Gallium and Indium under High Pressure

S. I. Simak, U. Häussermann, R. Ahuja, S. Lidin, and B. Johansson

1Department of Applied Physics, Chalmers University of Technology and Göteborg University, S-41296 Gothenburg, Sweden
2Department of Inorganic Chemistry, Stockholm University, S-10691 Stockholm, Sweden
3Condensed Matter Theory Group, Physics Department, Uppsala University, S-75121 Uppsala, Sweden

High pressure experiments have been extremely useful for the understanding of the crystal structures of the elements. The possibility to study structural stability as a function of volume has added a new dimension to the fundamental question concerning the relation between atomic and electronic structure. In particular, it has been established that for elements in the same group of the periodic table, compression of a lighter element gives rise in most of the cases to the same structures as observed for the heavier elements at ambient conditions or at least closely related structures (the corresponding-states rule) [1]. A further consequence of this rule is the tendency towards lower transition pressures for the heavier members of a group. A well-known example of this is yttrium (a IIIB element) which at high pressure attains the double hexagonal closed packed (dhcp) structure, which is the crystal structure of lanthanum at zero pressure [2]. At even higher pressures yttrium enters the face-centered cubic (fcc) closed-packed structure [2], as does lanthanum at much lower pressure. We will show that a radically different picture is needed for the understanding of the high pressure behavior of the IIIA metals. We note that already the trend in the ground-state structures of the IIIA metals is highly peculiar. Aluminum crystallizes in the fcc structure, whereas gallium has a rather complicated orthorhombic structure [3]. Indium crystallizes in a body-centered tetragonal (bct) structure which corresponds to a distorted fcc arrangement where the environment of 12 nearest neighbors is split into two sets.

The high-pressure behavior of the group-III elements Al, Ga, and In has recently become a very active topic of experimental and theoretical investigation, with various surprising results emerging. First, we note that for Al no structural change is observed up to a pressure of 220 GPa [4]. Ga adopts the bct-In structure in its GaIII modification at a pressure of about 14 GPa (at 300 K) [5,6]. At high pressures GaIII finally transforms to the fcc structure as discovered recently [5,7]. The experiment performed by Schulte and Holzapfel yielded a value of 82 GPa at 150 K [5], whereas Takeamura et al. determined it to be 120 ± 10 GPa (at 300 K) and supported their finding by theoretical calculations giving a transition pressure of ≈ 120 GPa (at 0 K) [7]. In contrast to gallium, indium remains in its bct crystal structure up to the highest applied pressure to date of 67 GPa [8]. In conclusion, the IIIA metals seem to display a totally opposite behavior as regards the corresponding-states rule. Al as the lightest representative attains already in its ground state a high symmetry dense packed structure, typical of elemental high pressure modifications. Further, the bct → fcc transition for Ga in a range between 82 to 120 GPa raises the strong expectation for In to exhibit such a transition in the pressure range examined in [8], or just slightly above. The nonobservation of this transition [9] is even more remarkable in light of our recent investigation of the structural stability of In at ambient conditions [10]. There we found that the stabilization energy of In obtained by the slight distortion of the fcc structure is only 2 meV per atom. That a structure with such an extremely small stabilization energy can remain stable over a pressure range of at least 67 GPa is most unexpected since high compression is known to favor high symmetry structures.

In the present Letter, we want to investigate the reason behind the different high pressure behaviors of Ga and In, using the ab initio full-potential linear muffin-tin orbital method. This method has proved to be one of the most accurate techniques concerning studies of structural transitions [11]. We investigated the total energy as a function of volume and as a function of the c/a ratio for both Ga and In, in the bct structure [12]. We started at experimental equilibrium volumes (V0) of the ground state structures α-Ga and In, respectively. The results are summarized in Fig. 1. Qualitatively the energy surfaces of the two elements have the same shape exhibiting a double-well behavior with respect to variations in c/a. Between the two minima there is a local maximum at a c/a ratio corresponding to the ideal fcc structure (c/a = √2). The minima at c/a > √2...
FIG. 1 (color). The total energy surface for bct Ga and bct In. $E - E_{\text{fcc}}$ differences are given in $\mu\text{Ry}$ ($1 \mu\text{Ry} = 13.6 \mu\text{eV}$) per atom. Differences above 200 $\mu\text{Ry}$ are truncated.

