Tetragonal distortion and structural stability of indium at high pressures

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A first-principles computation of tetragonal distortion, structural stability, and equation of state has been carried out for indium, using the linear muffin-tin orbital electron-band-theory technique. Results on the variation of tetragonal distortion (c/a) with compression show a broad maximum around $V/V_0 \approx 0.8$ (19 GPa) in agreement with experimental data. We do not find $5s5p$-to-$5d$ electron transfer as speculated to be the cause of the maximum in c/a. However, our results reveal that the core overlap resulting from broadening of the $4d$ states is the probable reason for the turnover in the c/a ratio. Within the atomic-sphere approximation we find the face-centered orthorhombic phase to be marginally stable beyond 56 GPa in accord with the experiments of Takemura *et al.*

Indium at 0.1 MPa has an unusual face-centered-tetragonal (fct) structure with axial ratio 1.076 (Ref. 1) which corresponds to a value of 1.52 in the equivalent body-centered structure. High-pressure x-ray-diffraction experiments[2–5] reveal that tetragonal distortion (axial ratio, c/a) initially increases with pressure reaching a maximum around 24 GPa, and then decreases with further increase of pressure. From the universal phase diagram for the group III B elements based on empty core pseudopotential theory and from the calculations of shear moduli, Hafner and Heine[6] showed that at normal pressure indium is located in a region which is unstable for close-packed fcc and hcp structures. Some distortion from these close-packed structures lowers the band-structure energy. Under the application of pressure indium moves through the stability region of the fct structure and approaches the boundary where the shear constant becomes negative, leading to rhombohedral distortion. However, the measurements of Takemura and co-workers[4,7] show the appearance of a face-centered-orthorhombic (fco) phase beyond 45 GPa which remains stable up to 100 GPa (Ref. 7) and which cannot be obtained by combination of tetragonal and rhombohedral distortions.

Recently Schulte and Holzapfel[8] have investigated indium for its equation of state and structural stability up to 67 GPa using the energy-dispersive x-ray-diffraction technique in a diamond-anvil cell. However, they do not observe any evidence of structural phase transition and the normal fct phase remains stable up to 67 GPa. These experiments used liquid nitrogen or mineral oil as pressure transmitting fluid in comparison to the angle-dispersive measurements of Takemura and co-workers,[4,7] which utilized the excellent features of the imaging plate as an area detector, with indium acting as its own pressure transmitter. There appears to be discrepancy between the recent and earlier experimental data for the maximum in the variation of axial ratio with compression.[2–5] A careful observation of various data sets under pressure show that recent measurements[4,5] on the axial ratio show only a weak maximum as compared to the previous data sets.[2,3] Also, the universal phase diagram of Hafner and Heine[6] suggests an increase in the c/a ratio but fails to explain its decrease with pressure. In absence of adequate theoretical work, Takemura[4,7] has speculated that there is a gradual change in the conduction-electron character of indium from sp to pd due to the $s \rightarrow d$ transfer under pressure in analogy with aluminium.[9]

Thus, discrepancies exist in high-pressure data in indium as far as the maximum in axial ratio and structural phase transition under pressure are concerned. Also the empty core pseudopotential theory used in addressing these discrepancies has its own limitations. Hence, in the present work we have attempted to study indium at high pressure by first-principles electron-band theory for the variation of its axial ratio, structural stability, and equation of state, with an aim to resolve the existing controversies in the experimental data and to arrive at a proper explanation for the turnover in the axial ratio.

We have employed the scalar-relativistic linear muffin-tin orbital (LMTO) method[10] for self-consistent electronic-structure studies. A frozen [Kr] core with a $5s^2 5p$ valence electron configuration is assumed with Barth-Hedin exchange correlation[11] with s,p,d,f components retained in the angular momentum expansion of the muffin-tin orbitals. The calculations include the combined corrections to the atomic-sphere approximation (ASA). The total energy is computed under the frozen-core approximation and is corrected for the electrostatic muffin-tin correction.

