High-pressure bct-fcc phase transition in Ga

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A high-pressure powder x-ray-diffraction experiment has been carried out on Ga up to 150 GPa at room temperature. The c/a axial ratio of the body-centered-tetragonal phase III continuously decreases with pressure and becomes $\sqrt{2}$ at 120 ± 10 GPa, where an fcc lattice is realized. There is no detectable volume change at the phase transition. The fcc phase Ga(IV) is stable to at least 150 GPa. Full-potential linearized augmented plane-wave calculations have been done to investigate the pressure dependence of the c/a axial ratio of phase III. The result of the calculation is in reasonable agreement with the present experiment. The energy band structure of fcc Ga has also been calculated with the pseudopotential method. The valence bands are found to touch the $3d$ core states at about 79 GPa. [S0163-1829(98)07129-X]

I. INTRODUCTION

Gallium metal has been the subject of much attention for its peculiar crystal structure. The ambient pressure phase Ga(I) is orthorhombic with eight atoms in the unit cell. In this structure a Ga atom is bonded to another Ga atom just like a diatomic molecule. However, since the next-near neighbors are located at the distances 10–13 % longer than the first-neighbor distance, Ga retains metallic properties. It is suggested that covalent and metallic bonds coexist in Ga(I).[1]

Gallium undergoes two structural phase transitions under high pressure. Because of the decrease of the melting temperature with pressure, Ga(I) melts at around 1.2 GPa at room temperature, and then transforms to Ga(II) at about 2.5 GPa.[2] The structure of Ga(II) was determined to be bcc with 12 atoms in a unit cell.[3] Ga(II) transforms to Ga(III) at about 14 GPa and at room temperature.[4,5] It should be noted that Ga(III) was first identified as a high-pressure high-temperature phase with the liquid–II–III triple point at 3 GPa and 45 °C.[6] The phase boundary between Ga(II) and (III) is thus supposed to have a negative slope dT/dP. Ga(III) has a body-centered-tetragonal (bct) structure.[3,7–9] Very recently Schulte and Holzapfel have measured the change in the c/a axial ratio of bct-Ga(III) under pressure up to 68 GPa.[5] The axial ratio continuously decreases with pressure. They predicted that the axial ratio will become $\sqrt{2}$ above 80 GPa at room temperature, where an fcc structure may appear. In order to examine whether the predicted bct-fcc transition will actually take place, we have carried out a powder x-ray-diffraction experiment on Ga under pressure up to 150 GPa at room temperature. In addition, full-potential linear-augmented plane-wave (FLAPW) calculation and norm-conserving pseudopotential (NCPP) calculations have been done on Ga to investigate the structural stability as well as the energy band structure under high pressure.

Another aim of studying Ga to ultrahigh pressures is to see whether the $3d$ core electrons may become delocalized to form valence electrons. The $3d$ core states of Ga are located close to the valence bands. Their energy levels are only 4 eV below the bottom of the $4s$ and $4p$ valence bands at atmospheric pressure. Since the width of the $4s$ and $4p$ valence bands increases under pressure, the valence bands may eventually overlap with the $3d$ core states. The valence electrons of Ga will then have a $3d$-character at high pressures, if the $3d$ bands further approach the Fermi level. The valence-core overlap is a precursor of the pressure ionization of core electrons, in which the core electrons are totally delocalized.[10] The critical pressure for the valence-core overlap in Ga has been estimated to be about 79 GPa in the present NCPP calculation. We are interested in detecting an evidence for the valence-core overlap in Ga through the experimental study of the crystal structure.

II. EXPERIMENTAL AND CALCULATIONAL METHODS

The angle-dispersive powder x-ray-diffraction experiment has been carried out under high pressure by using a diamond-anvil cell, synchrotron radiation, and an imaging plate. We used the synchrotron radiation on the bending magnet beam line 18C of the Photon Factory, National Laboratory for High Energy Physics (KEK).[11] The x-ray was monochromatized to 18.00 keV and focused to a beam size of 80×80 μm with two curved mirrors. The beam was finally reduced to a size of 40 μm with a pin-hole collimator. Details of the experimental setup and the data analysis have been described elsewhere.[12] Polycrystalline Ga (99.9999% purity) was enclosed in a hole of a Re gasket without a pressure medium. The pressure was determined on the basis of the ruby pressure scale.[13] At pressures above 100 GPa, the ruby luminescence was so weak that the pressure was estimated from the d spacings of the gasket. The uncertainty in pressure was about ±10 GPa in this case. The experiment was done at room temperature. Typical exposure times were 40 min.

