Melting and Polymorphic Transitions for Some Group II-VI Compounds at High Pressures

A. JAYARAMAN, W. KLEMENT, JR.,† AND G. C. KENNEDY*

Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California

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The fusion curves of HgTe, CdTe, and CdSe have been determined over portions of the pressure interval, 0–50 kbar, by differential thermal analysis. Solid-solid transitions in HgTe, HgSe, CdTe, CdSe, and CdS have been investigated by the volume-discontinuity method. The sequences of pressure-induced polymorphic transitions in the II–VI compounds have been described in terms of mean atomic number and electronegativity difference and also compared with previous correlations discovered for the Group VI elements and III-V compounds.

I. INTRODUCTION

DATA for the melting and polymorphic transitions of some Group IV elements and III–V compounds at high pressures have recently been presented by Jayaraman, Klement, and Kennedy.[1] Similarities among the phase diagrams and of the sequences of polymorphic structures were strikingly apparent from this investigation.[1]

The present paper reports determinations of the melting curves and solid-solid boundaries for some II–VI compounds. An attempt is made to delineate the sequence of structural transformations under pressure in these compounds, using the present results, the data from the optical and electrical resistance work of Drickamer and his colleagues,[2–5] data from the investigations of Bridgman,[6,7] and direct determinations,[8,9] of the structures of some high-pressure polymorphs.

II. EXPERIMENTAL PROCEDURES

Pressures up to 50 kbar were generated in a piston-cylinder apparatus previously described.[10] Friction corrections were made in the usual way[11] for the melting data and these pressures are believed accurate to ±1.0 kbar.

Melting was detected by means of differential thermal analysis (DTA). Temperatures were measured with the chromel-alumel thermocouples, using values from the standard tables. The DTA signal obtained on heating was taken for the melting point and these temperatures were determined to ±3°C. Because of the experimental difficulties such as shorting, deterioration of the thermocouples, etc., only a few data were successfully obtained above 1100–1200°C.

The solid-solid transitions were investigated with the volume-discontinuity method.[11] Since the II–VI compounds are brittle and have high shear strength, good quasihydrostatic pressures could not be obtained merely by placing the material directly in the pressure chamber, as for some metals previously studied.[12] Instead, the compounds were powdered and then dispersed in silver chloride, which transmits pressure almost hydrostatically. Typically, about 2 cm³ of powdered compound and about 3.5 cm³ of silver chloride were thoroughly mixed and pressed into a cylindrical pellet about $1\frac{3}{4}$ in. long by $\frac{1}{2}$-in. diam. Soft steel washers were used at both ends of the pellet to prevent extrusion. A thin lead foil was wrapped around the cylindrical pellet and the interior of the carboloy chamber coated with molybdenum disulfide to reduce friction at sample-chamber interface and at the walls, respectively. Piston displacement vs pressure was continuously recorded on an x-y recorder for cycles of increasing and decreasing pressure at several temperatures up to 169°C. At higher temperatures, the steel binding rings, with their larger coefficient of expansion, ceased to give adequate support to the shrunk-fit carboloy pressure chamber. Compression and decompression rates were in the range of 1–2 kbar/min.

The sluggishness of these solid-solid transitions makes the friction corrections more difficult than for rapidly running transitions. The compression curves for HgTe, as recorded at three temperatures, are presented in Fig. 1. At 23°C, the transition commences at (a) and proceeds over an interval of pressure up to (b) where it is ostensibly completed. Upon the release of pressure, the reverse transition starts at (c) and is essentially completed at (d). Similar stages in the pressure-induced

† Present address: Kungl. Tekniska Högskolan, Institutionen för Fasta Tillståndets Fysik, Stockholm 70, Sweden.

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[1] A. Jayaraman, W. Klement, and G. C. Kennedy, Phys. Rev. 130, 540 (1963).

[2] A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, J. Phys. Chem. Solids 11, 140 (1959).

[3] A. L. Edwards and H. G. Drickamer, Phys. Rev. 122, 1149 (1961).

[4] G. A. Samara and H. G. Drickamer, J. Phys. Chem. Solids 23, 457 (1962).

[5] S. Minomura, G. A. Samara, and H. G. Drickamer, J. Appl. Phys. 33, 3196 (1962).

[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 76, 55 (1948).

[7] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 21 (1940).

