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Effect of pressure on the lattice distortion of indium to 56 GPa

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The change in the axial ratio c/a of indium has been precisely determined under pressures up to 56 GPa at room temperature. The high-pressure powder-x-ray-diffraction techniques utilize an imaging plate and a synchrotron-radiation source. The axial ratio of the face-centered tetragonal lattice increases with pressure from the value at atmospheric pressure ($c/a=1.0757$), reaching a maximum of 1.091 around 24 GPa ($V/V_0=0.75$) and decreases with further compression. The bulk modulus and its pressure derivative have been determined as $B_0=41.8\pm0.5$ GPa and $B_0'=4.81\pm0.06$, respectively. The present result differs considerably from the previous measurements, in which a maximum in c/a was observed at pressures lower than 10 GPa. The origin of $(c/a)_{\max}$ has been discussed in terms of the pseudopotential of indium under pressure.

I. INTRODUCTION

Indium metal has an unusual crystal structure for a metallic element, namely, the face-centered-tetragonal structure (fct). The deviation from the face-centered-cubic structure (fcc) can be expressed by the tetragonal axial ratio c/a. It is 1.0757 at atmospheric pressure and at room temperature. One of the high-pressure phases of gallium also has a crystal structure similar to indium.[1] The tetragonal distortion of indium has been explained by the pseudopotential theory.[2] The nearest-neighbor distance for the hypothetical close-packed structures (fcc or hcp) of indium falls near a local maximum of the potential, resulting in the instability of the close-packed structures. Some distortion from the close-packed structures lowers the band-structure energy. Calculation of the shear moduli of indium further supports the tetragonal distortion.[2] The degree of the tetragonal distortion of indium is thus intimately related to the shape of the pseudopotential. If one applies pressure to indium, the potential energy changes through the change in the nearest-neighbor distance and, accordingly, the tetragonal distortion should also change. Accurate determination of the tetragonal distortion of indium under pressure may therefore serve as a rigorous test for constructing its pseudopotential.

Previous high-pressure experiments on indium are scarce. The pioneering work by Bridgman[3] focused on the measurements of volume and electrical resistance to 10 GPa. Vaughan and Drickamer[4] have measured the lattice constants to 34.5 GPa using x-ray-diffraction techniques. Similar measurements have been done by Vereshchagin *et al.*[5] to 11 GPa. Dudley and Hall[6] have determined the melting temperature of indium under pressures up to 7.5 GPa.[7] None of the previous works suggest any phase transitions in indium under pressure.

The change in the lattice constants of indium with temperature has been studied by several investigators. Graham *et al.*[8] have given numerical equations for the temperature dependence of the lattice constants a and c. The thermal expansion of the a axis is larger than that of the c axis, resulting in a continuous decrease of c/a with temperature. It does not, however, reach 1.0 (fcc) even before the melting. In addition, the c axis shows negative thermal expansion above about 20 °C.[8,9]

A primary purpose of the present study is to precisely determine the tetragonal distortion of indium under pressure. Secondary purposes are to measure the bulk modulus and its pressure derivative and to search for pressure-induced structural phase transitions.

II. EXPERIMENT

Indium powder of 99.999% purity obtained from Koch Chemicals Ltd. was loaded into the gasketed diamond anvil cell (DAC) without any pressure-transmitting medium. Pressure was determined by the ruby fluorescence method based on the pressure scale given in Ref. 10. Although the pressure was not truly hydrostatic, the low shear modulus of indium caused a small pressure gradient across the sample and a small broadening of the ruby fluorescence peaks, indicating a slight effect of nonhydrostaticity. The particle size of indium was initially 10–20 μm, giving poor powder-diffraction patterns with a nonuniform distribution of intensity along Debye-Scherrer rings at low pressures. At high pressures, however, the particles were crushed efficiently because of plastic flow of the gasket, which started around 5 GPa and ceased above 15 GPa. Such an effective reduction of the particle size was not possible if one used a pressure-transmitting medium.