are in accord with the experimentally observed structures. According to experiment GaIII, i.e., the bct structure, is not stable until a pressure of 14 GPa is reached, corresponding to $V/V_0 = 0.9$. At this point we calculated the stabilization of the bct structure ($c/a > \sqrt{2}$) with respect to the high symmetry fcc structure to be $\approx 4 \text{ meV}$ per atom, which is in agreement with the calculations of Takemura et al. [7]. With increasing pressure the two minima in the energy surface of GaIII become shallow, with the minimum at $c/a > \sqrt{2}$ remaining the more pronounced one. At a point $V/V_0$ slightly above 0.5, corresponding to a pressure of approximately 130 GPa, bct Ga transforms into the fcc structure which supports the results in Ref. [7]. As already mentioned, for In the maximum stabilization of the bct structure ($c/a < \sqrt{2}$) with respect to the fcc structure is only 2 meV per atom at ambient pressure ($V/V_0 = 1.0$).

In contrast to Ga, the shallower minimum at $c/a < \sqrt{2}$ becomes first more pronounced with increasing pressure attaining the same depth as the one at $c/a > \sqrt{2}$, after which both minima decrease steadily until the volume is as low as $V/V_0 = 0.3$. At this volume, which corresponds to the extremely high pressure of 800 GPa, bct In finally transforms into the fcc structure. It should be emphasized that the calculated energy changes portrayed as surfaces in Fig. 1 are extremely small. Therefore, there is a possibility that the bct $\rightarrow$ fcc transition may be observed at a lower pressure than the calculated one (which of course corresponds to a temperature of 0 K), because the thermal energy at room temperature ($\approx 26 \text{ meV}$) exceeds by far the energy differences between the bct and fcc structure for both Ga and In in the whole pressure range. However, if the difference between the entropy contributions for the structures with different $c/a$ ratios turns out to be even smaller than the total energy difference, the predicted transition pressures should be valid for room temperatures as well. A very good agreement between the calculated (at 0 K) and the measured (at higher temperatures) values of $c/a$ vs volume suggests that the latter is really the case [13].

The extremely high bct $\rightarrow$ fcc transition pressure of In compared to that of GaIII is puzzling since it does not follow the general behavior for elements in the same group of the periodic table. Therefore we need to establish in detail how pressure changes the electronic structure of Ga and In. Figure 2a displays the band structures for fcc Ga at the volumes $V/V_0 = 1.0, 0.6,$ and 0.5 and Fig. 2b the band structures for fcc In at the volumes $V/V_0 = 1.0, 0.6,$ and 0.4 [14]. We first notice the evolution of local band gaps due to the increasing interaction between the $s$ and $p$ valence bands ($s$-$p$ mixing) at the high symmetry points $Z$ and $X$ (which are degenerate), and $P$. The local band gap at $P$ is shifted—when approaching volumes closer to the transition pressure ($V/V_0 = 0.5$ for Ga and $V/V_0 = 0.3$ for In)—towards the Fermi level, yielding a band structure for fcc Ga and fcc In comparable to that of fcc Al at

FIG. 2. Band structures for fcc Ga (a) at $V/V_0 = 1.0, 0.6, 0.5$ and for fcc In (b) at $V/V_0 = 1.0, 0.6, 0.4$ [14]. The orbital character of some bands is indicated.
ambient pressure [10]. A second effect of pressure on the electronic structure of Ga and In is the broadening of the d core bands at compressed volumes, and at very high pressures they start to overlap with the bottom of the s valence band. For Ga this valence-core overlap is insignificant until the transition pressure is reached, but for In the band width of the 4d states becomes about 10 eV when reaching the transition pressure, and they mix strongly with the 5s band. Thus, pressure induces an ionization of core electrons in In (i.e., the 4d electrons become valence electrons) before the transition to the fcc structure takes place [15].

