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Transformations in Mercury at High Pressures*

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The liquid- α and α - β phase boundaries have been determined for mercury up to nearly 70 kbar with a newly developed technique of internally heated resistance measurements. The fusion curve and phase boundary diverge with pressure, thus eliminating the possibility of a triple point between the three phases. The structural distortions under pressure for Hg and some other anisotropic Group B elements are examined and an increase in coordination and packing efficiency within the given anisotropic structure is strongly suggested.

INTRODUCTION

MERCURY was the subject of one¹ of Bridgman's earliest and most comprehensive investigations of metallic elements at high pressures. In this work,¹ Bridgman determined the course of the fusion curve to about 12 kbar and also presented data for the compressibilities of the solid and liquid phases in the temperature interval, -40 to 20°C . Other workers^{2,3} have subsequently refined these fusion measurements and extended⁴ the melting-curve determination to about 20 kbar. In 1935, Bridgman⁵ investigated solid mercury up to pressures of about 40 kbar and down to liquid-nitrogen temperatures. A new polymorph (β) was discovered and its phase boundary with the well-known polymorph (α) is roughly parallel to the fusion curve. β Hg was expected to be stable at zero pressure from an extrapolation of the Bridgman data⁵ but only recently have Swenson and co-workers carefully established the low-pressure boundary,⁶ determined the crystal structure⁷ of β Hg, and pointed out the diffusionless nature of the transformation.⁸

The present investigation was undertaken in order to determine the fusion curve and solid-solid phase boundary to higher pressures. Because of the difficulty of handling mercury with previous techniques, it was necessary to develop a new technique of internally heated resistance measurement which is described here.

EXPERIMENTAL PROCEDURES

Pressures up to 45 kbar were generated in a piston-cylinder apparatus, previously described.⁹ Friction corrections were made by comparing the phase boundaries obtained upon compression and upon release of pressure; under the assumption that friction is approximately the same on the up- and down-stroke, the true phase boundary is found by interpolation. The double value of friction in the present experiments, i.e., difference between up- and down-stroke, was 4.1 kbar at 17 kbar, 4.8 kbar at 30 kbar, 5.6 kbar at 41 kbar, etc., in good agreement with previous experiments¹⁰ with the present geometry. Pressures are believed accurate to ± 0.5 kbar.

Pressures up to nearly 70 kbar were obtained with a double-stage apparatus, previously described.¹¹ These higher pressures are believed accurate to ± 2.0 kbar.

The technique of differential thermal analysis (DTA) is convenient in many ways for detecting phase trans-

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¹ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **47**, 347 (1911).

² A. Michels, B. Blaise, and G. Koens, *Physica* **9**, 365 (1942).

³ M. K. Zhokhovskii, *Izmeritel Tekhn.* **1955**, No. 5, 3 (1955).

⁴ M. K. Zhokhovskii and V. N. Razumikhin, *Izmeritel Tekhn.* **1957**, No. 4, 43 (1957).

⁵ P. W. Bridgman, *Phys. Rev.* **48**, 893 (1935).

⁶ C. A. Swenson, *Phys. Rev.* **111**, 82 (1958).

⁷ M. Atoji, J. E. Schirber, and C. A. Swenson, *J. Chem. Phys.* **31**, 1628 (1959).

⁸ J. E. Schirber and C. A. Swenson, *Acta Met.* **10**, 511 (1962).

⁹ G. C. Kennedy and R. C. Newton, *Solids Under Pressure* (McGraw-Hill Book Company, Inc., New York, 1963).

¹⁰ W. Klement, A. Jayaraman, and G. C. Kennedy, *Phys. Rev.* **129**, 1971 (1963).

¹¹ A. Jayaraman, W. Klement, R. C. Newton, and G. C. Kennedy, *J. Phys. Chem. Solids* **24**, 7 (1963).