[8] J. A. Kafalas, H. C. Gatos, M. C. Lavine, and M. D. Banus, J. Phys. Chem. Solids, 23, 1591 (1962).

[9] J. S. Kasper (unpublished) as quoted by W. B. Wilson (private communication).

[10] G. C. Kennedy and R. C. Newton, *Solids under Pressure* (McGraw-Hill Book Company, Inc., New York, 1963).

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

[12] G. C. Kennedy and P. N. LaMori, J. Geophys. Res. 67, 851 (1962).

TABLE I. Data for the solid-solid transitions in some II–VI compounds.

Compound	T (°C)	P (kbar)	Transition pressure (kbar) up-stroke	down-stroke	Width of transition (kbar) up-stroke	down-stroke	Volume change V/V_0 (%)	Reference
HgTe	23	14.0	15	13	~4 }		~6.0	
	160	14.0	15	13	~1 }			
	22	12.5					8.4	e
HgSe	23	7	8	6	3	2}	9.0	
	146	7.5	8.3	6.7		~1.5 }		
	RTª	7.5					9.6	e
	CO₂Tᵇ	7.1					9.2₆	
CdTe	RT		~7.5ᶜ	3	~4.5		8.6ᵈ	f
	23	33	34	32		12 }	10	
	125	31	34	28	10	~6}		
	RT		35	20				g
	RT	30–35						h
CdSe	23	23	28	17		3.5	9	
	RT	~19	27	~16	10			g
CdS	23	20	28	11	5	~4}	~10	
	143	21	25	15		4 }		
	RT	~19	27.5	10	~12	~10		g
	RT	~20						h

ª RT =room temperature.
ᵇ CO₂T = −78°C.
ᶜ At liquid-nitrogen temperature, greater than 13 kbar.
ᵈ The low-temperature data have apparently not been corrected to RT.

ᵉ See reference 7.
ᶠ See reference 8.
ᵍ See reference 3.
ʰ See reference 4.

transition are evident for the 70 and 162°C loops, although the enclosed area decreases with increasing temperature. For rapidly running transitions (as idealized by the sketch in Fig. 1), the displacements essentially coincide for the onset and reverse completion—(a) and (d)—and for the completion and reverse onset—(b) and (c)—of the transition, which runs in both directions at essentially constant pressures. It is
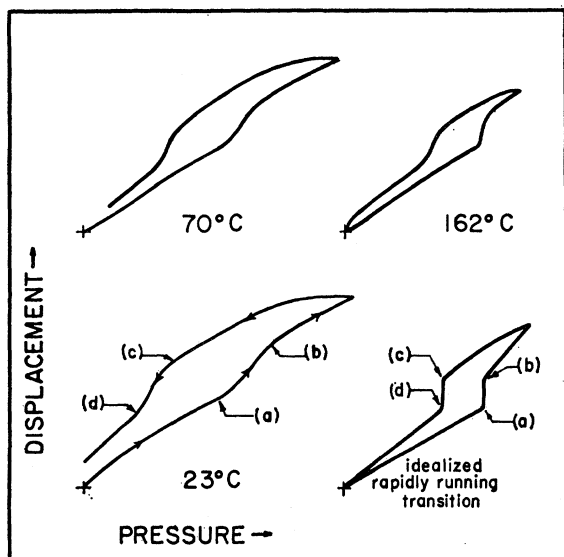

FIG. 1. Displacement vs pressure for HgTe at 23, 70, and 162°C. For comparison with these sluggish transitions, the idealized course of a rapidly running transition is also portrayed.

then only necessary to correct for friction in such a rapidly running transition.

It is evident that the total hystereses in these solid-solid transitions decrease with increasing temperature. This may be mainly attributed to the speeding up of the diffusion-related nucleation and growth processes and also to a decrease in friction, mostly due to the increased plasticity of silver chloride. With the assumption that both friction and "overshooting" are symmetrical, the "pressure" of the transition is taken as the mean of the pressures at (a) and (c); the limits corresponding to (a) and (c) are also tabulated. The volume change for the transition is obtained by extrapolating the pretransition compression curve from (a) to the pressure corresponding to (b) or similarly for the reverse transition (cf. Fig. 1). This takes into account the compression of the transformed material over the range of the transition, (a) to (b) or (c) to (d). These several transition data are collected in Table I, with further comments given below.