We identify the increasing s-p mixing of the valence bands under pressure, as the actual driving force for the bct → fcc transition of Ga and In. The importance of s-p mixing is easy to understand when assuming the band energy as the dominating structure determining factor [16], and according to [10] this assumption is valid for the third main group metals. Imagine a close-packed arrangement with unhybridized bands. Then the valence electrons of these metals will produce a completely occupied with unhybridized bands. Then the valence electrons of these metals will produce a completely occupied s valence band for a considerable part of the Brillouin zone with a large antibonding contribution (at the top of the band). Thus, for the third main group metals it is favorable to attain a structure where the s-s antibonding states are raised above the Fermi level for the largest possible part of the Brillouin zone, or equivalently where the number of p states below the Fermi level is increased. For Al and In at ambient conditions we made the observation that the degree of s-p mixing, which can be quantified with the ratio of the number of p and s states Np/Ns calculated inside the muffin-tin spheres [17], parallels the trend in the changes of the band energy under a tetragonal distortion of the fcc structure [10]. From Fig. 3, which shows the changes of Np/Ns as a function of c/a, we see that fcc Al at its equilibrium volume has already attained a maximal s-p mixing (minimum band energy) with respect to a tetragonal distortion. For Ga and In at their equilibrium volumes s-p mixing is increased by distortion where some atoms move closer to each other, thereby gaining valence electron bond energy. This distortion is balanced by the remaining (electrostatic) parts of the total energy, which favor a high symmetry structure. In Ref. [10] we found that the weaker tendency of In to form s-p hybridized bands at equilibrium volume originates in its lower lying and less dispersed s valence band compared with Al. Focusing again on the bct → fcc transition of Ga and In a very revealing trend emerges: at low pressures the Np/Ns curves have a minimum at a c/a ratio of \( \sqrt{2} \) corresponding to the fcc structure. When approaching volumes close to the bct → fcc transition the shape of the Np/Ns curves change and they start to develop a maximum at c/a = \( \sqrt{2} \) (Fig. 3).

Now we understand immediately the high-pressure behavior of Ga and In: bct-Ga and bct-In should transform to the fcc structure at such a compressed volume that the amount of interaction (hybridization) between the s and p valence bands becomes comparable to that for fcc Al at equilibrium. For Ga the change of the shape of the Np/Ns curves coincides exactly with the transition bct → fcc, whereas for In this change occurs already at a value of V/V0 slightly above 0.4, i.e., before the actual transition pressure is reached. This “delay” of the structural transition can be traced back to the different development of the s-p hybridization gaps under pressure for Ga and In at the high symmetry k points X(Z) and P. This fact can be extracted from Fig. 2. It may be seen that especially due to a faster increase of the gap at X(Z) for In a peculiar flat second valence band is produced along the direction X-P around the point of optimum s-p mixing for a structural transition bct → fcc (see Fig. 2b). This flat band yields a van Hove singularity in the density of states close to the Fermi level, thus indicating a structural instability. A distortion to a low symmetry structure would shift this singularity away from the Fermi level [18]. As can be seen in Fig. 4a such a shift is easily achieved by the tetragonal distortion. However, as soon as this part of the band is moved above the Fermi level for the fcc structure the latter finally

![FIG. 3. Variations of the ratio of the number of p states and s states in the muffin-tin spheres (Np/Ns, in per cent with respect to the fcc structure) as a function of c/a for Al (top panel), GaIII (middle panel), and In (low panel) at different volumes V/V0 as indicated in the figure.](image)
becomes stable. This situation is obtained at a compression of $V/V_0 = 0.3$ (see Fig. 4b) which coincides with the pressure where In transforms to the fcc structure. The reason for the different evolution of the $s$-$p$ hybridization gaps of Ga and In turns out to be connected to the relativistic effects. Though very small, mass velocity and Darwin terms contribute to the energy changes on the scale considered in the present Letter. When we “switch off” those effects and perform nonrelativistic calculation, the development of the indium bands completely corresponds to the one of Ga, and the transition to the fcc structure happens when the $N_p/N_q$ develops the maximum for $c/a = \sqrt{2}$, without any “delay” as revealed for “relativistic” In. The transition pressure in this case is estimated to be slightly below the one obtained for Ga, and therefore relativistic effects turn out to be responsible for a huge increase of the transition pressure.

