PHYSICAL REVIEW B VOLUME 11, NUMBER 8 15 APRIL 1975

Theory of melting in the group-IV semiconductors*

G. L. Warren† and W. E. Evenson
Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602

(Received 2 December 1974)

We have calculated the melting curves of germanium and silicon. A model of the group-IV semiconductors was used for which the solid consists of interacting systems of ions, conduction electrons, and covalent bond charges. The liquid state of these elements is metallic, and the model used to describe it consists of interacting systems of ions and conduction electrons. Variational calculations were performed to obtain Gibbs free energies for the solid and liquid states. Three adjustable parameters were necessary to describe the interactions between the various components of the models which are yet insufficiently understood for *ab initio* treatment. Excellent agreement with experiment was obtained for calculations of the melting curves up to 46 kbar for Ge and 21 kbar for Si. The physical origin of the negative-slope melting curve lies in the relatively open diamond-crystal structure and the covalent bonding which stabilizes this structure. The diamond structure is sufficiently openly packed that the liquid finds it energetically favorable to be more dense than the solid in these materials.

INTRODUCTION

The group-IV semiconductors crystallize in the diamond structure and have the little-understood property that they become more dense on melting. Since the liquid phase of these materials is more dense but has higher entropy than the solid phase, their melting-temperature–versus–pressure curves have negative slopes as predicted by the Clausius-Clapeyron equation. Negative-slope melting curves have not previously been successfully studied within the framework of fundamental rather than phenomenological theories. We report here the results of a fundamental calculation which does produce negative-slope melting curves for Ge and Si in excellent agreement with experiment and which elucidates the mechanisms responsible for this phenomenon.

A fundamental theory of melting must calculate the Gibbs free energies G_s and G_l for the solid and liquid phases as functions of temperature and pressure. Equality of G_s and G_l along a line in the P-T plane then determines the melting curve. In the neighborhood of this line the phase with lower Gibbs free energy is stable.

We follow the approach of Stroud and Ashcroft[1] who calculated the melting curve of the free-electron metal sodium. As they did, we consider the calculation of G_s and G_l as two separate problems, which is possible because melting is a first-order phase transition. The work of Stroud and Ashcroft on Na and the follow-up work of Jones[2] on simple metals seemed to us to indicate that viable calculations of melting in more complicated systems, such as the semiconductors, could now be attempted, with the *caveat*, however, that one may yet need to introduce an additional adjustable parameter or parameters to account for insufficient understanding of the interionic forces and interactions with covalent bonds.

The theory of melting is a long-standing problem of great interest and importance for understanding the physics of solids and liquids. Serious theoretical work started on this problem in 1903 with Tamman's work,[3] followed by Lindemann's important paper in 1910,[4] and has been proceeding ever since. Only recently, however, have advances in the theories of solids and liquids and in high-speed computing techniques made it possible to confront experiment and fundamental theory, based on a detailed analysis of the cohesive energy and entropy of a realistic model of the solid and liquid states. Reviews of melting theories with rather complete references are found in the work of Hoover and Ross,[5] Rowlinson,[6] and Stishov.[7]

The recent work of Van Vechten[8] considers melting in semiconductors from a semiempirical point of view. He develops a scaling theory of melting in semiconductors which fits experiment very well. He considers basic semiconductor properties, including covalent bonding, the semiconductor band gap, and an optical as well as acoustic phonon mode, in his calculation. These are the same properties we include in our more fundamental calculation of the melting curve in this work.

THEORY

We first summarize our approach and then will follow with a detailed discussion of the theory as applied to Ge and Si. A few years ago, Phillips[9] suggested a model of the solid semiconductor which treats the covalent bonds as quasiparticles, reflecting the sharp localization of electronic charge density in covalent bonds.[10–13] Microscopic theories of covalent bonding were considered by Bennemann[14,15] using scattering theory and pseudopotential theory, and by Herbert.[10] These calculations, as well as the work of Heine and Jones,[16] support this quasiparticle approach to covalent bonds. In addition, Phillips's model, with a modified dielectric function which included electron exchange in Hubbard's approximation,[17] was employed by Martin[18] to describe the lattice vibrational spectrum of silicon with fair agreement with experiment. Nelin[19] used a model similar to Martin's, but with the addition of a "valence-force field" which assumes that the bond charges interact approximately harmonically with one another and with the ions. His results for the phonon spectrum of Ge compare very well with experiment.

We have chosen to describe the solid state of the group-IV semiconductors by a model similar to that employed by Nelin,[19] i.e., a refinement of Phillips's model. We assume the solid to be well described by a three-component system with interactions between the three components: ions, an electron gas, and covalent-bond charges. The free energy of the solid is assumed to be the sum of (a) the Madelung energy arising from the Coulomb interaction between the ions (at finite temperature, so we include a Debye-Waller-type factor), (b) the kinetic, exchange, and correlation energies of the electron gas, (c) the Madelung energy arising from the Coulomb interaction between the bond charges, (d) the ion–electron-gas (i.e., the band-structure energy), the ion–bond-charge, and the electron-gas–bond-charge interaction energies, and (e) the phonon kinetic energy and entropy contribution (TS_{ph}). Cohen and Bergstresser[20] showed that the valence-electron–ion pseudopotential can be approximated well by a local pseudopotential for Ge and Si. In this work, we use local pseudopotentials to describe the ion–electron-gas and electron-gas–bond-charge interactions. We introduce two free parameters, however, into the solid Gibbs free energy through these pseudopotentials: one to describe the long-wavelength limit of the ion-electron pseudopotential, and the second to describe the effective size of the bond charges in the electron-gas–bond-charge pseudopotential.

