

High-pressure bct to fcc structural transformation in Ga

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(Received 31 March 2000)

The equation of state, electronic structure, and phonon dispersions for bct Ga(III) and fcc Ga(IV) phases under high pressure have been studied by first-principle pseudopotential plane-wave calculations. We did not find sufficient dynamical and electronic signatures that may indicate a first or second thermodynamic phase transition from the bct to fcc phase.

Gallium has a rather complicated phase diagram with many stable and metastable phases. At ambient pressure, The α -Ga(I) phase is orthorhombic with eight atoms in the unit cell of *Cmca* symmetry. In addition, a number of metastable phases have been identified as β , γ , δ , and ϵ .^{1,2} Gallium undergoes several structural phase transitions under pressure. Ga(I) transforms to Ga(II) phase at about 2.5 GPa.³ The structure of Ga(II) was determined to be body-centered-cubic with 12 atoms in the unit cell. At about 14 GPa, Ga(II) transforms to Ga(III) of body-centered-tetragonal (bct) structure.^{4,5}

Schule and Holzappel⁵ measured the c/a ratio of bct-Ga(III) phase under pressure up to 68 GPa. The axial ratio decreases continuously with pressure, and they predicted that the c/a ratio will approach $\sqrt{2}$ above 80 GPa at room temperature, where a face-centered-cubic (fcc) structure may appear. More recently, Takemura, Kobayashi, and Arai⁶ conducted a high-pressure x-ray-diffraction experiment on Ga(III) up to 150 GPa at room temperature. They found that the c/a ratio of Ga(III) decreased monotonically with pressure and converged to $\sqrt{2}$ at about 120 GPa. However, there is no detectable volume change at the phase transition, suggesting that the mechanism for bct-Ga(III) to fcc-Ga(IV) phase is at least second order. The electronic structure for several phases of Ga has been studied in detail^{7,8} and the full-potential linear-augmented plane wave (FLAPW) has been employed to investigate the Ga(III) under pressure.⁶ It was noted from previous theoretical calculations that fcc and bct Ga have an almost identical equation of state.^{8,6} Since the $3d$ core state of Ga is very shallow, it is anticipated that $4s$ and $4p$ bands may touch the $3d$ core states under pressure, driving the bct-to-fcc structural change. The experimental observation, however, is in contradiction to Laudau's theory for phase transition, where the bct-fcc transition is expected to be first order. The absence of discontinuity in the volume and the calculated energy of the bct-Ga(III) to fcc phase is surprising. This unusual feature leads to questions on the thermodynamic origin and the driving mechanism for the structural change.

In this paper, we examine the equation of state and electronic structure of bct Ga(III) and fcc Ga under pressure by the *ab initio* pseudopotential plane-wave method. Phonon dispersions of bct and fcc phases of Ga at several pressures are also obtained from a direct method using supercell calculation. The purpose is to investigate the physical mechanism for the phase transition between the bct and fcc phases.

Calculations of total energy and Hellmann-Feynman forces were carried out by using the VASP (Ref. 9) program. The VASP code applies the standard method in which the Kohn-Sham equation is solved self-consistently using the pseudopotential and plane-wave basis, based on the density-functional theory in the local-density approximation.¹⁰ We employed an ultrasoft pseudopotential¹¹ for Ga, which was generated with the atomic configuration of $3d^{10}4s^24p^24f^0$ and a cutoff radius of 1.19 Å. The Ga $3d$ state was explicitly included in the valence shell. A cutoff energy of 400 eV was used in the calculations. The summation over the Brillouin zone was performed on a $25 \times 25 \times 25$ Monkhorst-Pack¹² k -point mesh.

For the calculation of phonon dispersions, we used a 54-atom supercell for bct Ga and a 108-atom supercell for fcc Ga. The Hellmann-Feynman forces were calculated for all atoms in the supercell with one atom displaced from the equilibrium position by about 0.5–1.0 % of the lattice constant. From the Hellmann-Feynman forces, the interatomic force constants can be generated by establishing the symmetry of the unit cell. The interaction range was limited to the distance from the central atom of the supercell to the surface atom. The dynamical matrix was constructed to calculate the phonon frequencies. Details of the calculations of force constants and phonon dispersions have been described in Ref. 13. This method has been successfully applied to calculate the phonon spectra for not only insulators¹⁴ and semiconductors¹⁵ but also for metals¹⁶ and alloys^{17,18} as well.

Figure 1 shows the equation of state (EOS) and the pressure-volume relation for bct Ga and fcc Ga. In agreement with previous theoretical studies,^{6,8} the energy difference over the volume range from 9.5 to 14.5 Å³ is very small, less than 4 meV, with the bct phase slightly more stable until it merges smoothly into the fcc EOS at $V \approx 9.6$ Å³ (130 GPa). Experimentally, it was noted⁶ that a structural change from bct to fcc occurs at about $V = 0.97$ Å³ (120 ± 10 GPa) based on the c/a ratio variation. Furthermore, in agreement with theoretical calculations, there is no volume discontinuity in the experimental equation of state.