The FLAPW calculation has been carried out with the WIEN97 programs.[14] The zone integration has been performed carefully to obtain well-converged total energy, because the energy difference between the bct and fcc structures is quite small as shown in Ref. 15. We used the tetrahedron method with as many as 4200 k points in the irreducible zone.

The total-energy NCPP calculation has been done based on the local-density approximation[16] in the density-functional theory.[17] The basis functions were expanded in

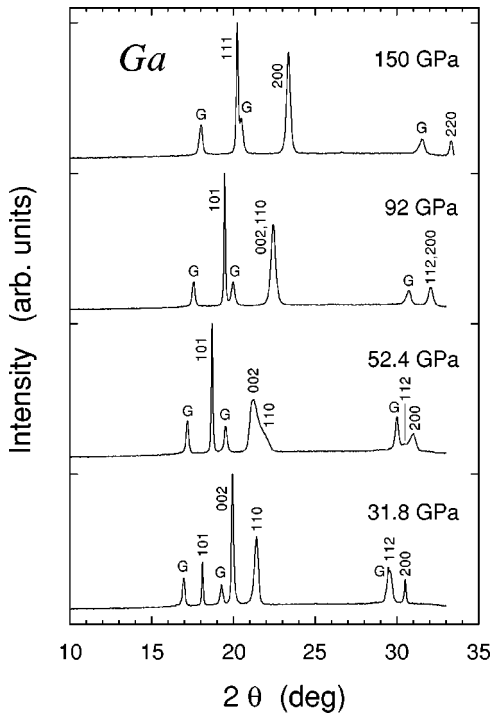

FIG. 1. Powder x-ray-diffraction patterns of Ga(III) and (IV) at high pressures. The x-ray energy was 18.00 keV. *G* denotes the diffraction peaks of the Re gasket. The diffraction pattern at 150 GPa is indexed to the fcc structure of Ga(IV).

plane waves. The optimized pseudopotential for Ga proposed by Troullier and Martins[18] was used in order to reduce the number of plane waves. Nonlocal parts of s, p, and d pseudopotentials were transformed to separable forms[19] without ghost bands. Two kinds of pseudopotential are constructed in order to investigate the effect of the shallow core $3d$ states. One pseudopotential considered the core $3d$ states as valence states. Another pseudopotential considered the $3d$ states as part of the frozen core. The pressure is determined directly by using calculated values of stresses acting on unit-cell surfaces.[20] A partial core correction was considered.[21] The energy cutoff was set at 81–144 Ry for both cases of pseudopotentials. The total energies and stresses are sufficiently converged at 81 Ry. The number of k-point samplings was 819 and 89 in the 1/16 and 1/48 of the Brillouin zone for bct and fcc, respectively.

III. RESULTS

A. X-ray-diffraction experiment

Figure 1 shows representative x-ray-diffraction patterns of Ga under high pressure. The raw diffraction images of phase III recorded on imaging plates were smooth, in good contrast to spotty ones of low-pressure phase II. The 002 and 110, as well as 112 and 200 reflections gradually approach each other and merge into single peaks. This means that the bct structure continuously approaches the fcc structure. Figure 2 shows the change in the peak width at half maximum as a function of pressure. The heavily overlapped peaks above 75 GPa (002+110 and 112+200 reflections) are fitted as single peaks with a Gaussian profile. The peak width of the 002+110 and 112+200 reflections decreases under pressure, while the width of the 101 single peak continuously increases, indicating an increased pressure gradient. The decrease of the peak width of the 002+110 and 112+200 reflections saturates at around 120 GPa.

