

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

Komsilp Kotmool^{a,b}, Bing Li^{c,d,e}, Sudip Chakraborty^f, Thiti Bovornratanaraks^{b,g}, Wei Luo^f, Ho-kwang Mao^{c,d,h,1}, and Rajeev Ahuja^{f,i,1}

^aDepartment of Physics, Mahidol Wittayanusorn School, Nakhon Pathom 73170, Thailand; ^bThailand Center of Excellence in Physics, Commission on Higher Education, Bangkok 10400, Thailand; ⁶High Pressure Synergetic Consortium, Carnegie Institution of Washington, Argonne, IL 60439; ^dCenter for High Pressure Science and Technology Advanced Research, Shanghai 201203, China; ^eCenter for the Study of Matter at Extreme Conditions, Department of Mechanical and Materials Engineering, Florida International University, Miami, FL 33199; ^fCondensed Matter Theory Group, Department of Physics and Astronomy, Uppsala University, S-75120 Uppsala, Sweden; ^gExtreme Conditions Physics Research Laboratory, Department of Physics, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand; ^hGeophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015; and ⁱApplied Materials Physics, Department of Materials and Engineering, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Contributed by Ho-kwang Mao, July 30, 2016 (sent for review June 1, 2016; reviewed by Naurang Saini and Ali Zaoui)

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 (TI) 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 ($\sqrt{2 \times a} - c$)/c lowered by 1% using an angledispersive X-ray diffraction technique. The density functional theory (DFT)-based calculations suggest that s-p mixing states and the valence-core overlapping of 6s and 5d 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

igh-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 \pm 10 GPa (1). For Ga, there was an isostructural phase transformation from bodycentered 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 momoclinic (*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 Å⁻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.

Author contributions: R.A. designed research; K.K., B.L., S.C., T.B., and R.A. performed research; K.K., B.L., S.C., T.B., W.L., H.-k.M., and R.A. analyzed data; K.K., B.L., S.C., H.-k.M., and R.A. wrote the paper.

Reviewers: N.S., Sapienza Università di Roma; A.Z., Polytech Lille.

The authors declare no conflict of interest.

¹To whom correspondence may be addressed. Email: mao@gl.ciw.edu or rajeev.ahuja@ physics.uu.se.



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 minimumbasis (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 $V_0 = 27.23 \text{ Å}^3$, $B_0 = 40.80 \text{ GPa}$, and $B'_0 = 6.30 \text{ for the h.c.p. phase}$ and $V_0 = 26.95 \text{ Å}^3$, $B_0 = 42.94 \text{ GPa}$, and $B'_0 = 6.20 \text{ for the f.c.c.}$ 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 (~26 meV). The structural parameters of b.c.t. phase are fitted to be $V_0 = 26.92 \text{ Å}^3$, $B_0 = 45.30$ 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. 3.4. 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 Tl 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, l = 14 ...). Therefore, our XRD results indicate that the highpressure 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 Tl is very small, to characterize this distortion quantity, and the parameter ($\sqrt{2}$ × (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 \sim 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 Å³, $B_0 = 35$ GPa, and $B_0 = 5.7$.

To understand the phase transition of Tl under high pressure, the electronic band structures and partial density of states (PDOSs) of the h.c.p. and f.c.c. phases of Tl 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 $\Gamma \rightarrow M \rightarrow K \rightarrow \Gamma$ and $L \rightarrow H$ directions; meanwhile, *s*-*p* mixing states are seen along $\Gamma \rightarrow A \rightarrow L$ and $H \rightarrow A$ directions. In the lower energy range between -15 and -10 eV, the spinorbit (SO) splitting evidently is attributable to two energy levels 5 $d_{5/2}$ and 5 $d_{3/2}$ 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-pbonding 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 partialvalence 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-pbonding states and the minority of s-p mixing and valence-core overlapping states. The flat band, below the Femi level, that lies along the $X \to K$ and $L \to W \to X$ 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 5 $d_{3/2}$ 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 highpressure phase transition of Tl 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 alreadyexisting 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 5*d* 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 5*d*-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 (L(S)DA-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 × 19 × 12 and 16 × 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 × 19 × 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 μ m beveled to 300 μ m with 8.5° beveled angle. Tungsten foil with initial thickness of 250 μ m 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