The band structures of bct and fcc phases at the $V = 0.97$ Å³ have been calculated in order to examine the difference in the electronic structure between these two phases. At this volume, the optimized c/a ratio is 1.44 for bct Ga. Again as shown in Fig. 2 and Fig. 3, there are no significant differences in the band structure and electron density of states (DOS). In Fig. 2 it is shown that $4s$ and $4p$ states

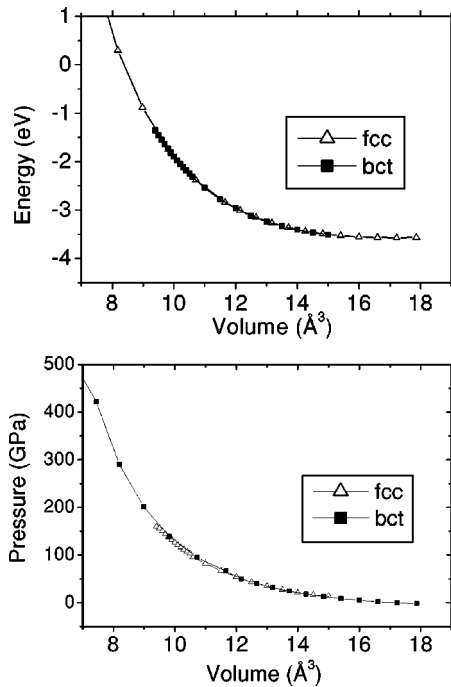


FIG. 1. Equation of states and pressure-volume relation of fcc Ga and bct Ga.

touch the $3d$ core states at $V=9.97 \text{ \AA}^3$. It should be noted that the band touching begins even before the critical volume found by Takemura *et al.*⁶ This observation implies that the $3d$ state is not the driving force for the transition from bct to fcc phase. Moreover, the band crossings of the fcc structure occur at the Γ point. From the site symmetry ($m\bar{3}m, O_h$) of the Ga atom, the symmetries of $4s(a_{1g})$, $4p(t_{1u})$ and

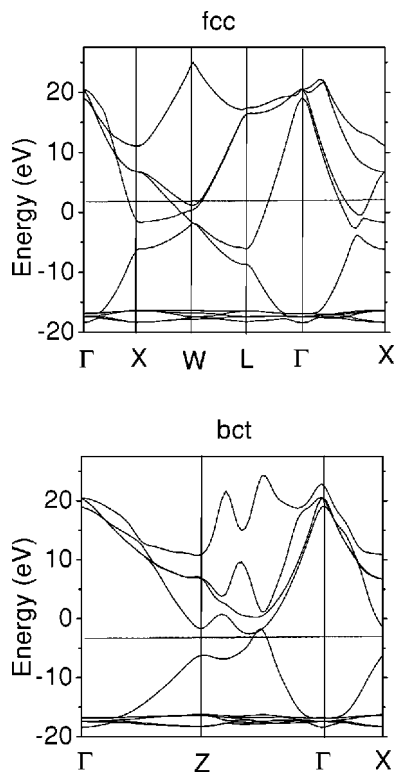


FIG. 2. Band structure of fcc Ga and bct Ga at $V=9.70 \text{ \AA}^3$.

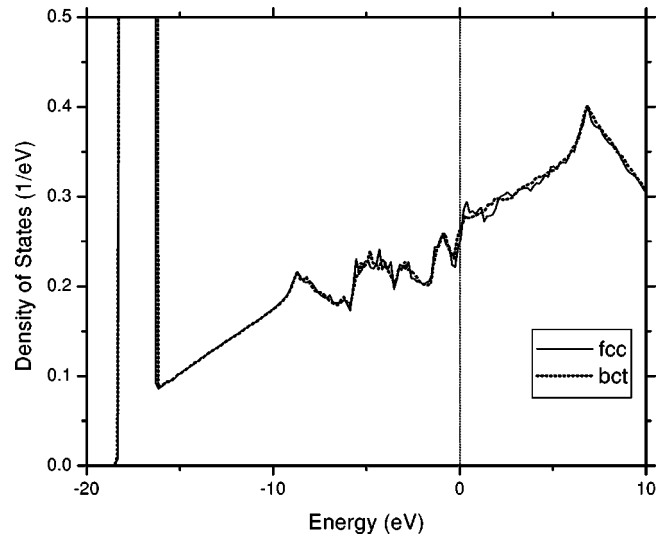


FIG. 3. Electronic density of states of fcc Ga and bct Ga at $V=9.70 \text{ \AA}^3$.

$3d(e_g, t_{2g})$ orbitals are all different and no mixing is allowed.