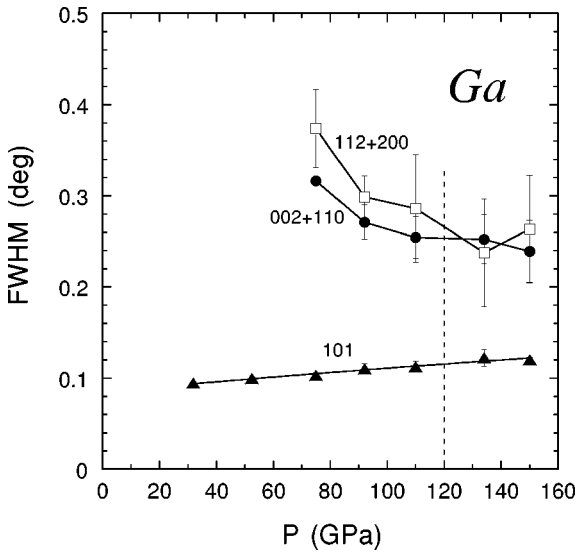

FIG. 2. The full width at half maximum of the diffraction peaks of bct-Ga(III) as a function of pressure. As the bct structure approaches fcc, the width of overlapping peaks (002+110 and 112+200) decreases, while the width of a single peak (101) slightly increases due to the increased pressure gradient. The curves are drawn for the guide of eyes. The dashed line indicates the estimated transition pressure to fcc-Ga(IV).

The lattice parameters a and c of Ga(III) are obtained by a least-squares method. Figure 3 shows the change in the c/a ratio of Ga(III) as a function of pressure. The axial ratio gradually decreases with pressure and approaches the value $\sqrt{2}$ at about 120 ± 10 GPa. We thus conclude both from Figs.

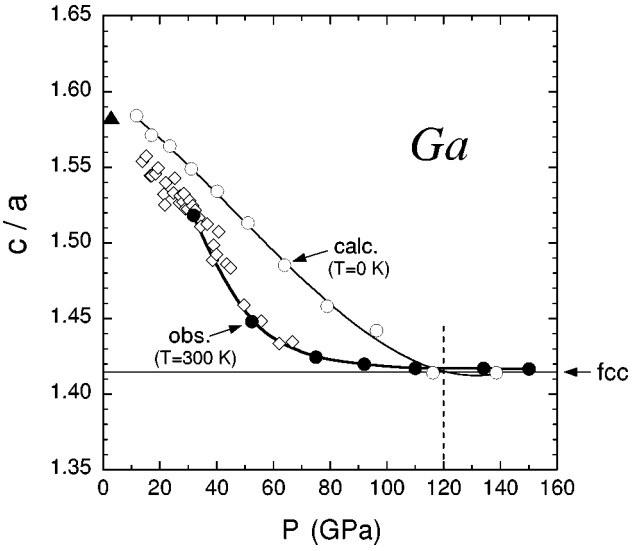

FIG. 3. The change in the c/a axial ratio of bct-Ga(III) as a function of pressure. The solid circles indicate the present experimental result, the triangle from Ref. 3, and diamonds from Ref. 5. The curves are drawn for the guide of eyes. The fcc phase Ga(IV) is stabilized above 120 GPa. The open circles indicate the c/a ratios at $T=0$ K calculated with the FLAPW method in the present work.

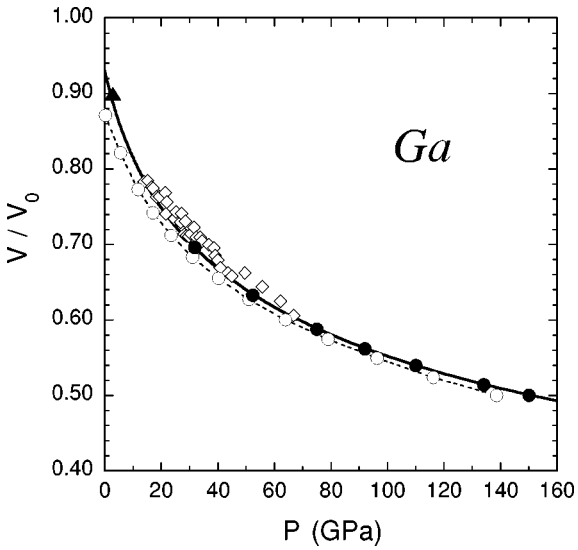

FIG. 4. The pressure-volume relationship of Ga. The solid circles indicate the present experimental result, the triangle from Ref. 3, and diamonds from Ref. 5. The solid curve shows a fit with the Birch-Murnaghan equation of state with $B_0=55$ GPa, $B_0'=4.7$, and $V/V_0=0.93$. The open circles and dashed curve indicate the equation of state for fcc Ga at $T=0$ K calculated with the FLAPW method in the present work.