The irreducible wedge of the body-centered-tetragonal (bct) Brillouin zone (BZ) was computed at 462 $\mathbf{k}$ points. The total energies computed for various c/a values at normal volume (i.e., $V/V_0 = 1.0$) are shown in Fig. 1. It is seen that the LMTO-ASA values combined with the electrostatic muffin-tin corrections show a minimum energy at a c/a value different from the known experimental value.[1] However, it is known that the correction due to intercellular electrostatic interaction may not always be adequate.[12,13] Hence we adjusted it to reproduce the experimental c/a value of 1.52 at $V/V_0 = 1.0$. It was then kept fixed for subsequent compressions. We display

our calculated c/a values for different compressions in Fig. 2. A weak maximum around $V/V_0 \approx 0.8$ is seen which is in agreement with the recent experimental observations of Takemura[4] and Schulte, Nikolaenko, and Holzapfel.[5] However we do not find a pronounced maximum in the variation of the axial ratio with compression as found in the past.[2,3,14] Further, our calculated c/a values when compared with the various data sets in Fig. 2 are seen to agree within 2–3 %.

In order to find the cause of the maximum in the tetragonal distortion, we analyzed the details of our band-structure results. We noticed that the Fermi level lies near a valley in the density of states. Hence we investigated whether the maximum in the axial ratio could be related to the changes in the proximity of the Fermi surface to the BZ boundary like in Hume-Rothery phases in alloys.[15] However, in our calculations along some directions in the BZ, we did not find significant changes (<20 mRy) in energy eigenvalues near the Fermi level, with change in the axial ratio from 1.47 to 1.52 for volume fraction 0.7. Hence we do not expect much change in the Fermi-surface topology in this range of axial ratio.

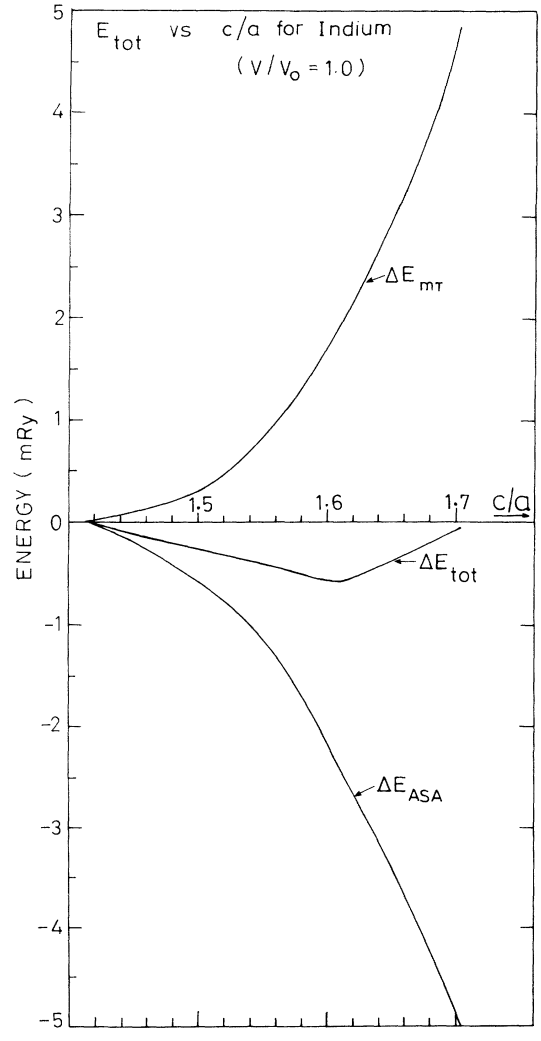

FIG. 1. Variation of the atomic-sphere-approximation contribution and muffin-tin correction to the total energy as a function of c/a at $V/V_0 = 1.0$.

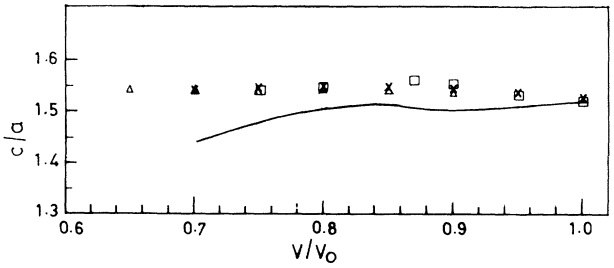

FIG. 2. The c/a variation with V/V_0 for Indium. The solid line is calculated from total-energy calculations and is compared with the three experimental data sets (□, Ref. 3; △, Ref. 4; ×, Ref. 5).

In order to look for the possible *sp*-to-*d* transfer of electrons under pressure in indium as a mechanism for the axial ratio maximum, we have plotted Fermi energy, the top of the 5*s*, 5*p* bands, and the bottom of the 5*d* band as a function of compression in Fig. 3. It is seen that these levels remain well separated above the Fermi level and hence we rule out the possibility of *sp*-to-*d* transfer causing a change in the conduction-electron character. We thus do not support the speculation made by Takemura[4] that even a small admixture of *d* character in the 5*s*5*p* conduction band of indium would be enough to change the shape of the pseudopotential, possibly giving rise to a turnover in the tetragonal distortion.