High-purity polycrystalline compounds were used in this work. HgSe and CdTe were prepared by heating stoichiometric proportions of high-purity elements together in a sealed silica tube.

III. EXPERIMENTAL RESULTS AND DISCUSSION

HgTe and HgSe

Bridgman[7] did not obtain time-independent compression data for HgTe at room temperature and for pressures up to about 50 kbar. He, however, suggested that there was a transition near 12.5 kbar at 22°C with
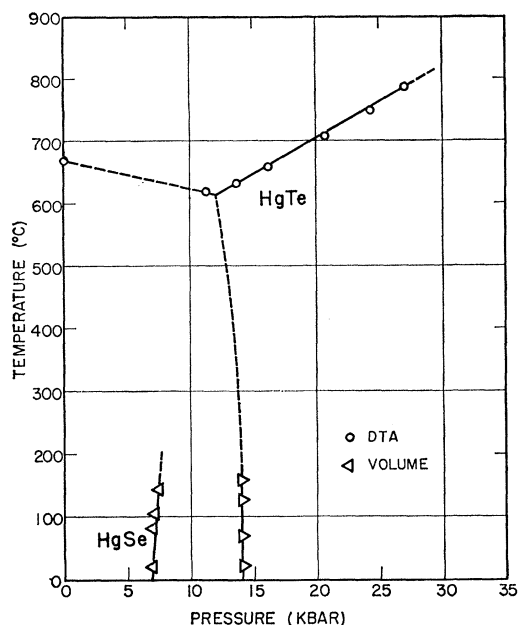
FIG. 2. The melting curve of HgTe, as determined by DTA, with the phase boundary determined by the volume-discontinuity method extended to the triple point. The phase boundary for HgSe determined by volume discontinuity is also plotted.

a volume change of ~8.4% and further proposed that this transition was obscured by the progressive decomposition of HgTe into its constituent elements. Other evidence for this interpretation was the reported detection of the $\alpha-\beta$ transition in free mercury produced in the hypothesized pressure-induced decomposition. Because of Bridgman's procedure[7] whereby volume decrements were measured only at certain pressures, no continuous record of displacement vs pressure is available for comparison with the present data.

The present compression experiments indicate that the solid-solid transition is somewhat sluggish but reversible; the transition is clearly diffusion controlled as indicated by its increasing rapidity at the higher temperatures (Fig. 1). The coordinates of the transition are plotted in Fig. 2, with pertinent data collected in Table I. Bridgman's arguments for the decomposition of HgTe upon isothermal compression are not verified by the present work. The structure of the high-pressure polymorph of HgTe is expected[7] to be of the cinnabar type and this has been verified by Kasper.[9]

DTA signals for the melting of HgTe in molybdenum and tantalum containers were of poor quality in 5 technically sound runs. Data from the best run are plotted in Fig. 2. For a normal melting point of 670°C,[13] the melting slope of the zincblende polymorph is about $-4.6°C/kbar$ until a triple point near 615°C and 12.0

[13] D. R. Mason and D. F. O'Kane, in *Proceedings of the International Congress on Semiconductor Physics—Prague 1960* (Academic Press Inc., New York, 1961), p. 1026.

kbar is reached; the melting slope of the cinnabar polymorph is then about 11.5°C/kbar up to at least 27 kbar. The volume-discontinuity data at lower temperature have been connected with the DTA melting determinations by means of the dashed boundary in Fig. 2. The actual curvature in the zincblende-cinnabar boundary necessary for this connection is probably not as exaggerated as shown, but rather reflects the difficulty of the interpolation and the lack of precision of the lower temperature determinations.

Bridgman's compression studies[7] of HgSe suggested a sharp transition near 7.4 kbar at both room and dry ice temperature with volume changes of 9.6 and 9.26%, respectively. Kafalas et al.[8] have found by resistance measurements that the room-temperature transition commences at 7.5 kbar and is extended to about 12 kbar; the transition is accompanied by an increase in resistance of several orders of magnitude. Below $-100°C$, the reverse transition is so sluggish that the high-pressure polymorph can be retained at zero pressure. The present compression experiments verify that the transition in HgSe is sluggish—but less so at the higher temperatures (Fig. 2; Table I). It is difficult to understand how this transition could be considered as sharp, especially at CO_2 temperatures. It may be that a good deal of shear within the packed powder contributed to the rapidity of the transition. Friction within the material can be reduced by intimately mixing silver chloride with the sample, as in the present experiments. Kafalas et al.[8] have determined the structure of the HgSe polymorph as being of the cinnabar type and report the volume change as 8.6%.