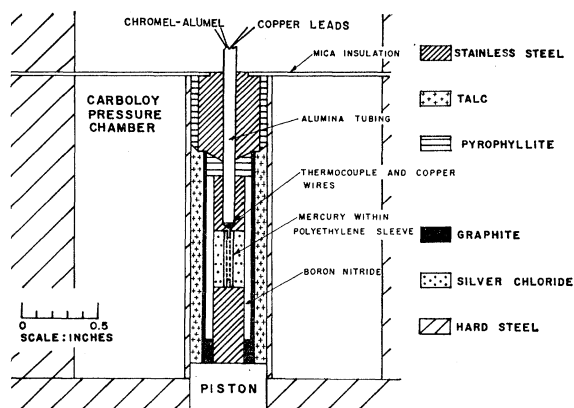


FIG. 1. Diagram of the internally heated resistance (IHR) arrangement.

formations at high pressures and has been extensively used in this laboratory. This technique requires that one of the thermocouples is in contact with, or slightly separated by a good thermal conductor from, the sample being investigated. In practice, direct contact is usually not feasible for melting studies. The problem is then to make a suitable thin-walled container of some material which is sufficiently ductile, which is a relatively good thermal conductor and which does not react with either thermocouple or sample. The latter condition is especially difficult to satisfy for many of the liquid metals. Another constraint on the applicability of the DTA technique is that minimum heating and/or cooling rates of about $2^{\circ}\text{C}/\text{sec}$ are necessary in order to obtain discernable signals. Since many solid-solid phase transitions are sensitive to the heating and cooling rates, the "equilibrium" transformations may be obscured by hysteresis effects.¹⁰

Liquid metals have been successfully contained at high pressures, provided the capsule is properly sealed during the initial compression of the solid sample. Experiments with the melting of mercury were at first carried out with the DTA method, using containers fabricated from tantalum, molybdenum, and iron and including a variety of press-fitted and screw-cap designs. Despite these efforts at encapsulation, mercury inevitably escaped from the container during the initial compression at room temperature. It is believed that the escaped mercury intermittently short-circuited the thermocouple with the graphite heating sleeve. This resulted in barely readable DTA signals. The thermocouples failed completely after 2 to 10 meltings in 4 separate runs. The signals, such as they were, indicated melting temperatures 5°C or more too low to be consistent with a reasonable extrapolation of the fusion curve^{3,4} from lower pressures. In brief, mercury could not be effectively encapsulated and those DTA signals actually obtained were unreliable.

To overcome these difficulties, a technique of internally heated resistance (IHR) measurements was devel-

oped. The experimental arrangements are depicted in Fig. 1, which is drawn to scale.

Liquid mercury was contained within a piece of polyethylene tubing of about 25-mil bore, the ends being sealed by slightly oversize stainless steel pins. Pressure was transmitted to the sample through the polyethylene and the surrounding sheath of silver chloride. Temperature was measured by means of a chromel-alumel thermocouple, located near the sample in a well, drilled into the upper stainless steel end piece.

Electrical insulation between the resistance circuit and the internal heating circuit was effected by means of alumina tubing, pyrophyllite, and boron nitride or talc, from top to bottom (Fig. 1). The lower stainless steel end piece passed through a graphite annulus and was in direct contact with the piston, which served as the common terminal for the heater current as well as the direct current through the sample. Heater current of up to a few hundred amperes was supplied through the upper pressure plate to the stainless steel plug and thence through the graphite sleeve. Two copper wires, brought in through the four hole alumina tubing and in intimate contact with the upper stainless steel end piece, served to carry direct current of a few hundred milliamperes from a dry cell across the mercury sample. Potential drop across the sample was continuously plotted against temperature on an x-y recorder.