- Akahama Y, Nishimura M, Kinoshita K, Kawamura H, Ohishi Y (2006) Evidence of a fcc-hcp transition in aluminum at multimegabar pressure. *Phys Rev Lett* 96(4):045505.
 Degtyareva O, McMahon MI, Allan DR, Nelmes RJ (2004) Structural complexity in
- gallium under high pressure: Relation to alkali elements. *Phys Rev Lett* 93(20):205502. 3. Schulte O, Holzapfel WB (1993) Effect of pressure on atomic volume and crystal
- structure of indium to 67 GPa. Phys Rev B Condens Matter 48(2):767–773. 4. Simak SI, Haussermann U, Ahuja R, Lidin S, Johansson B (2000) Gallium and indium
- under high pressure. *Phys Rev Lett* 85(1):142–145. 5. Mikhaylushkin AS, Häussermann U, Johansson B, Simak SI (2004) Fluctuating lattice
- constants of indium under high pressure. *Phys Rev Lett* 92(19):195501.
- Mikhaylushkin AS, Simak SI, Johansson B, Hussermann U (2006) The role of orthorhombic distortions in gallium under high hydrostatic pressure. J Phys Chem Solids 67(9-10): 2132–2135.
- Kenichi T, Kazuaki K, Masao A (1998) High-pressure bct-fcc phase transition in Ga. Phys Rev B 58(5):2482–2486.
- Greenblatt M, Li S, McMills LEH, Ramanujachary KV (1990) Chemistry and superconductivity of Thallium-based cuprates. *Studies of High Temperature Superconductors*, ed Narlikar A (Nova Science, New Brunswick, NJ), pp 143–170.
- 9. Hatton J (1955) Effect of pressure on the superconducting transition temperature of thallium. *Phys Rev B* 100(6):1784.
- Olsen JS, Gerward L, Steenstrup S, Johnson E (1994) A high-pressure study of thallium. J Appl Cryst 27:1002–1005.
- Schulte O, Holzapfel WB (1997) Effect of pressure on the atomic volume of Ga and TI up to 68 GPa. *Phys Rev B* 55(13):8122–8128.
- Schulte O, Nikolaenko A, Holzapfel W (1991) Pressure-volume relations for Zn, Cd, Ga, In and Tl at room temperature to 30 GPa and above. *High Press Res* 6(3):169–182.
- 13. Leger J, Redon A (1991) Volume compression of thallium to 45 GPa. High Press Res 6(4):233-240.

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 μ m by 9 μ m, 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).

ACKNOWLEDGMENTS. We acknowledge The Swedish National Infrastructure for Computing (SNIC), High Performance Computing Center North (HPC2N), and Uppsala Multidisciplinary Center for Advanced Computational Science (UPPMAX) for providing computing time. B.L. thanks Dr. Wenge Yang and Cheng Ji for experiment assistance and helpful discussions. K.K. and T.B. acknowledge support from the Thailand Research Fund (TRF) through Royal Golden Jubilee PhD Program Grant PHD/0277/2552. T.B. acknowledges support from the National Research Council of Thailand and TRF Contract RSA5880058. S.C. and R.A. acknowledge support from the Swedish Research Council and the Swedish Energy Agency. The experiment was performed at HPCAT (Sector 16), APS, Argonne National Laboratory. HPCAT operations are supported by Department of Energy (DOE) National Nuclear Security Administration Award DE-NA0001974 and DOE Basic Energy Sciences Award DE-FG02-99ER45775, with partial instrumentation funding from the National Science Foundation.

- Poole TR, Kemeny PC, Liesegang J, Jenkin JG, Leckey RCG (1973) High resolution photoelectron studies of the d bands of some metals. J Phys F: Met Phys L46.
- Ley L, Pollak R, Kowalczyk S, Shirley DA (1972) The onset of relativistic effects in the density of states of the 6s6p elements Tl, Pb, and Bi. *Phys Lett A* 41:429–430.
- Koepernik K, Eschrig H (1999) Full-potential nonorthogonal local-orbital minimumbasis band-structure scheme. *Phys Rev B* 59(3):1743–1757.
- Opahle I, Koepernik K, Eschrig H (1999) Full-potential band-structure calculation of iron pyrite. *Phys Rev B* 60(20):14035–14041.
- Oganov AR, Glass CW (2006) Crystal structure prediction using ab initio evolutionary techniques: Principles and applications. J Chem Phys 124(24):244704.
- Glass CW, Oganov AR, Hansen N (2006) USPEX evolutionary crystal structure prediction. Comput Phys Commun 175(11-12):713–720.
- Kresse G, Furthmüller J (1996) Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys Rev B Condens Matter 54(16):11169–11186.
- Kresse G, Furthmuller J (1996) Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput Mater Sci* 6(1): 15–50.
- 22. Birch F (1947) Finite elastic strain of cubic crystals. Phys Rev 71(11):809-824.
- Togo A, Oba F, Tanaka I (1996) First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂ at high pressures. *Phys Rev B* 78(13): 134106.
- Hrubiak R, Sinogeikin S, Rod E, Shen G (2015) The laser micro-machining system for diamond anvil cell experiments and general precision machining applications at the High Pressure Collaborative Access Team. *Rev Sci Instrum* 86(7):072202.
- Holmes NC, Moriarty JA, Gathers GR, Nellis WJ (1989) The equation of state of platinum to 660 GPa (6.6 Mbar). J Appl Phys 66(7):2962–2967.
- Larson AC Dreele RBV (2000) General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR:86-748.