Mercury selenide normally melts at 798°C.[13] No DTA signals could be observed in any of 4 technically sound
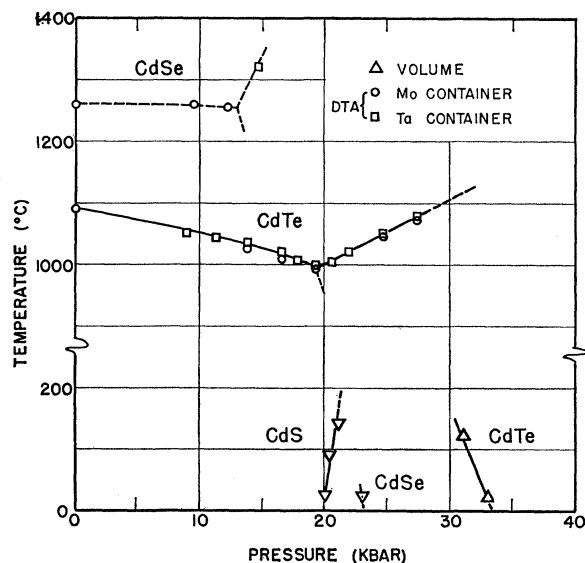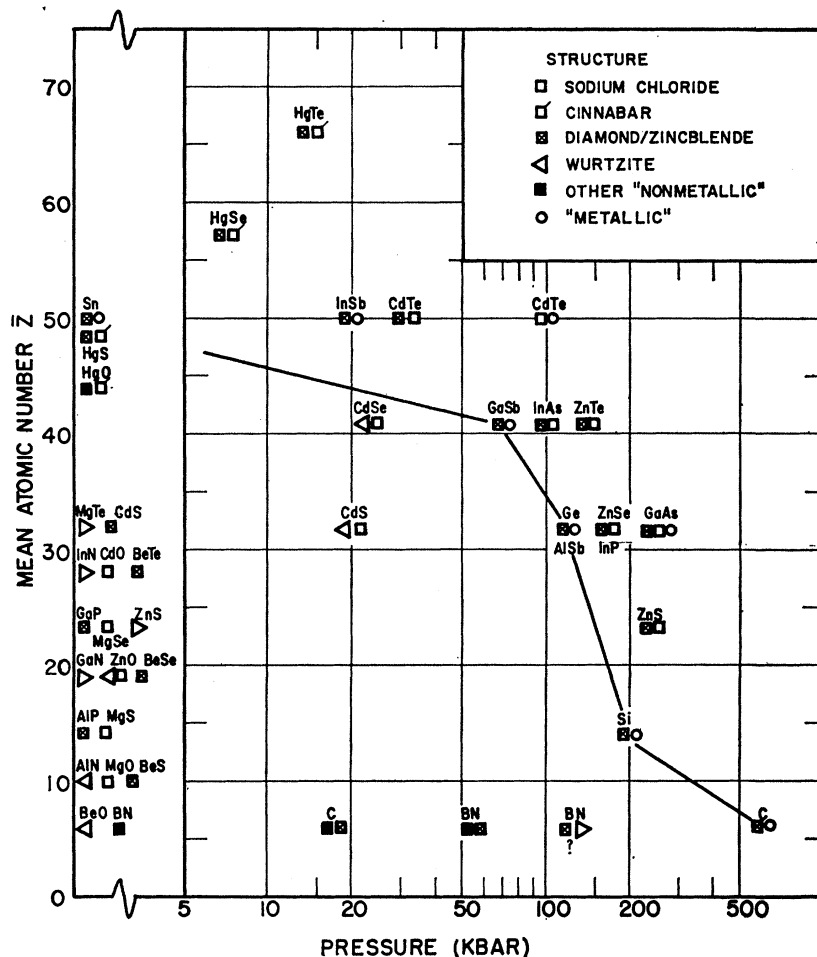

FIG. 3. Melting curves of CdTe and CdSe, as determined by DTA, and the solid-solid transitions for CdTe, CdSe, and CdS, as determined by volume discontinuity.