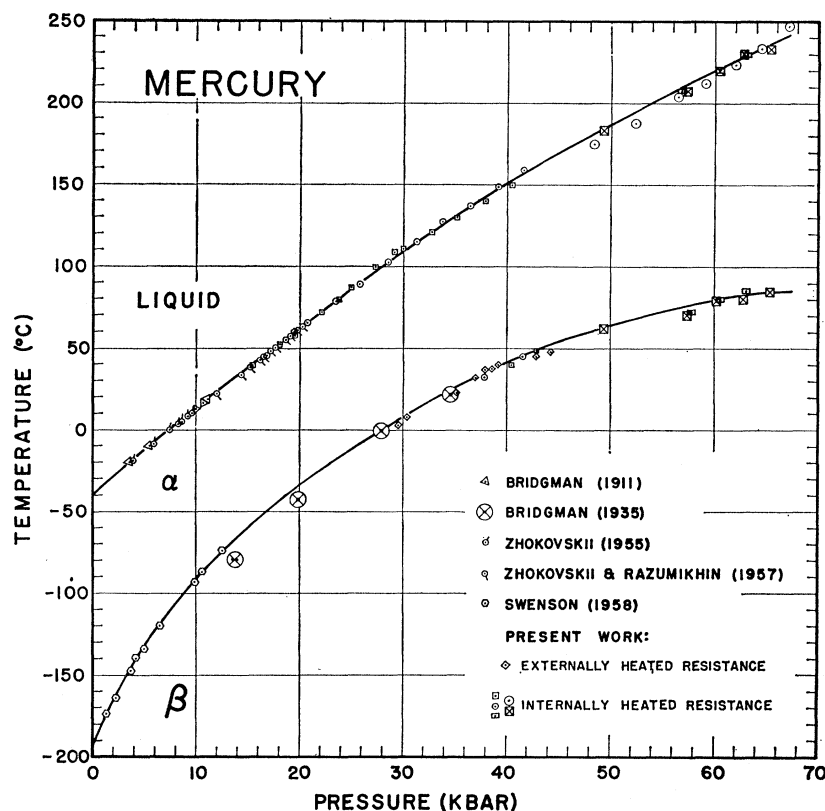
A marked advantage of this technique is that liquids can be contained effectively at high pressure. Perhaps the greatest advantage is that the signals are usually very distinct and the discontinuities in resistance, characteristic of even rather subtle transitions, are readily detected. Very low heating and cooling rates are possible and this is of some advantage in studying solid-solid transitions with rate-dependent hystereses. The primary limitation appears to be the lack of tubing materials—which are required to be electrically insulating, nonreactive, plastic enough to transmit pressure well and suitable for a range of temperature. Polyethylene, for example, is probably only useful to a few hundred degrees Centigrade; with Teflon, this range could be increased somewhat.

Prior to the development of the IHR technique, a few runs were made with mercury contained as in Fig. 1, but with heating and/or cooling accomplished externally with a heating tape or with dry ice.¹¹

EXPERIMENTAL RESULTS

The results of several runs are plotted in Fig. 2, together with some of the data^{1,3-6} obtained by previous workers. The IHR signals detected on heating were taken for the melting-point determinations; these signals were usually sharp and distinct, with the resistance of the liquid phase many times that of the solid. The resistance increments were not reproducible and this may be attributed to variations in contact resistance and, possibly, also preferred orientation in the

FIG. 2. Phase diagram of mercury to about 70 kbar. Many of the precise data of Michels *et al.* (reference 2) to 3 kbar, of Zhokhovskii (reference 3) and of Zhokhovskii and Razumikhin (reference 4) for the fusion curve have been omitted in the interest of clarity.



anisotropic solid. Temperatures were determined with a precision of $\pm 1-2^\circ\text{C}$; values from the standard tables were taken for the chromel-alumel thermocouples, in the absence of reliable pressure corrections. The most uncertain data lie in the interval, 45–55 kbar—at pressures greater than single-stage determinations and yet lower than the most accurate region of the double-stage apparatus.

