Corresponding Member of the Academy of Sciences of the USSR L. F. VERESHCHAGIN, S. S. KABALKINA,

Z. V. TROITSKAYA

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

PHYSICS

Corresponding Member of the Academy of Sciences of the USSR L. F. VERESHCHAGIN, S. S. KABALKINA,
Z. V. TROITSKAYA

THE EFFECT OF HIGH PRESSURE ON THE STRUCTURE OF GALLIUM AND INDIUM

The elements Al, Ga, In, Tl, despite belonging to the same group of the periodic system, possess different crystalline structures. Al has the face-centered cubic structure usual for a metal. Ga is characterized by a rhombic structure, which formally may be regarded as "molecular," since each atom has one nearest neighbor at a distance of 2.44 Å and six at distances of 2.71–2.80 Å. Gallium exhibits a number of features connected with its complex structure: an extremely low melting point (29.8°), the ability to undergo prolonged supercooling; the curve of the dependence of the melting temperature of gallium on pressure has a negative slope. Melting of gallium is accompanied by a transition to a more densely packed structure with an increase in coordination, which is also connected with an increase in electrical and thermal conductivity (^{1}). In has a tetragonal structure, which in the face-centered aspect may be regarded as a distorted closest cubic packing ($c/a = 1.075$).

Fig. 1. Shortest interatomic distances d in elements of group III B. a—at atmospheric pressure, b—at p = 30–40 kbar

Under ordinary conditions thallium corresponds to a close-packed hexagonal structure (α-Tl), which at $T > 230°$ transforms into body-centered cubic (β-Tl) (^{2}). At $p > 37$ kbar and room temperature, after the phase transition Tl has a face-centered cubic structure (^{3}).

We have carried out an X-ray diffraction investigation of the structure of gallium and indium at high pressures: Ga at 30–40 kbar and In up to 110 kbar. In the work a special X-ray camera was used (^{4}, ^{5}), the main part of which is a tablet of "amorphous" boron with a channel for the specimen; the tablet was placed between two anvils made of hard alloy VK-6. Calibration of the chamber with respect to pressure by recording jumps in the electrical resistance of Bi during three phase transitions made it possible to fix the pressure with an accuracy of ±3–5 kbar.

Gallium. It is known that at pressures above 12 kbar and temperatures below 2.4° gallium undergoes a transition to a new modification, named by Bridgman Ga II (^{6}). It has also been found (^{7}) that at $p > 30$ kbar and $T > 50°$ there exists a third form—Ga III (Bridgman' s GaII′). The equilibrium phase diagram of gallium up to 75 kbar in the temperature interval from −50 to 150° is given in (^{7}). The authors of that work observed that, in the region of high pressures, during the transition in the solid phase GaIII → GaII, strong supercooling (20-25°) took place. In a number of cases in the region of stability of GaII, crystallization of GaIII occurred from the melt. The transition GaI → GaII, according to the same authors, occurs without delay.

In the present investigation, whose aim was to determine the structure of GaII, the authors used the method of photographing at high pressure and room temperature. The powder for the experiments was prepared by

grinding gallium in a metal mortar cooled with dry ice, and sifting through a sieve (200 mesh); filling the pellet with powder was carried out at −40 to −50°. The chamber with the pellet was cooled with dry ice, then quickly transferred into the press, where a pressure of 30-40 kbar was produced. At the moment the pressure was produced, the temperature of the specimen was about −20 to −30°. Thus, at a pressure of 30-40 kbar and a temperature below 0°, we succeeded in carrying out the transition GaI → GaII, bypassing melting, and in removing the high-pressure phase, i.e., GaII, at room temperature (Cu radiation). It should be noted that a considerable number of X-ray patterns of Ga obtained in this way either turned out to be blank or contained individual spots, which is apparently associated with recrystallization of gallium at room temperature. Nevertheless, in 5 cases identical X-ray patterns were obtained, the principal lines of which (excluding the lines of boron and of the anvil material) could be indexed in the indium structure with cell parameters: $a = 3.96 \pm 0.02$ Å and $c = 4.37 \pm 0.03$ Å, $c/a = 1.104$.

Table 1

I	hkl	d_{hkl}
strong	101	2.34
very weak	002	2.18
medium	110	1.96
medium	112	1.47
very weak	200	1.40

Table 1 gives the intensities, indices, and values of the interplanar spacings of 5 reflections of GaII at $p = 30$ kbar.

Table 2 presents data for In, GaI, and GaII. The structure of In and GaII is considered in the face-centered aspect.