Fig. 4. Transition pressures for the polymorphic transitions of several Group IV elements, III-V, and II-VI compounds plotted vs mean atomic number, $\bar{Z}$; the identified or expected structures bracket the transition pressures, which are usually the room-temperature values.

runs in molybdenum and tantalum containers. Although Bridgman's contention[7] that HgTe decomposes under compression at room temperature has been shown unlikely, it is possible that some sort of decomposition phenomena may be entering into the melting of HgSe at high pressures. The difficulties in obtaining melting signals for HgTe may also be due to some such factor.

Cd-VI Compounds

Compression runs were made at several temperatures for CdTe, CdSe, and CdS, originally occurring in the zincblende, wurtzite structures, respectively. Data are collected in Table I and plotted in Fig. 3. Also listed in Table I are the transition data of Edwards and Drickamer,[3] of Edwards, Slykhouse, and Drickamer[2] from optical absorption studies, and of Samara and Drickamer[4] from resistance measurements.

Because the presently determined volume changes in the transitions in all of the Cd-VI compounds are very similar, i.e., about 9–10%, it is proposed that the transitions are *to* phases of similar structure. This state-

ment is made in cognizance of the fact[14,15] that the difference in volume between the zincblende and wurtzite polymorphs of the same substance is rarely more than 3%. It has been established[16] that AgI, which is isoelectronic with CdTe, transforms near 3 kbar at room temperature from the wurtzite or zincblende structure to the denser NaCl structure. Likewise, CuI transforms[17] near 16 kbar at room temperature from the zincblende to the NaCl structure. It is, thus, suggested that the pressure-induced polymorphs in the Cd-VI compounds in the region of 0–40 kbar have the NaCl or some closely related structure, such as that of cinnabar, and also are still semiconductors. This latter suggestion is qualitatively consistent with the optical data since there is observable transmission and thus the high pressure phases are nonmetallic.

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[14] M. Hansen and K. Anderko, *Constitution of Binary Alloys*, (McGraw-Hill Book Company, Inc., New York, 1958).

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

[16] L. H. Adams and B. L. Davis, Proc. Nat. Acad. Sci. 48, 982 (1962).

[17] A. Jayaraman (unpublished).

However, there may be objections because of the positive temperature coefficient of resistance reported for CdSe.[5,18] It may also be relevant to note that extrinsic semiconductors exhibit a temperature range where the coefficient of resistance is positive.

Samara and Drickamer[4] have reported a further transition in CdTe near 100 kbar. This polymorph is believed[4,5] to be typically metallic and is further discussed in the classification attempted in Sec. V. This phase transformation is probably less sluggish than the others previously studied in the Cd-VI compounds, which are clearly diffusion controlled and rather sluggish near room temperature in these high-melting materials.

The melting experiments with CdTe were carried out in molybdenum and tantalum containers. There was no evidence of contamination with these metals although considerable alloying, and consequently lower melting points, was found from a run in a nickel container. For a normal melting point of 1092°C,[19] the melting slope is approximately −5°C/kbar up to a triple point near 19.2 kbar and 996°C; the melting slope of the high pressure polymorph is about +10°C/kbar (Fig. 3). The slope of the fusion curve of the zincblende polymorph of CdTe is less negative than for isoelectronic InSb, in accord with the observations recorded previously.[1]

Cadmium selenide was encapsulated in molybdenum and in tantalum for the fusion curve determinations. Post-run examinations did not suggest any reaction with the containers. For a normal melting point of 1258±3°C,[13] the melting curve is almost flat up to 12 kbar with a steep positive slope at somewhat higher pressures (Fig. 3). The triple point is estimated to be near 13±1 kbar and 1252°C.

Zn-VI Compounds

Bridgman's compression studies[7] of ZnTe and ZnSe suggested somewhat irregular transitions with very small volume changes near 40 kbar. No such discontinuities were evident from the optical studies of Edwards et al.[2] or from the resistance measurements of Samara and Drickamer[4] and thus Bridgman's suggested transitions are not corroborated. It is likely that the effects were due to nonstoichiometry.