The IHR results for the α - β transition are the mean of the signals detected on heating and cooling at rates of about $0.5-2.0^\circ\text{C}/\text{sec}$. The resistance of the α phase is slightly higher than that of the β phase but, again, the increment was not readily reproducible. The hysteresis interval for the α - β transformation was about 6°C at 42 kbar, with no detectable variation for different cooling rates.

The single melting point determined at 19.4 kbar with the externally heated setup is in excellent agreement with the IHR result and with the Zhokhovskii and Razumikhin datum⁴ (Fig. 2). Most of the measurements made in the externally heated apparatus were concerned with the resistance discontinuities, characteristic of the α - β transition, which appeared under increasing or decreasing pressure. The transformation was found to be somewhat smeared out but, nevertheless, there is good agreement with the IHR results and the results of Bridgman⁵ in the respective pressure intervals (Fig. 2).

DISCUSSION

As seen from Fig. 2, the low-pressure portions of the presently determined phase boundaries are in good agreement with the actual and extrapolated data from previous investigators.^{3,4,6} At the higher pressure, curvature continues to be apparent for the fusion curve and pronounced for the α - β boundary. The temperature interval of stability of α mercury is about 150°C at 1-atm pressure, decreases to a minimum of about 86°C near 18 kbar and is about 153°C near 66 kbar, the highest pressure attained in this investigation. The divergence of the boundaries with increasing pressure is obvious and it may reasonably be assumed that an α - β -liquid triple point does not exist.

Three possible courses may be suggested for the phase diagram of mercury at pressures above 70 kbar. First, the intervention of another, more dense polymorph and an α - β - γ triple point is the most conventional expectation. Second, the gross curvature in the α - β phase boundary invites the idea that the β field may become closed off. Third, the lack of *actual* measurements concerning the crystallographic distortions with temperature and pressure (however, see discussion below) for both α and β Hg does not rule out the possibility that the α - β phase boundary terminates in a critical point, the phases, thus, being indistinguishable at higher

pressures; the only critical point presently known in a solid element is that in cerium.^{12,13}

Structural Considerations for Mercury at High Pressure

Some insight into the relative compressibilities of the several phases can often be obtained by consideration of the coordinates existing in the different structures, as emphasized recently by Jayaraman, Klement, Newton, and Kennedy.¹¹

For liquid mercury, the work of Kruh *et al.*¹⁴ suggests that there are about 7.5 nearest neighbors per atom, which would be considered as rather open packing.

The α form of mercury is rhombohedral, with one atom/unit cell and $\alpha \approx 70.6^\circ$. There are 6 nearest and 6 next nearest neighbors, with about 16% difference in interatomic distance between the sets. The variation of the rhombohedral angle with temperature has not been clarified,⁶ but apparently is not large.¹⁵ This rhombohedral crystal structure has been described, at times, as a distortion from simple cubic ($\alpha = 90^\circ$), but is actually more closely related to the face-centered cubic (fcc) structure ($\alpha = 60^\circ$ for the rhombohedral primitive cell). The elastic moduli data from Gruneisen and Sckell¹⁶ for α Hg at -190°C suggest an approximately 5-fold greater stiffness along the trigonal axis than perpendicular to it. Thus, the rhombohedral angle would decrease with increasing hydrostatic compression and it is suggested that the α Hg structure continuously distorts toward fcc with pressure.

The structure of β Hg, as determined by Atoji, Schirber, and Swenson,⁷ is body-centered tetragonal (bct) with two atoms/unit cell, $c/a \approx 0.707$ at -196°C . [The only other element presently known to crystallize in a similar structure is proactinium,¹⁶ with $c/a \sim 0.825$ at room temperature. There may exist a good deal of analogy between Pa and Hg, akin to that^{10,11} recently pointed out between U and Ga, especially since Zachariasen¹⁶ has deduced that 5f electrons are not involved in the bonding in these actinides.] The coordination is 2 nearest and 8 next nearest neighbors, some 8% further away. There are no measurements of the elastic moduli or of the variation in axial ratio with temperature.