Powder-x-ray-diffraction patterns were mostly obtained with synchrotron radiation (SR) on the beam line 6B at the Photon Factory National Laboratory for High Energy Physics (KEK), in an angle-dispersive mode. The white x-ray beam from the bending magnet was monochromatized with Si(111) double crystals to an energy of 18.00 keV. The second Si crystal was bent sagittaly to focus the beam to the position of the sample. A pinhole collimator with 80-μm diameter was inserted in the beam path in order to reduce the beam size further. An imaging plate[11] (IP) with a 200×250-mm^2 area was held flat about 140 mm apart from the sample. Special care has been taken to achieve high accuracy in determining the lattice constants. The flatness of the IP as well as its alignment against the x-ray beam have been checked by taking diffraction patterns of standard specimens prior to the high-pressure experiments. The positions of the DAC and the IP were monitored with dial gauges, which ensured reproducibility of setting them within ±20 μm. The exact value of the sample-to-plate distance was determined for the DAC under pressure by taking a diffraction pattern of a standard specimen (Ag powder in our case), which was glued on the table surface of the diamond anvil on the exit side. The total experimental error in the sample-to-plate distance was estimated to be ±0.02%. A detailed description of the experimental system and the error estimation will be reported elsewhere.[12] Some diffraction patterns at low pressures have been obtained with a conventional sealed-off x-ray tube with a molybdenum target equipped with a position-sensitive detector. All the measurements have been done at room temperature.

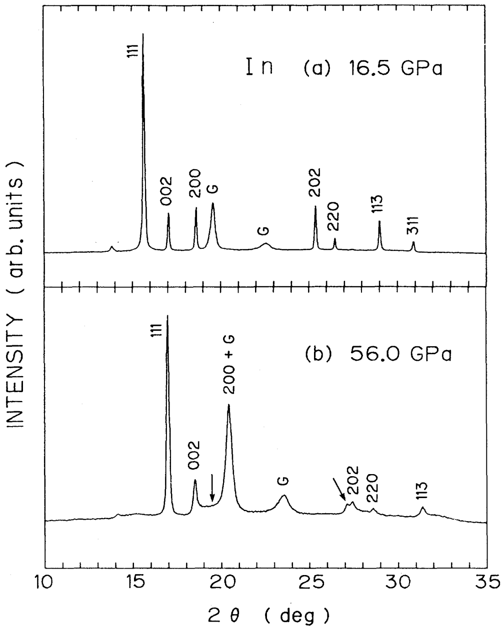

FIG. 1. Powder-x-ray-diffraction patterns of indium at (a) 16.5 GPa and (b) 56.0 GPa. The x-ray energy was 18.00 keV. The exposure time for each pattern was 5 and 2 h, respectively. The weak peak around $2\theta=14°$ in both patterns is probably due to indium oxides present in the specimen. The peaks marked *G* are from the gasket. Note the appearance of a new peak on the left-hand side of the 202 reflection in (b) as well as the increase in the intensity between the 002 and the 200 reflections, which indicate the onset of a structural phase transition.