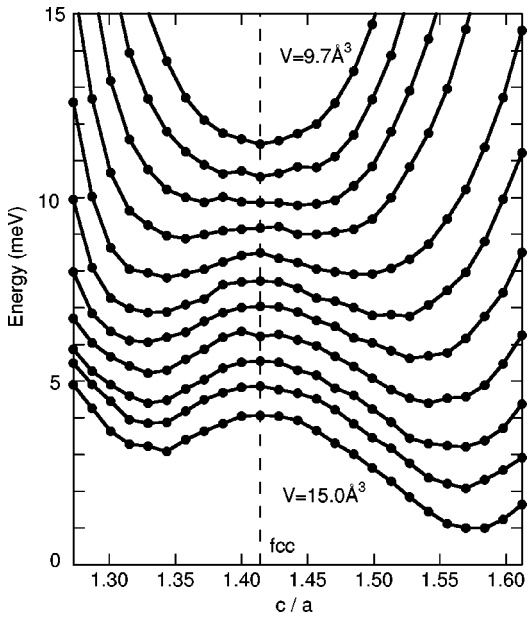

FIG. 5. The total energy of bct Ga as a function of the c/a ratio at different volumes calculated with the FLAPW method. For each curve, from top to bottom, the volume per atom is fixed to 9.7, 10.2, 10.7, 11.2, 11.7, 12.2, 12.7, 13.3, 13.8, 14.4, and 15.0 Å^3, respectively. The dashed line indicates the position for fcc at $c/a=\sqrt{2}$. The curves are arbitrarily shifted in the vertical direction for clarity.

2 and 3 that bct-Ga(III) transforms to fcc-Ga(IV) at 120 ± 10 GPa. The presently found fcc phase Ga(IV) is stable to at least 150 GPa.

The pressure-volume relationship is shown in Fig. 4. The bulk modulus B_0, its pressure derivative B_0', and the relative volume V/V_0 of bct-Ga(III) at atmospheric pressure are determined by fitting the P-V data with the Birch-Murnaghan equation of state. Since the volume change at the bct-fcc transition is negligibly small, we used all the data up to 150 GPa for the fitting. We obtain the values $B_0=55\pm5$ GPa, $B_0'=4.7\pm0.5$, and $V/V_0=0.93\pm0.01$.

B. Total energy and band-structure calculations

We first calculated the total energy of hypothetical fcc Ga at atmospheric pressure with the FLAPW method in order to check the accuracy of the calculation. We obtained the equilibrium lattice constant $a_{\rm fcc}=7.71$ a.u. (4.08 Å) and bulk modulus $B_0=64$ GPa, which are in good agreement with the previous pseudopotential calculation.[15] The lattice constant is 2% smaller than the hypothetical experimental value, which is obtained by extrapolating the equation of state of the fcc phase to atmospheric pressure based on the present experimental data. Such a deviation is common to the local-density approximation.

We then calculated the total energy of bct Ga as a function of the c/a ratio for various volumes. As shown in Fig. 5, the total energy has two local minima around $c/a=1.34$ and 1.58 at large volumes. Hence the fcc structure ($c/a=1.41$ as bct) is unstable at low pressures, and the bct structure with $c/a>\sqrt{2}$ is realized. The energy difference between fcc and bct is about 4 meV at 12 GPa ($V=15.0$ Å^3). As the volume decreases (pressure increases), the two local minima become shallow, and the energy difference between bct and fcc becomes small. Above about 115 GPa ($V\leqslant10.2$ Å^3), there is only one minimum at $c/a=\sqrt{2}$ and Ga becomes fcc. In Fig. 3, the calculated axial ratios are plotted with open circles. The agreement between the calculation and the experiment is reasonable. Here we obtained pressures from the equation of state calculated for the fcc structure. This can be justified, because the energy difference between the bct and fcc structures is so small (~1 meV) that the equations of state for both phases would be almost the same (see Fig. 4). The fcc structure appears at $P\approx120$ GPa in our calculation. We found no discontinuous changes in the calculated c/a ratio and in the equation of state at the bct-fcc transition.

The energy band structures of Ga have been calculated for the fcc structure with the NCPP method and are shown in Fig. 6 for two different pressures. The shallow $3d$ core states were included as valence states in this case. The width of the $4s$ and $4p$ valence bands increases at high pressures, and the bottom of the valence bands touches the $3d$ core states at a pressure of 79 GPa.