Although liquid mercury is only loosely packed, not too much curvature is manifested in the fusion curve because of the high compressibility of α mercury. The least compressible of the condensed phases is β Hg and

this is probably related to the facility with which 10-fold coordination can be achieved, i.e., $c/a \rightarrow \sqrt{2/3} = 0.817$. As the packing in α Hg tends, with pressure, toward the 12-fold characteristic of the fcc structure, this phase is initially more compressible than the β form; at the higher pressures, the difference in compressibility decreases rapidly and consequently the α - β phase boundary exhibits less curvature. If the packing in the liquid does not increase at a rate commensurate with the realization of closest packing in the α polymorph, the curvature in the melting curve does not diminish as rapidly as for the boundary. The consequences of these rationalizations are in accord with the present experimental results (Fig. 2).

Atoji *et al.*⁷ have noted that β Hg is isomorphous with the phase found over a wide range of composition in the Hg-Cd alloy system.^{17,18} Actually, it is likely that a continuous solid solution exists from β mercury to very near pure cadmium although it is rather difficult to attain equilibrium at the lower temperatures. Lattice spacings for these β Hg-Cd alloys have been reported by several workers,^{17,19} none of which are in particularly close agreement. The data of Schubert *et al.*¹⁷ are the most recent and self-consistent and will, therefore, be used for the present discussion. According to Schubert *et al.*,¹⁷ the axial ratios of the β Hg-Cd structures vary almost linearly with composition; by extrapolation to pure mercury, the axial ratio of β Hg may be estimated as ~ 0.704 at room temperature. Considering the reported value⁷ of $c/a \approx 0.707$ at -196°C ; it then appears that the axial ratio of β Hg decreases slightly with increasing temperature.

The data of Schubert *et al.*¹⁷ are not so readily extrapolated to pure cadmium for an inquiry into the possible appearance of this element in the β Hg structure at high pressure. Although an axial ratio of ~ 0.82 might be expected for " β Cd," the uncertainty as to the molar volume (by extrapolation) relative to the hexagonal close-packed (hcp) polymorph effectively frustrates this approach. The zero pressure difference in free energy and in entropy at 25°C between β Cd and the stable polymorph may be estimated as 0.16 ± 0.10 kcal/mole and -0.8 ± 0.7 eu, respectively, by extrapolation of recent selected β Hg-Cd thermodynamic data²⁰ in the manner employed by Klement.²¹ This suggests that β Cd, if it exists, is stable at low temperature—an observation that might have been made immediately from the Hg-Cd equilibrium phase diagram.¹⁸

¹² E. G. Poniatovskii, Doklady Akad. Nauk S.S.S.R. **120**, 1021 (1958) [translation: Soviet Phys.—Doklady **3**, 498 (1958)].

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¹⁴ R. F. Kruh, G. T. Clayton, C. Head, and G. Sandlin, Phys. Rev. **129**, 1479 (1963).

¹⁵ C. S. Barrett, Acta Cryst. **10**, 58 (1957).

¹⁶ E. Gruneisen and O. Sckell, Ann. Physik **19**, 387 (1934); Solid State Phys. **7**, 284 (1958); W. H. Zachariasen, Acta Cryst. **5**, 19 (1952).

¹⁷ K. Schubert, U. Rösler, W. Mahler, E. Dörre, and W. Schütt, Z. Metallk. **45**, 643 (1954).

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¹⁹ W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958).

²⁰ R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, Inc., New York, 1963).

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TABLE I. Effects upon dimensionless structural parameters for some noncubic Group B elements. Parentheses denote uncertain data.