As demonstrated above, there is insufficient electronic evidence indicating a genuine phase transition from bct to fcc structure. The volume, energy, electronic structure, and chemical bonding for bct Ga converge smoothly into the fcc phase with increasing pressure. We now focus on the dynamical instability, and to this end, we calculated the phonon

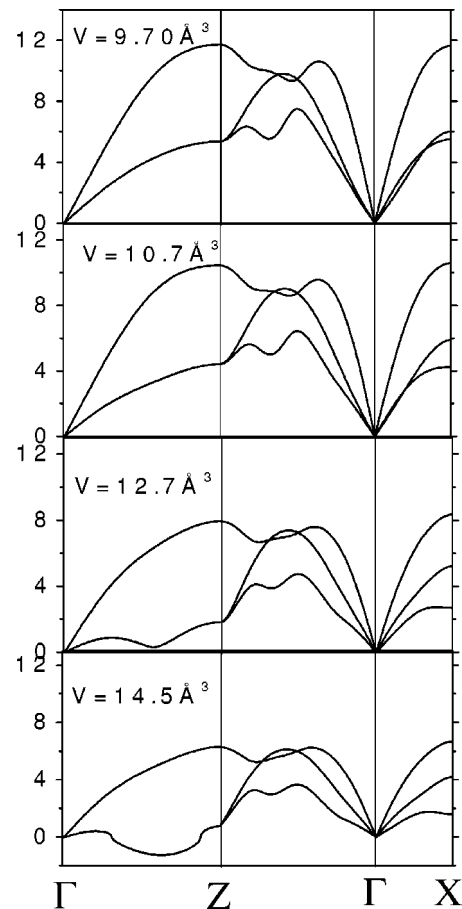


FIG. 4. Phonon dispersions of bct Ga at different volumes.

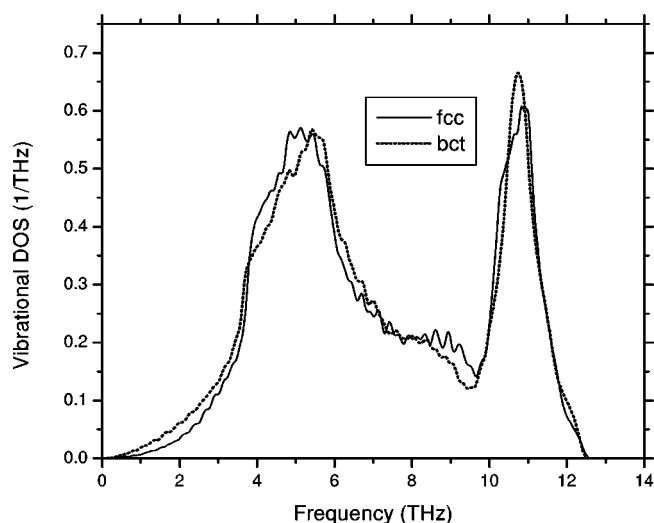


FIG. 5. Phonon density of states of fcc Ga and bct Ga at $V = 9.70 \text{ \AA}^3$.

dispersions of bct and fcc Ga at several pressures. If it is a second-order phase transition from bct to fcc, we would expect there will be a soft phonon mode near the zone center because both the bct and fcc structures have only one atom in the respective unit cell. Figure 4 shows the phonon dispersions of bct Ga along symmetry directions calculated at four volumes: 14.5, 12.7, 10.7, and 9.7 \AA^3 . It is noted that the transverse mode along [001] becomes imaginary at about (0, 0, 2/3) at volume $V = 14.5 \text{ \AA}^3$. This observation indicates the bct structure at this volume is dynamically unstable and will transform to another structure with more than one atom in the unit cell. This instability, however, is unrelated to the bct-fcc phase transition. In fact, it is connected with the reversible transformation to the low-pressure bcc-Ga(II) struc-

ture. In contrast, the bct structure is stabilized as the volume decreases (pressure increases) below $V = 12.7 \text{ \AA}^3$. At the critical volume of the bct-fcc transition, determined by Takemura *et al.*'s experiments to be $V = 9.7 \text{ \AA}^3$, no soft modes were observed in the Brillouin zone, indicating that the bct Ga structure is dynamically stable. A similar soft mode hardening with pressure was also observed in bcc tellurium.¹⁹ Earlier, Bernasconi, Chiarotti, and Tossati⁸ have calculated the total energy of Ga for various structures. They found that the bct-Ga transforms to fcc at about 25 GPa due to dynamical instability. This result disagrees with our calculations and the experiments. The phonon densities of states for bct and fcc Ga at $V = 9.7 \text{ \AA}^3$ are compared in Fig. 5. Once again, we found very similar vibrational properties for both structures. The lack of discontinuity in the vibrational energy and the static energy indicates that the free energy of the system is also continuous at the critical pressure as well.

In conclusion, the only indication of a possible phase transition from bct Ga to fcc Ga under pressure is the observation of the convergence of the c/a ratio to $\sqrt{2}$ and a change in crystal symmetry at about 120 GPa from both experiment and theory. Present *ab initio* calculations on the equation of state, electronic structure, and vibrational properties of bct and fcc Ga show that the structural transition from bct to fcc is very smooth without any electronic or dynamical evidence satisfying the conventional conditions for a first- or second-order thermodynamic phase transition.

ACKNOWLEDGMENTS

Z.Q.L. would like to thank Professor K. Parlinski and M. Sluiter for very helpful discussion in lattice-dynamics theory. J.S.T. wishes to thank Dr. Takemura and Dr. Kobayashi for comments.

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