Fig. 2. Dependence of c/a of indium on p

Figure 2: Fig. 2. Dependence of c/a of indium on p

Thus, at pressures exceeding 12 kbar, GaI apparently transforms into a structure of the indium type, more symmetrical and denser; the coordination number increases in this process. A consequence of the same transition is apparently the decrease in electrical resistance during the transition GaI → GaII.

On the basis of the structural data, the following interatomic distances were obtained for GaII at 30 kbar: $4d_1 = 2.79$ Å, $8d_2 = 2.95$ Å. In Fig. 1,a the dependence of the shortest interatomic distances on the atomic number Z in the elements of group IIIB Al, Ga, In, Tl at atmospheric pressure is presented; in Fig. 1,b, the same dependence at 30–40 kbar. Examination of the curve shows that the shortest interatomic distances in the elements of group IIIB under high pressure change smoothly as a function of Z, whereas at atmospheric pressure for Ga a certain anomaly is observed—the points corresponding to it fall significantly out of the general course of the curve. Thus, pressure "removes" the anomaly in the interatomic distances.

Fig. 2. Dependence of c/a of indium on p

Considering the general character of the change in the structure of elements under high pressure in subgroups IVB and VB, we see that the transition of gallium into the indium structure is a confirmation of the general tendency: under pressure an element acquires the structure of the element located below it.

Indium. As was mentioned above, the indium structure can be obtained by stretching a face-centered cube along a fourth-order axis—

Table 2

Element	Pressure p	a, Å	b, Å	c, Å	c/a	Number of atoms in the elementary cell	Density, g/cm^3
In	1 bar	4.585	–	4.941	1.075	4	7.31
GaII	30 kbar	3.96 ± 0.02	–	4.37 ± 0.03	1.104	4	6.8
GaI	1 bar	4.524	4.523	7.661	–	8	5.9

by 8%. Taking into account the smooth character of the change with pressure of such physical properties of In as the volume (8), electrical resistance (9), and

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

melting temperature (7), one might have expected that pressure gradually removes the distortion of the structure, as a result of which, with increasing p, there would be a gradual decrease of c/a from 1.075 to 1.0. We carried out a detailed x-ray study of indium (Mo radiation) up to 110 kbar, which showed that in fact the influence of pressure on the structure of indium is more complicated.

Thus, it follows from Fig. 2 that, as the pressure is increased to ~ 70 kbar, c/a increases somewhat (from 1.075 to 1.088), then passes through a maximum, and only at higher pressures (100-110 kbar) is there a tendency toward its decrease.

Fig. 3. Dependence of the coefficients of linear compressibility of indium $\frac{1}{a_0}\frac{\partial a}{\partial p}$ (a) and $\frac{1}{c_0}\frac{\partial c}{\partial p}$ (b) on p

In Fig. 3 are presented the coefficients of linear compressibility of indium

$$\frac{1}{a_0}\frac{\partial a}{\partial p} \quad \text{and} \quad \frac{1}{c_0}\frac{\partial c}{\partial p},$$

at pressures up to 110 kbar. The values obtained from this by extrapolation to $p = 0$,

$$\frac{1}{a_0}\frac{\partial a}{\partial p} = (9.1 \pm 0.7) \cdot 10^{-7}\ \text{bar}^{-1}$$

and

$$\frac{1}{c_0}\frac{\partial c}{\partial p} = (7.0 \pm 0.7) \cdot 10^{-7}\ \text{bar}^{-1},$$

agree, within the errors of the experiment, with the values calculated from elastic moduli (10):

$$\frac{1}{a_0}\frac{\partial a}{\partial p} = 8.6 \cdot 10^{-7}\ \text{bar}^{-1}$$

and

$$\frac{1}{c_0}\frac{\partial c}{\partial p} = 6.6 \cdot 10^{-7}\ \text{bar}^{-1}.$$

Fig. 4. Dependence of the volume compressibility of indium on p.
a—our data, b—Bridgman' s data (8)

In Fig. 4 the volume compressibility of In up to 110 kbar is shown, and Bridgman' s data (8) are also plotted. The x-ray data exceed Bridgman' s data by 7% in the pressure range 40-60 kbar and by 2% in the region of higher pressures ($\sim$ 100 kbar). These discrepancies are evidently due to the deviation of the experimental conditions from hydrostatic ones, as well as to errors in the determination of the pressure.

Thus, on the basis of the data obtained, it may be considered highly probable that removal of the distortion in the structure of indium will occur at pressures considerably exceeding 100 kbar.

Institute of High Pressure Physics
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.