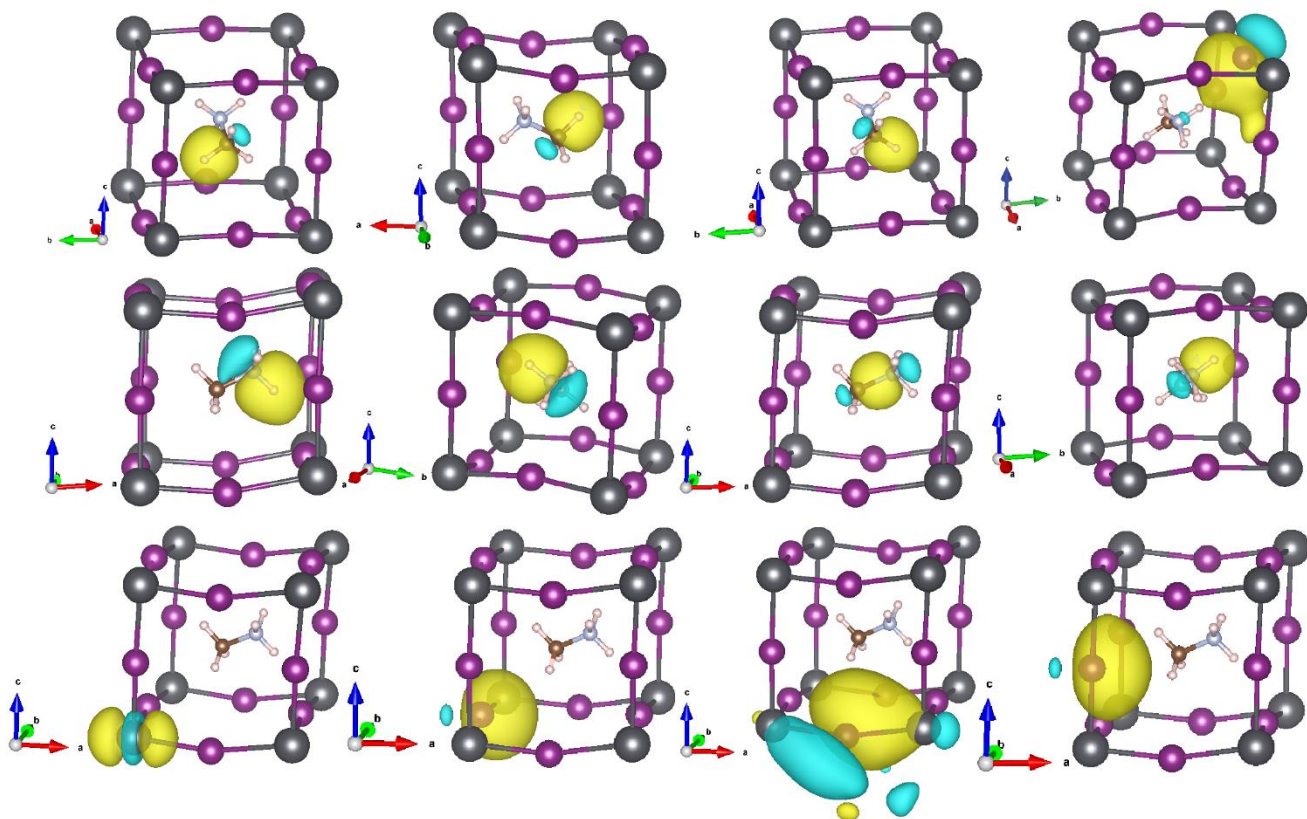


Figure S. 8 Complete isosurfaces of maximally localised Wannier functions of the optimized structures calculated with applications of PBEsol and vdW-DF-cx exchange correlation functionals at $\theta = 0^\circ, 40^\circ, 60^\circ$.



Thiti Bovornratanaraks <thiti.b@gmail.com>

Scientific Reports: Decision letter for SREP-17-54917B

1 message

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Mon, Aug 13, 2018 at 5:46 PM

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