In conclusion, we have shown that the structural competition between the high symmetry fcc and low symmetry bct structure for the IIIA metals Al, Ga, and In originates from electronic properties, namely the optimization of $s$-$p$ hybridization of the valence bands. As a consequence the high pressure behavior of these metals appears reversed to the corresponding-states rule: For Al the fcc structure for the IIIA metals appears reversed from electronic properties, namely the optimization of the Brillouin zone ($BZ$) we used the special $k$-points in the full $BZ$. For volumes corresponding to the transition regions up to 74 088 $a^3$, the bct structure was reported by K. Takemura and H. Fujihisa, Phys. Rev. B 47, 8465 (1993), and not observed by Schulte and Holzapfel [8]. We find the extremely small total energy difference between this postulated orthorhombic structure and the bct-In structure at this pressure to be beyond the accuracy of available first-principles methods.

We are grateful to Professors K. Takemura and W. B. Holzapfel for valuable discussions. The Swedish Natural Science Research Council (NFR), the Swedish Foundation for Strategic Research, and the Swedish Materials Consortium No. 9 are acknowledged. U. H. and S. L. wish to thank the Göran Gustafsson Foundation for financial support.

[6] In the pressure range between 2 and 14 GPa a complex mixed phase region $i$ of $\beta$-Ga and GaII is observed [5].
[9] A phase transition of indium at 45 GPa to a face-centered orthorhombic structure was reported by K. Takemura and H. Fujihisa, Phys. Rev. B 47, 8465 (1993), and not observed by Schulte and Holzapfel [8]. We find the extremely small total energy difference between this postulated orthorhombic structure and the bct-In structure at this pressure to be beyond the accuracy of available first-principles methods.
[12] The calculations were based on the local-density approximation (LDA) in the form given by L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971). Basis functions, electron densities, and potentials were calculated without any shape approximation. We made use of 3, 4, 5, and 6 valence band basis functions for both Ga and In, with 3d pseudocore states for Ga and 4d (and for very high compressions 4p) pseudocore states for In included in the corresponding basis as well. For sampling the irreducible wedge of the Brillouin zone ($BZ$) we used the special $k$ points with a Gaussian smearing of width 5 to 20 mRy. The extremely small total energy differences considered in the present work required extreme precautions as regards convergence. All necessary tests were carried out. The most crucial parameter turned out to be the number of $k$-points in the summation over the $BZ$. For volumes corresponding to the transition regions up to 74 088 $k$-points in the full bct $BZ$ were taken into account.
[13] K. Takemura (private communication); W. B. Holzapfel (private communication).
[14] For calculating the band structures we used a tetragonal body centered (bct) unit cell with the appropriate $c/a$ ratio of $\sqrt{2}$.
[15] It is known that the LDA usually gives rise to a semicore state which is higher in energy compared to experimental data due to the self-interaction. However, our tests treating semicore states as atomiclike and employing a self-interaction corrected (SIC) functional show that the energy vs $c/a$ dependence is qualitatively unaffected.
[17] The ratios $V_{MT}/V_0$ between the volume of the muffin-tin sphere ($V_{MT}$) and the considered volume ($V_0$) was always kept constant for all $c/a$ at a particular volume.
[18] The occurrence of superconductivity could also be a possibility to remove the van Hove singularity at the Fermi level. The simultaneous presence of steep and extremely flat band portions at the Fermi level has been recognized as “fingerprint” for a potentially superconducting compound by Simon [A. Simon, Angew. Chem. Int. Ed. Engl. 36, 1788 (1997)]. It is therefore quite possible that the superconductivity of In ($T_c = 3.38$ K) will be considerably enhanced under pressure.