We then considered the effect of 4*d* core electron contribution to bonding and pressure. We estimated the approximate 4*d* core pressure as a function of compression using the procedure given by Sikka and Godwal,[16] while the 4*d* bandwidths were estimated from the LMTO out-

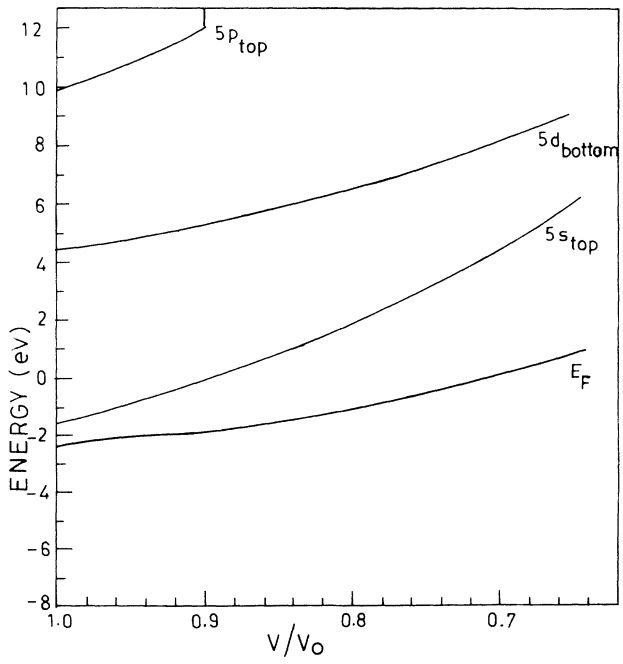

FIG. 3. Fermi energy, the top of the 5*s*, 5*p* bands, and the bottom of the 5*d* band as a function V/V_0.

puts. The results of such calculations are shown in Fig. 4. It is clear that there is a continuous increase in the 4*d* bandwidth with compression and a rapid rise in 4*d* core pressure beyond the compression of $V/V_0=0.8$. We also noted that up to the compression of $V/V_0=0.8$, it was possible to obtain proper c/a values from total-energy minimization using only $5s5p$ panels for conduction electrons. However, beyond this compression for proper convergence of total energy, it was essential to include the 4*d* electrons in the conduction band in a separate panel (as is also supported by Fig. 4). We thus suggest that the probable cause of turnover in the axial ratio is the core overlap mechanism arising from the broadening of the 4*d* core orbitals under pressure to the extent that beyond $V/V_0=0.8$, they no longer can be treated as core states but have to be considered as a part of the conduction states for reliable estimates of axial ratios.

We also investigated the relative structural stabilities between fct and fco phases by total-energy calculations.[17] The difference in energies as a function of compression is plotted in Fig. 5. This shows that fct and fco phases are of comparable stability with fco phase becoming marginally stable beyond $V/V_0\approx0.625$ supporting the experimental findings of Takemura and Fujihisa.[7] It is to be noted that the orthorhombic distortion is quite small [the b/a changes from 1 for fct to 1.018 for fco (Ref. 17)] and the overlap among atomic (Wigner-Seitz) spheres are 25.48 and 26.68 %, respectively, for the fct and fco phases which are within the accepted 30% overlap limit for LMTO-ASA calculations. This may be compared with the corresponding overlap values of 19.06 and 24.11 % for face-centered-cubic and body-centered-cubic structures. We thus expect LMTO-ASA estimates of total energies to be reasonable. However in view of the small energy differences between fct and fco phases it is desirable to have full potential total-energy LMTO calculations to confirm the LMTO-ASA simulations of fct-fco phase transition.