IV. DISCUSSION

Hafner and Heine have investigated the trends in the crystal structures of the elements based on the interatomic potential constructed from the empty-core pseudopotential.[22] According to their universal phase diagram for the group IIIb elements, Ga is expected to transform from the orthorhombic to tetragonal structure, and then to a close-packed structure (hcp or fcc). This prediction is qualitatively justified in the present experiment.

Bernasconi, Chiarotti, and Tosatti have calculated the total energy of Ga for various structures with the pseudopotential method.[15] They predicted that cubic Ga(II) transforms to fcc at about 15 GPa and at 0 K. The bct phase Ga(III) has practically the same total energy as fcc, and is calculated to

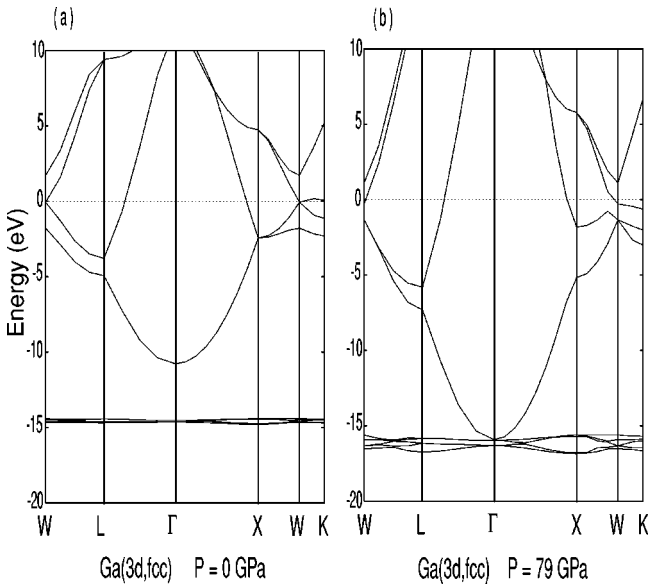

FIG. 6. The energy band structures of fcc Ga at (a) 0 GPa (lattice constant $=4.29$ Å) and (b) 79 GPa (lattice constant $=3.65$ Å) calculated with the NCPP method.

be mechanically unstable above 25 GPa. The present experiment shows that Ga(II) first transforms to bct Ga(III) and then to fcc Ga(IV) at 120 GPa, a substantially higher pressure than their calculation. The bct-fcc transition pressure is however in good agreement with the present FLAPW calculation. Since the calculated energy difference between the bct and fcc structures is extremely small in the vicinity of the phase transition, a large number of k-point samplings would be necessary for energy calculation to get a reliable transition pressure.

It should also be mentioned that the transition pressure is higher than the value predicted by Schulte and Holzapfel ($\sim$80 GPa), which was estimated from the extrapolation of their data of the c/a ratio.[5] The difference comes from the asymptotic behavior of the pressure dependence of the c/a ratio near the bct-fcc transition.

There is no detectable discontinuity in the experimental axial ratio and in volume at the bct-fcc transition (Figs. 3 and 4). The FLAPW calculation also indicates the continuous approach of the bct structure to fcc. Hence we are tempted to consider that the bct-fcc phase transition in Ga is of the second order. However, Landau's theory for phase transition suggests that the bct-fcc transition should be of the first order.[23,24] The absence of a discontinuity in the calculated bct-fcc transition could partly be due to the numerical accuracy. The energy difference between bct and fcc Ga at $P \approx 100$ GPa is less than 1 meV. The number of k points would not be sufficient to find the discontinuity at the phase transition. We conclude at least that the discontinuity at the transition is quite small.

The pressure dependence of the c/a ratio is qualitatively different between the experiment and numerical calculation (Fig. 3). The experimental c/a ratios decrease faster than the calculated values and asymptotically approach $\sqrt{2}$. This may be due to the difference of temperature. The calculation represents the behavior at $T=0$ K, while the experiment has been performed at room temperature $T \approx 300$ K ($E \approx 26$ meV). Since the thermal excitation energy at room