Large drops in the room temperature resistances of ZnTe, ZnSe, and ZnS were found near 140–145, 165,

and 240–245 kbar, respectively, by Samara and Drickamer.[4] Minomura et al.[5] reported positive temperature coefficients of resistance for ZnTe at 180 kbar and ZnS at 310 kbar. Despite these data and the estimated resistivities[4] of 10^{-3} to 10^{-4} Ω cm for the high pressure polymorphs of these Zn-VI compounds, it is believed that the transformation is from the zincblende to a NaCl-type structure in all cases—in analogy with the sequence postulated for the Cd-VI compounds.

IV. FURTHER DISCUSSION

In a previous paper[1] dealing with the Group IV elements and III-V compounds, it was suggested that the sequence of polymorphic structures found with increasing pressure and/or atomic number reflected increased coordination as: graphite → wurtzite and/or diamond/zincblende → white tin → sodium chloride → body-centered cubic or cesium chloride → closest packing (face-centered cubic, hexagonal close packed). For the II-VI compounds, it is necessary to take into account the proportionally greater ionic contributions to the bonding in considering this sequence.

Before some semiquantitative correlations are offered, several qualitative structural features for the elements and compounds centered around column IV B of the periodic table may be briefly cited:

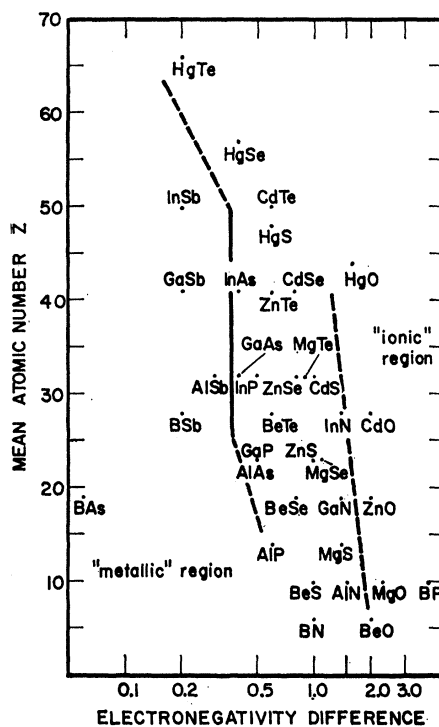(a) The graphite structure, known only in C and

FIG. 5. Electronegativity difference, after Haissinsky (reference 20), plotted vs mean atomic number, $\bar{Z}$, for III-V and II-VI compounds. The classification into "metallic" intermediate and "ionic" regions is discussed in the text.

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[18] Professor Drickamer has informed us that it is very difficult to be sure that the temperature coefficient of resistance determinations on CdSe have been made isobarically, especially close to the transition where readjustment of the anvils due to heating could cause a slight shift to lower pressures favoring the low-pressure, high-resistance polymorph. In these circumstances, it is difficult to assess the over-all significance of the relative resistivities at 120 and 25°C reported because a calculation (for a measured resistance of about 0.06 Ω and specimen dimensions of 2-mil thickness by 50-mil diam) suggests specific resistivities of ~10^{-2}Ω cm compared to the claimed value[5] of 10^{-4}Ω cm.

[19] M. R. Lorenz, J. Phys. Chem. Solids **23**, 939 (1962).

BN, does not occur in compounds formed of heavier elements or elements further apart in the periodic table.

(b) The wurtzite structure is apparently stable only in the more ionic compounds and seems to have a wider range of stability at higher temperatures (i.e., higher entropy) than the closely related zincblende structure. Also, the wurtzite structure is absent in compounds of the heavier elements.

(c) The white tin structure may be limited to components similar in electronegativity, with the stability of this metallic structure due, in an important way, to the interactions of the nearly free electrons rather than to any ionic factors.

(d) The sodium chloride structure is increasingly favored for those components which differ more in electronegativity

(e) For a given isoelectronic sequence, greater pressures are required to attain a metallic phase and less to reach the stability region of a NaCl-type phase as the difference in electronegativities of the constituent atoms increases.