Finally we calculated the pressure[18–20] from the contributions resulting from the electronic pressure arising from the conduction electrons evaluated in the atomic-sphere approximation (ASA) by the linear muffin-tin orbital (LMTO) method;[10] due to intercellular Coulomb interaction beyond ASA;[12,13] at higher compressions the core pressure from 4*d* core states was also included.[16] These results in the fct and fco phases are compared in Fig. 6 with the recent high-resolution angle-dispersive data of Takemura and co-workers.[4,7] We find reasonable agreement between the two in the fct phase. However in the fco phase at high compressions we notice systematic deviations of our estimated pressure from the experimental data. This perhaps is due to the fact that we have used the same structural parameters as obtained around 50 GPa at high pressures.[17] We also notice that there is almost no volume discontinuity in the fct–fco transition supporting Takemura's results.[4] We also found the equilibrium volume to agree within 4% by including zero-point and room-temperature lattice thermal contributions

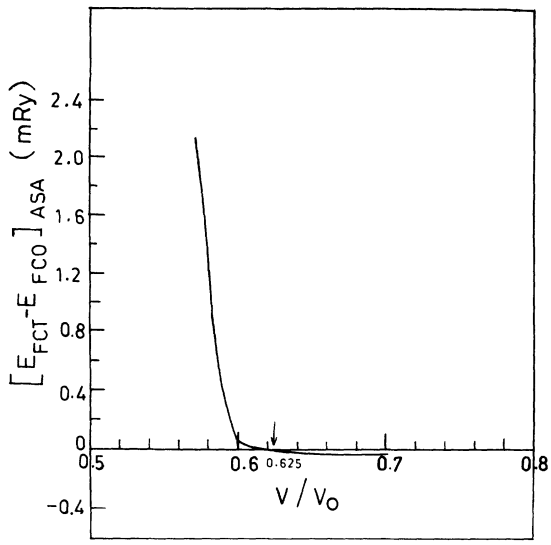

FIG. 5. Variation of the ASA value of total energy in indium in the fct phase relative to the fco phase with V/V_0.

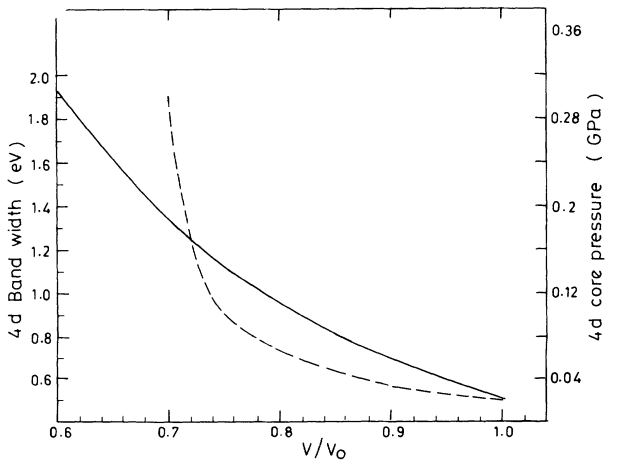

FIG. 4. Variation of 4*d* bandwidth (solid line) and 4*d* core pressure (dotted line) with V/V_0.

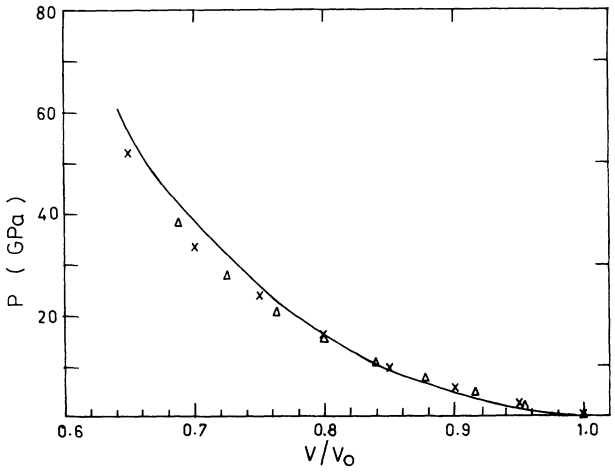

FIG. 6. Pressure versus V/V_0. The solid line is from our calculations in the fct and fco phases and is compared with experimental data sets (△, Ref. 5; ×, Ref. 7).

to the ASA and muffin-tin-corrected values of pressure. The bulk modulus (B) and its pressure derivatives (B') were found to be 35.6 and 4.5, respectively, which can be compared with their experimental values of 41.8 and 4.8.[4]

The results of our present studies show that there is a weak maximum in the c/a ratio with compression. The possible cause of it seems to be the core overlap resulting from the broadening of the $4d$ core orbitals. We do not find the ($5s5p$) to $5d$ electron transition. Thus indium does not behave like aluminium under pressure. Based on LMTO-ASA estimates of total energy we find the fco phase to be marginally stable purely under hydrostatic environment. Also, this transition occurs with very small volume discontinuity. This should not be interpreted as a second-order transition in view of discontinuity in the lattice constants and the large region of coexistence of fct and fco phases.[4]

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