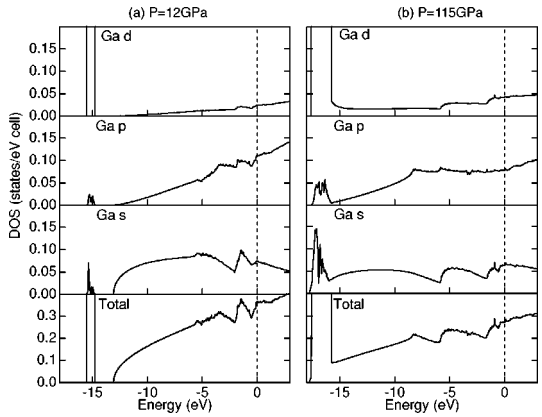

FIG. 7. The calculated total and partial density of states of fcc Ga at (a) 12 GPa and (b) 115 GPa. The Fermi energy is set to $E_F=0$.

temperature is greater than the energy difference between bct and fcc, lattice dynamics may affect the behavior at finite temperature.

Finally, we discuss the origin of the bct-fcc transition from the electronic structure calculation. In Fig. 7 the total and partial density of states (DOS) for fcc Ga are plotted at $P=12$ and 115 GPa. The Fermi energy is set at $E_F=0$. The peaks at $E<-10$ eV are from the $3d$ bands and most of the weights in the valence bands is from $4s$ and $4p$ orbitals. For $P=12$ GPa, a small dip exists in the total DOS just below the Fermi energy. Figure 8 compares the total DOS near the Fermi energy for the bct structure with different c/a ratios. As c/a becomes larger, the Fermi energy shifts into the dip and finally comes to the local minimum of the total DOS at $c/a \approx 1.56$. This change of the Fermi energy stabilizes the bct structure at low pressures. At high pressures, the dip becomes small as shown in Figs. 7(b) and 8(b). The energy gain by the tetragonal distortion vanishes at higher pressures, and the fcc structure is realized.

The $3d$ orbitals slightly hybridize with the valence bands, which is seen as the small but finite bandwidth of the $3d$

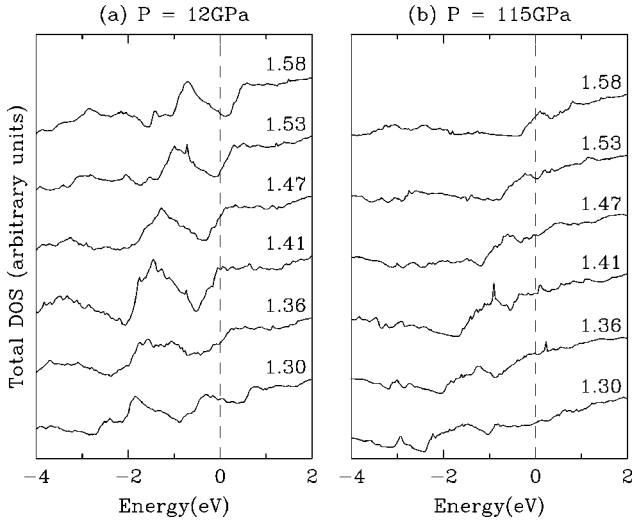

FIG. 8. The calculated total density of states near E_F of bct Ga at (a) 12 GPa and (b) 115 GPa. The numerical values in the figures indicate the c/a ratio.

bands and the d component of the partial DOS around the Fermi energy [Fig. 7(a)]. An important question is whether the $3d$ orbitals have influence on the bct-fcc structural transition. In order to clarify this, we performed NCPP calculations by excluding the $3d$ orbitals from the valence bands. The calculations required longer computational time than the FLAPW calculations, and we could not achieve numerical accuracy comparable to the FLAPW calculation. However the bct phase was always found to transform to the fcc phase at about 100–150 GPa even by treating the $3d$ orbitals as core states. Thus the $3d$ electrons play no essential role in the bct-fcc structural transition and would contribute only to quantitative differences such as the transition pressure.

V. CONCLUSIONS

We have studied the crystal structure of Ga up to 150 GPa at room temperature with the powder x-ray-diffraction techniques. The bct phase Ga(III) continuously transforms to the fcc structure above about 120 GPa, which remains stable to at least 150 GPa. The structural properties as well as the energy band structures of bct and fcc Ga have been studied with the FLAPW and NCPP calculations. The FLAPW calculation shows that bct Ga(III) continuously transforms to the fcc structure at high pressures, in good agreement with the present experiment. The NCPP calculation suggests that the valence bands of Ga overlap with the core $3d$ states above about 79 GPa. However the bct-fcc transition would not be directly driven by the valence-core overlap.

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