Element	Structural parameter	Increase	Alloying ^a Decrease	Hydrostatic pressure ^b $\xi = \left(\frac{c}{a}\right) \left(\frac{C_{33}-C_{13}}{C_{11}+C_{12}-2C_{13}} \right)$	Temperature ^a
Zn	axial ratio	Cd, Hg, Al	Cu, Ag	0.25, 0.26, 0.28; decrease	increase
Cd		Hg, (Si)	Mg	0.17, 0.22, 0.22, 0.27; decrease	increase (maximum near melting point)
β Hg	rhombohedral angle	Cd	no data	no data	no data
α Hg				$\left(\frac{C_{33}-C_{13}}{C_{11}+C_{12}-2C_{13}} \right) \approx 4.7$; decrease	no data
In	axial ratio	Sn, Pb, Bi	Cd, Hg, Tl	see text	(decrease)
Tl		Sn, Sb, In ^d	Cd ^e	2.0 ^e ; increase	(decrease)
Sn	axial ratio	Zn, Cd, Hg, In	Pb, Bi, Sb	0.49, 0.57, 0.78, 0.92; decrease	increase
Mg	axial ratio	Cd, Al, (Ga), (Si), In, Tl, (Ge), Sn, Pb, (As), Bi	Ag, (Au), (Zn), (Hg), (Sb), (Te)	1.51, 1.52, 1.56, 1.71; increase	increase

^a Data from reference 19, unless otherwise noted.^b Data from references 16 and 23, unless otherwise noted. Values from all sources have been considered to obtain an estimate of the uncertainties. The small corrections from adiabatic to isothermal moduli have been ignored.^c See reference 24.^d See reference 25.^e See reference 26.

Structural Correlations among some Anisotropic Group B Elements

In order to further elucidate the structural phenomena in mercury, it is worthwhile to consider briefly some of the effects of pressure, temperature, and alloying on several of the anisotropic Group B metals. Gallium, bismuth, antimony, etc., are omitted from this discussion because the coordination within these structures depends upon certain positional parameters, which have usually not been measured with sufficient precision under the different conditions.

The mercury congeners—zinc, cadmium, and also magnesium—crystallize in the hcp structure, with the axial ratios of the former differing considerably from ideal, i.e., $c/a = 1.85$ – 1.90 vs 1.6330 . There is, however, no decisive evidence at present for any polymorphic transitions at high pressure for Cd, Zn, or Mg. (For single crystals of cadmium, Bridgman²² found slight discontinuities in volume and electrical resistance which have neither received satisfactory explanation nor been detected in polycrystalline material. These subtle discontinuities may be related to the type of transition discussed near the end of this paper.) The initial variation with pressure of the axial ratio (or of any dimensionless structural parameter for a noncubic structure) may be estimated from the elastic moduli. Quantitatively,

$$\frac{\partial}{\partial p} \left(\frac{c}{a} \right) \propto \left\{ \left(\frac{c}{a} \right) - \frac{(\partial c / \partial p)}{(\partial a / \partial p)} \right\},$$

which may be recast in terms of ξ ;

$$\xi \equiv \left(\frac{c}{a} \right) \left(\frac{C_{33}-C_{13}}{C_{11}+C_{12}-2C_{13}} \right),$$

²² P. W. Bridgman, Proc. Am. Acad. Arts Sci. 60, 305 (1925).

where $\xi > 1$ means an increase and $\xi < 1$ a decrease in the axial ratio for hexagonal, tetragonal, or trigonal structures under hydrostatic pressure. From the room temperature elastic moduli,^{16,23} it may be expected that the axial ratios of Cd and Zn decrease markedly with pressure while that of Mg increases slightly from $c/a \sim 1.624$. The extensive fields of stability of the hcp structures of Cd, Zn, and Mg under pressure are, thus, characterized by distortion toward ideal packing. Many of these data and those pertinent to the following discussion have been collected in Table I.^{24–26}

The overriding effect of hydrostatic pressure is to increase the coordination in the noncubic structures—from $6+6 \rightarrow 12$ for Mg, Zn, Cd, and α Hg, as mentioned, and also for Tl, and from $4+2 \rightarrow 6$ for Sn. The data are uncertain for In when the errors in the moduli measurements are considered; the only measurements for In appear to be those of Winder and Smith.²⁷ In a previous paper,¹¹ it was suggested that hydrostatic pressure decreased the axial ratio for indium, but this statement was based on an erroneous calculation. It would be physically plausible and consonant with the other anisotropic elements if the axial ratio for indium *did* decrease with pressure. It may be, however, that the axial ratio initially increases due to some overlap and then decreases at higher pressures.