III. RESULTS

Figure 1 shows representative diffraction patterns of indium at high pressures: (a) at 16.5 GPa and (b) at 56.0 GPa, both taken with the SR and the IP. These patterns were obtained by integrating the intensity of the raw image data along each Debye-Scherrer ring on the basis of the method developed by Shimomura *et al.*[12] It should be noted that there was evidence for a structural phase transition in indium around 45 GPa. In the diffraction patterns taken above 44.5 GPa, weak peaks were observed around $2\theta=19.2°$ and 27.1° [see arrows in Fig. 1(b)]. Intensities of these peaks increased with increasing pressure. However, the slow growth rate of the high-pressure phase has prevented us from doing the structure analysis. In the present study we concentrate on the structural change of the low-pressure phase. Five to seven reflections have been used to calculate the lattice constants a and c depending on the pressure range. No systematic deviations have been found in the lattice constants when different sets of reflections were used. Experimental uncertainty in a and c was ±0.02%, yielding errors of ±0.06 and ±0.04 % in volume and in c/a, respectively. These values are an order of magnitude smaller than the typical errors obtained by the energy-dispersive method, mainly because of the high resolution inherent in the angle-dispersive method. In addition, characteristic to the IP, the large sample-to-plate distance ($\simeq 140$ mm) reduces the relative error of the distance associated with setting and removing the DAC and the IP in each experimental run. Crystal data are summarized in Table I. The lattice constants measured at the lowest pressure agree reasonably well with the values found in the literature. Both a and c show smooth changes with pressure without any anomalies. The equation of state (EOS) is shown in Fig. 2. The present data are fitted with the Birch-Murnaghan equation of state with the bulk modulus $B_0=41.8\pm0.5$ GPa and its pressure derivative $B_0'=4.81\pm0.06$, both at atmospheric pressure. These values are compared favorably with those measured with ultrasonic methods [$B_0=41.13$ GPa (Ref. 14); $B_0=40.34$ GPa, $B_0'=6.16$ (Ref. 15)], as well as with the volumetric method [$B_0=39.08$ GPa, $B_0'=5.24$ (Ref. 16)]. Figure 3 shows the change in the axial ratio c/a as a function of volume. A maximum appears around $V/V_0=0.75$ and $P=24$ GPa with a value $(c/a)_{\max}=1.091$. The previous measurements by Vaughan and Drickamer[4] are shown by the dash-dotted curve. They differ considerably from the present results, having a maximum $(c/a)_{\max}=1.101$ around 8 GPa ($V/V_0=0.88$). The reason for the discrepancy is not clear. They have claimed that there was a slight irregularity in a and c near $V/V_0=0.95$, which seems to be the main cause of their $(c/a)_{\max}$. Since the present results show only smooth changes in a and c, their irregularity could be erroneous. The data by Vereshchagin *et al.*[5] are shown by the dashed curve.[17] They agree fairly well with the present results up to about 10 GPa, but fall off rapidly at higher pressures. Again, the position and the value of $(c/a)_{\max}$ ($V/V_0=0.86$, $P=9$ GPa, $c/a=1.089$) are different from the present results. Also shown in Fig. 3 is the temperature dependence of the tetragonal distortion at atmospheric pressure plotted as a function of relative volume.[8] Further discussion will be given in the next section.

TABLE I. The lattice constants a and c, relative volume V/V_0, and axial ratio c/a of indium under pressure at room temperature. The unit-cell volume at atmospheric pressure and at room temperature (V_0) is calculated to be 104.63 Å^3 from the lattice constants given in Ref. 13 ($a_0=4.5990$ Å and $c_0=4.9470$ Å for fct), which are the average of values reported by various investigators.

P (GPa)	a (Å)	c (Å)	V/V_0	c/a
0.3(1)	4.5946(12)	4.9407(20)	0.9968(7)	1.0753(8)
3.8(2)[a,b]	4.4742(37)	4.8438(49)	0.9268(18)	1.0826(20)
6.1(1)	4.4213(20)	4.7976(35)	0.8963(11)	1.0851(13)
6.7(2)[a]	4.3982(25)	4.7836(40)	0.8844(12)	1.0876(16)
7.7(2)[a]	4.3765(15)	4.7683(16)	0.8729(7)	1.0895(8)
9.8(2)[a]	4.3287(23)	4.7263(25)	0.8464(11)	1.0919(11)
12.2(2)	4.3011(5)	4.6873(6)	0.8287(2)	1.0898(3)
16.5(1)	4.2495(4)	4.6326(6)	0.7995(2)	1.0902(2)
18.2(2)[a]	4.2221(18)	4.6109(34)	0.7856(9)	1.0921(13)
19.8(2)	4.2076(8)	4.5884(14)	0.7764(4)	1.0905(5)
23.0(3)[a]	4.1706(12)	4.5500(23)	0.7564(6)	1.0910(8)
25.8(3)	4.1450(4)	4.5216(7)	0.7425(2)	1.0908(3)
31.2(2)	4.0937(3)	4.4661(6)	0.7153(1)	1.0910(2)
38.2(4)	4.0470(10)	4.4121(18)	0.6906(4)	1.0902(7)
44.5(6)	4.0059(7)	4.3667(9)	0.6697(3)	1.0901(4)
50.6(12)	3.9705(12)	4.3258(14)	0.6518(4)	1.0895(6)
56.0(8)	3.9441(20)	4.2930(22)	0.6383(7)	1.0885(11)

[a] Data taken with a conventional x-ray tube and a position-sensitive detector.