It is desirable to quantify these observations, explicitly taking into account the ionic characters and the positions of the components in the periodic table. The parameters employed here are the mean atomic number, $\bar{Z}$, and the electronegativity differences, as taken directly from Haissinsky.[20] Transition pressures[21] (on a logarithmic scale), usually at room temperature, are plotted in Fig. 4 for the several identified or suggested structures of the Group IV elements and the III–V and II–VI compounds. Structures also reported[14,15] at zero pressure and structures of substances not yet found to undergo pressure-induced polymorphic transitions or not yet investigated at high pressures are shown on the left-hand side of Fig. 4. Figure 5 is a plot of the electronegativity difference vs mean atomic number for many binary combinations of the elements of Groups III and V and of Groups II and VI.

In this discussion, "metallic" refers to the white tin, disordered body-centered cubic and close-packed type structures. The solid knee-shaped line in Fig. 4 represents the lowest pressure, for a given $\bar{Z}$, at which a "metallic" structure becomes stable. For compounds with appreciable ionic character, "metallic" polymorphs are obtained only at pressures somewhat greater than those corresponding to points on the knee. The graphite

structure is stable only for the substances of lowest $\bar{Z}$ and at the lowest pressures. It is difficult to delineate adequately the stability region of the wurtzite structure because of the lack of data. The wurtzite structure is, however, apparently limited to $\bar{Z} \leqslant 41$ and electronegativity difference between 0.8 and 2.0 (Figs. 4 and 5). It has been pointed out[22,23] that larger deviations from the ideal axial ratio in the wurtzite structure are associated with greater differences in electronegativity of the constituent atoms. Little is known about the variations in axial ratios with pressure and not too much can be said about the stability of the wurtzite structure relative to the zincblende structure. In the limit of predominantly ionic bonding, however, the Madelung constant[23] for wurtzite with an ideal axial ratio is slightly larger than for zincblende. For compounds of moderately ionic character, the sequence of pressure-induced polymorphic transformations may be; initially, wurtzite and/or zincblende; next, a pressure range in which the sodium chloride structure is stable and, at still higher pressures, a "metallic" phase. This sort of behavior has probably been observed already for CdTe, CdSe, and GaAs. With increasingly greater electronegativity difference between the constituent atoms, typically ionic structures such as the NaCl type are stable to very high pressures. Some semiquantitative expression can be given to these statements by reference to Fig. 5. For the so-called "metallic" region of the plot of $\bar{Z}$ vs electronegativity difference, InSb, GaSb, and AlSb transform, with pressure, to a "metallic structure"—in this case, that of white tin.[24,25] For the intermediate region (Fig. 5), the several compounds are expected to occur, with pressure, in the NaCl type structure or a distortion thereof, such as the cinnabar structure, before becoming "metallic". Jamieson[24] has shown that the first pressure-induced polymorphs of InAs and GaAs have the NaCl structure and, indeed, it was this dissimilarity in structural behavior relative to InSb, GaSb, and AlSb that most prompted the present attempts at classification. For the so-called "ionic" region of Fig. 5, the compounds are initially in the NaCl structure and it is expected that very high pressures are required for transformations to "metallic" phases. As indicated by the dotted lines, the boundaries between the various regions in Fig. 5 are rather uncertain. For instance, the electronegativities change with pressure due to the different compressibilities of the electron clouds of the respective ions, and this may significantly alter the pattern of polymorphic transitions suggested here. The correlations depicted in Figs. 4 and 5 are well suited to the needs of the experimentalist, since the only variable is

[20] M. Haissinsky, J. Phys. Radium **7**, 1 (1946).

[21] Taken from the following sources: present work: HgSe, HgTe, CdSe, CdS, CdTe; Jayaraman, Klement, and Kennedy (reference 1): GaSb; Jayaraman, Newton, and Kennedy [Nature **191**, 1288 (1961)]: InSb; S. Minomura and H. G. Drickamer [J. Phys. Chem. Solids **23**, 451 (1962)]: Si, Ge, AlSb, GaAs, InP, InAs; Samara and Drickamer (reference 4): ZnS, ZnSe, ZnTe, CdTe; B. J. Alder and R. H. Christian [Phys. Rev. Letters **7**, 367 (1961)]: C; F. P. Bundy and H. M. Strong [Solid State Phys. **13**, 81 (1962)]: C; F. P. Bundy [Program AIME Symposium, Dallas, 1963, p. 79]: BN; R. H. Wentorf [Progress in Very High Pressure Research (John Wiley & Sons, Inc., New York, 1960)]: BN.