The effects of temperature are often intuitively thought of as opposing those of pressure. Indeed, the temperature and pressure-induced variations in axial

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ratio for Zn and Sn are opposed (Table I); however, there may be complications in the thermal expansion¹⁹ (well above the Debye temperatures) for Cd and In. There is a slight increase in c/a for Mg with temperature, as well as pressure, and this emphasizes the difficulty in generalizing about the temperature effects for those elements with complex Fermi surface-Brillouin zone interactions.

Likewise, the effects of alloying upon the dimensionless structural parameters of these anisotropic elements might be expected to be complex but, surprisingly, some limited generalizations are possible. As indicated by the scanty data in Table I, the coordination is increased for Zn, Cd, and β Hg by alloying with B-group elements to the left and above in the periodic table and decreased for the others. The coordination is increased for In, Tl, Sn, and Mg by alloying with elements to the right and below and decreased for the others. Subtleties for very dilute solid solutions (such as claimed for Mg alloys¹⁹) are ignored here. The only exceptions arise from the In-Tl system^{19,25} and from some Mg-alloy work, which is not thoroughly verified.

For β Hg then, the decrease in axial ratio with temperature and increase with pressure, as suggested above, are still plausible in view of these correlations. The decrease in rhombohedral angle with pressure suggested for α Hg is possibly associated with a slight increase in α with temperature. The complexities of the Fermi surface-Brillouin zone interactions in several of these phases, especially In and Mg, may invalidate many of the naïve correlations herein outlined.

Schirber and Swenson⁸ have put forth a mechanism for the diffusionless α - β transition, which leans heavily on the observation that c/a for β Hg at -196°C is 0.707 or very nearly $1/\sqrt{2}$. More caution is necessary in such deductions since it is very probable that the axial ratio varies both with temperature and pressure, the geometrical considerations then becoming more complex.

It would be especially useful to have more data for the alloys. No lattice spacings for α Hg-rich solid solutions are available, apparently, while, for β Hg, only the Cd alloys have been investigated. For investigations

of β Hg requiring single crystals, it may be necessary to rely on extrapolations from the Hg-Cd alloys since the problems in obtaining suitable unicrystals of β Hg are formidable.⁸

Although indium does not fit in well with many of the correlations discussed above, recent work on the In-Cd²⁸ and In-Hg²⁹ alloy systems has brought up a problem of great importance and pertinence for the distortions in many anisotropic elements under pressure. It has been known¹⁹ for some time that Cd or Hg dissolved in In decreases the axial ratio steadily toward unity; upon further alloying, c/a remains unity, i.e., the fct structure becomes fcc. Heumann and Predel²⁸ and Coles *et al.*²⁹ have shown definitively, however, that there is really a narrow two-phase region separating the fct and fcc phases. It thus appears that indium does not gradually pass from fct to fcc but that a distinct, first-order phase transition is required. According to the packing principle outlined in this paper, there are definite tendencies for many of the anisotropic structures to distort, with pressure, towards the ideal coordination, e.g., $c/a = (8/3)^{1/2}$ for hcp structures. Whether this distortion can proceed continuously to the ideal coordination, which then obtains at higher pressures, is now open to some doubt. It may be that a subtle phase transition occurs between the distorted and the ideal structures. Such a phase change would probably be difficult to detect because of the small changes in volume, entropy, resistance, etc., expected across the transition.

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²⁸ T. Heumann and B. Predel, *Z. Metallk.* **53**, 240 (1962).

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