[b] Data taken in the course of decreasing pressure.

IV. DISCUSSION

The change in the axial ratio c/a of indium under pressure can be interpreted primarily within a framework of the pseudopotential theory at least at low pressures. As was discussed by Hafner and Heine,[2] the degree of the tetragonal distortion of indium should be very sensitive to subtle curvatures of the pseudopotential. This is because the elastic shear constants C and C', which are related to the rhombohedral and the tetragonal distortion of the fcc structure, respectively, can be expressed by a

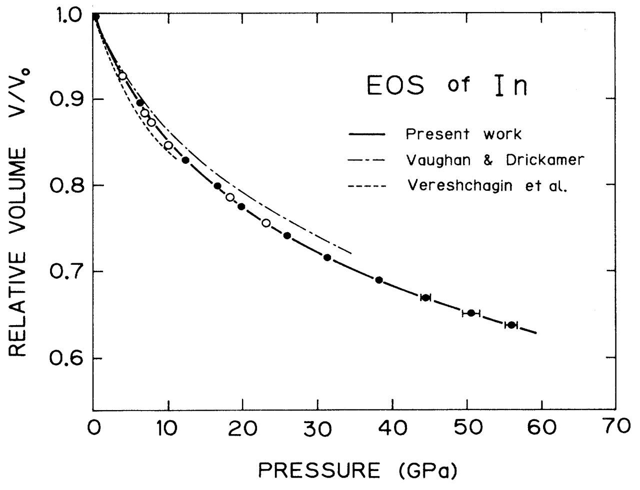

FIG. 2. The equation of state of indium up to 56 GPa. The present results are shown by the solid and open circles: the data were taken either with the SR and the IP (solid circles) or with a conventional x-ray source and a position-sensitive detector (open circles). The error bars in relative volumes are smaller than the size of the circles. The solid curve is a fit with the Birch-Murnaghan equation of state ($B_0=41.8$ GPa and $B_0'=4.81$). The dash-dotted and dashed curves show the previous data by Vaughan and Drickamer (Ref. 4) and by Vereshchagin *et al.* (Ref. 5), respectively.

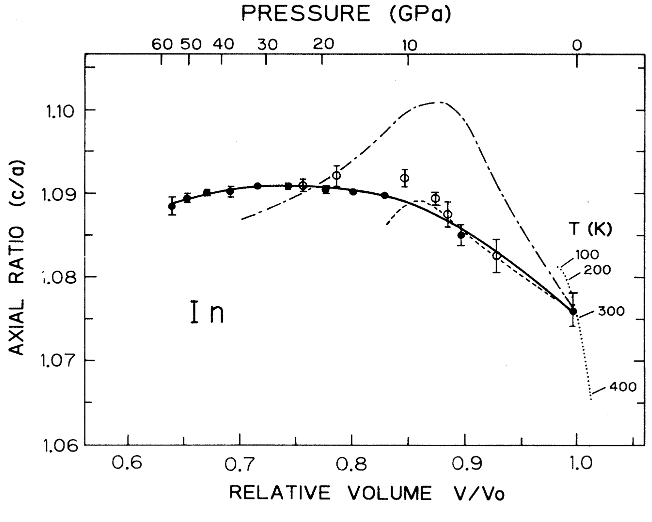

FIG. 3. The change in the axial ratio c/a of indium with relative volume V/V_0, where V_0 denotes the volume at atmospheric pressure and at room temperature. The corresponding pressures are indicated on the upper abscissa. The present results are shown by the solid and open circles, which have the same meaning as in Fig. 2. The previous data by Vaughan and Drickamer (Ref. 4) (dash-dotted curve) and by Vereshchagin *et al.* (Ref. 5) (dashed curve) are also shown. The temperature dependence of c/a at atmospheric pressure is shown by the dotted curve as a function of relative volume on the basis of the data by Graham *et al.* (Ref. 8).