[22] G. A. Jeffrey, G. S. Parry, and R. L. Mozzi, J. Chem. Phys. **25**, 1024 (1956).

[23] F. Keffer and A. M. Portis, J. Chem. Phys. **27**, 675 (1957).

[24] J. C. Jamieson, Bull. Geol. Soc. Am. (1962), p. 76a; and Science **139**, 845 (1963).

[25] P. L. Smith and J. E. Martin, Nature **196**, 762 (1962).

pressure, $\bar{Z}$ and the electronegativity difference being immediately known for a given compound.

Many predictions of polymorphic transitions stem from the present correlations. According to Figs. 4 and 5, MgTe is very similar to CdS and there may be a close similarity in the pressure-induced transitions. Beryllium oxide may be expected to transform to the NaCl structure at only a few hundred kbar. Boron nitride will require considerably higher pressures than is required for the conversion of carbon to a "metallic" form, etc.

Correlations beyond those obtained by Jayaraman, Klement, and Kennedy[1] are not apparent from the yet scanty data for the melting slopes and/or phase boundaries among the several polymorphs common to

these elements and compounds. Likewise, there is no attempt here to examine the behavior under pressure of the I–VII compounds which, in any case, should be considerably simpler because of the generally predominant ionic character of the bonding.

Deformation Potentials in Silicon. II. Hydrostatic Strain and the Electron-Phonon Interaction*

Leonard Kleinman

Department of Physics and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania

The hydrostatic pressure dependence of the energy of $\Gamma_{25'}$, the top of the valence band in Si, is calculated and expressed in terms of the deformation potential constant D_d^v. There are three types of terms which contribute to D_d^v: those involving the valence wave functions explicitly, a term involving the over-all zero of the crystal potential and an exchange and correlation term depending on the average valence charge density. It is shown that to obtain the correct change in the zero of energy with strain one may take the usually arbitrary zero of energy appearing in the Hartree-Fock self-consistent potential to be equal to the total energy of the ions in their equilibrium position divided by the number of electrons. The first term is determined by applying perturbation theory to the wave functions calculated previously by Kleinman and Phillips. The second term is calculated using the Ewald summing technique and the third term is determined from the Bohm-Pines approximation. Our calculated value of the pressure dependence of the $\Gamma_{25'} - L_1$ energy gap in Si is similar to the experimental value obtained in Ge. Our absolute energy shifts lie between those estimated by Herring from transport data, and those of Bagguley et al., who determined the relaxation times appearing in Herring's theory from cyclotron resonance.

I. INTRODUCTION

THE three deformation potential parameters describing the strain dependence of the fourfold degenerate level at the top of the valence band in the covalently bonding semiconductors are the independent components of the hole-phonon coupling tensor for long-wavelength acoustic phonons.[1] Of these, only the parameter D_d^v describing the hydrostatic pressure dependence is not amenable to independent experimental determination. (In I[2], we calculated the other two parameters; see the references therein for their experimental determination.) If there exists a temperature range low enough for the optical phonon scattering to

be negligible and at the same time high enough for the acoustical phonon scattering to be large compared to impurity scattering, then in principle D_d^v can be determined from a variety of transport properties of the holes; in actual fact, the only experimental estimate of D_d^v is obtained from optical[3] determinations of $D_d^v - D_d^c$. D_d^c is the equivalent parameter for the bottom of the conduction band and has been estimated by Herring et al.[4] from a careful study of the transport properties of electrons in Ge. Recently, using cyclotron resonance, Bagguley, Flaxen, and Stradling[5] have meas-

* Supported in part by the Advanced Research Projects Agency.
[1] G. Bir and G. Picus, Fiz. Tverd. Tela **2**, 2287 (1960) [translation: Soviet Phys.—Solid State **2**, 2039 (1961)].
[2] L. Kleinman, Phys. Rev. **128**, 2614 (1962). Referred to as I in this paper.

[3] W. Paul and D. M. Worschauer, J. Phys. Chem. Solids **4**, 89 (1958).
[4] C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956); C. Herring, T. H. Geballe, and J. E. Kunzler, Bell System Tech. J. **38**, 657 (1959).
[5] D. M. S. Bagguley, D. W. Flaxen, and R. A. Stradling, Phys. Letters **1**, 111 (1962). I should like to thank Dr. S. Koenig for calling this work to my attention.