combination of the first and the second derivative of the potential with respect to the interatomic distance. In case of indium, C' is negative, leading to the fct structure. Hafner and Heine[2] have further proposed a universal phase diagram of the group IIIb elements classified by R_s and R_c/R_s, where R_c is the core radius and R_s is related to the atomic radius R_a and the valence Z through the formula $R_s = R_a Z^{-1/3}$. Although they did not provide the pressure (or volume) dependence of the c/a ratio of indium numerically, their universal phase diagram suggests an increase in tetragonal distortion of indium under pressure, since R_c/R_s approaches the region of more negative C' values for smaller R_s (smaller volumes). This seems to be consistent with the present result of *increasing* c/a with pressure at the initial stage of compression. The *decrease* of c/a at higher pressures, however, cannot be accounted for by this simple argument based on the elastic shear moduli alone. In the following we consider two possible explanations for the decrease in the tetragonal distortion.

The first possibility is an effect of the core repulsion at higher pressures. As the interatomic distance decreases with pressure, the potential becomes increasingly steep dominated by the core repulsion. Energy increases rapidly for smaller interatomic distances, and, hence, the splitting of the nearest-neighbor distance into two by the tetragonal distortion does not lower the crystal energy at all. Any distortion from the close-packed structures is thus unfavorable. This is in accord with the general trend of the structural changes of simple metals under pressure toward close-packed arrangements in the absence of electronic transitions. It should be noted that the ingredient of this trend is, in part, the spherical symmetry of the potential for *sp* electrons, which allows for the model of hard-sphere packing, and thus is not necessarily relevant to transition metals.

The second possibility stems from a comparison of the electronic structure of indium with that of Al under extreme pressure. According to the calculation by McMahan and Moriarty,[18] the conduction electrons of Al gradually change their character from *sp* to *pd* or *d* at very high pressures. The overall *sp* to *d* electronic transition in Al is caused by the downward movements of the $3d$ bands relative to the $3s3p$ bands under pressure and is expected to also occur in indium under pressure, for which the $5s5p$ to $5d$ is a possible transition. The *sp* to *d* electronic transition proceeds rather continuously with pressure because of the hybridization. For the case of Al, it is calculated to start around $V/V_0 = 0.5$, corresponding to a pressure above 300 GPa. In indium, the energy separation between the $5s5p$ and the $5d$ bands is smaller than that of the $3s3p$ and the $3d$ counterparts of Al, suggesting that the starting pressure of the *sp* to *d* transition could be lower. On the other hand, the inner $4d$ core bands of In should prevent the downward movements of the unfilled $5d$ bands because of the orthogonality,[19] postponing the *sp* to *d* transition. Consequently, it is not clear whether the electronic transition in In occurs at a lower or higher pressure than Al. If it occurs, even a small admixture of the *d* character in the conduction band would be enough to change the shape of the pseudopotential, possibly giving rise to a turnover in the tetragonal distortion.

Here we have to recall that the pseudopotential calculations are done at zero temperature. For the total energy and the lattice distortion of indium at room temperature, we should consider the contribution by phonons as well. In this regard, the comparison of the pressure and the temperature dependence of the c/a ratio is quite interesting. As seen in Fig. 3, the effect of temperature on the tetragonal distortion of indium is far more remarkable than the effect of pressure. This demonstrates the importance of phonon energy in determining an equilibrium distortion of indium at finite temperature. Further experimental determination of the lattice distortion of indium over a wide pressure-temperature range will clarify the electronic and the lattice dynamical origin of the tetragonality of indium. Theoretical investigations of this problem would prove desirable.

In summary, the lattice constants of indium have been precisely determined under pressure to 56 GPa at room temperature. The c/a axial ratio has a maximum around 24 GPa, suggesting a qualitative change of bonding character of indium at high pressures. Two explanations are proposed: (i) the increasing contribution of the core repulsion and (ii) the *sp* to *d* electronic transition analogous to aluminum under pressure. Evidence for a structural phase transition above 45 GPa is noted.

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