We determine the phonon frequencies through a variational principle which is approximately self-consistent. As discussed below, the variational approach we have used maintains thermodynamic self-consistency to a very close approximation, avoiding the problem encountered in other work (e.g., Stroud and Ashcroft[1]) where the slope of the melting curve as calculated by the Clausius-Clapeyron equation differs from an interpolation between the calculated melting points. This problem, while present, is not particularly serious in the work of Stroud and Ashcroft; however, in the semiconductors which we study here, their procedure leads to very serious discrepancies between the calculated and interpolated slopes. We approximate the phonon spectrum by a Debye spectrum for the acoustic modes plus an Einstein spectrum for the optical modes. We use a fixed relationship between the sound velocity of the Debye modes and the frequency of the Einstein modes, so the contributions to the free energy due to ionic motions are described by a single parameter, the Debye temperature Θ. All effects of ionic motions at a given temperature and volume are included in Θ, i.e., not only the phonon spectrum, but also anharmonic effects are included because of the self-consistency of the calculation. Nelin and Nilsson[21] have recently shown that anharmonic effects can be taken into account very well in Ge up to at least 300 K below the melting temperature by assuming a temperature-dependent harmonic vibrational spectrum as proposed by Barron.[22] Barron suggested that the shift in the harmonic vibrational spectrum due to a change in temperature is proportional to the harmonic vibrational energy of the crystal. His results suggest that a quasiharmonic description of the solid, such as we have used, will be suitable even closer to the melting temperature than has been checked by Nelin and Nilsson's experiments.

The book by Glazov *et al.*[23] reviews many of the properties possessed by liquid silicon and germanium. They conclude that the solid-liquid transition of these elements is a semiconductor-metal transition in that the solid state acts like a semiconductor and the liquid state like a metal. Accordingly, we describe the liquid state of the group-IV elements as a liquid metal, calculating the free energy in a way similar to the calculation of Stroud and Ashcroft for liquid sodium. We take the liquid structure factor to be the Percus-Yevick approximation[24,25] to the hard-sphere structure factor. Ashcroft and Lekner[25] have compared this structure factor to the experimental structure factor for liquid metals like Li, Na, K, Rb, Cs, and In. Their results indicate that the hard-sphere reference system describes the structure of liquid metals fairly well. We have compared this structure factor with the experimental results of Poltavtsev[26] on the radial distribution functions of Si and Ge and those of Hendus[27] on the structure factor of Ge. While agreement is not as good in this case as for the simple liquid metals, especially since any tetrahedral short-range order is neglected, the agreement obtained is sufficiently good that we have felt justified in taking advantage of the relative simplicity of the Percus-Yevick hard-sphere structure factor in our calculation.

The liquid free energy is then taken as a sum of (a) the Madelung energy of the ions, using the structure factor, $\mathcal{S}(\vec{k})$, described above, (b) the kinetic, exchange, and correlation energies of the electron gas, (c) the ion–electron-gas interaction energy, (d) the ion kinetic energy, and (e) the entropy contribution, taken as the entropy of the hard-sphere gas as discussed below. We introduce a third free parameter into the theory at this point to describe the long-wavelength limit of the ion-electron pseudopotential in the liquid. Because the liquid is metallic and fundamentally different from the solid, we do not expect this parameter to be the same as in the solid. We determine the hard-sphere packing fraction variationally by minimizing the free energy, as did Stroud and Ashcroft.[1]

Solid state

We calculate the Helmholtz free energy of the solid, $F_s(T, V, N)$, and its volume derivative

$$P=-\left(\frac{\partial F_s}{\partial V}\right)_{T,N}, \tag{1}$$

where T, V, N, and P are temperature, volume, number of ions, and pressure. Then, we obtain the Gibbs free energy of the solid,

$$G_s(T, P, N)=F_s(T, V(T, P), N)+PV(T, P). \tag{2}$$

We first calculate the solid Helmholtz free energy as a function of Debye temperature Θ, then minimize with respect to Θ to obtain the best approximation to the free energy of our model. We use the Gibbs-Bogoliubov variational principle[28]

$$F\leqslant F_0+\langle H-H_0\rangle_0, \tag{3}$$

where subscript 0 indicates the reference system, no subscript indicates the true system, H and H_0 are the Hamiltonians, and

$$\langle\cdots\rangle_0\equiv e^{\beta F_0}\operatorname{Tr}(e^{-\beta H_0}\cdots). \tag{4}$$

We will use a reference-system Hamiltonian that differs from the true H only in the potential-energy terms, so $H-H_0=U-U_0$, where U and U_0 are the potential-energy operators. Then, since $F_0=\langle H_0\rangle_0-TS_0$, and we can write $H_0=K+U_0$, we have

$$F\leqslant E_{0\,\mathrm{kin}}+\langle U\rangle_0-TS_0, \tag{5}$$

where $E_{0\,\mathrm{kin}}\equiv\langle K\rangle_0$.

We use the harmonic approximation to the ions in a diamond lattice plus a free-electron gas as the reference system for the solid. Since we will use only a one-parameter phonon spectrum, the right-hand side of Eq. (5) will be a function of the Debye temperature Θ, which we vary to minimize our model free energy. We will define

$$f_s(T, V, N, \Theta)\equiv E_{0\,\mathrm{kin}}+\langle U\rangle_0-TS_0. \tag{6}$$

Then, our approximate free energy for the solid is

$$F_s(T, V, N)=f_s(T, V, N, \Theta_0(T, V, N)), \tag{7}$$

where $\Theta_0(T, V, N)$ is the value of Θ at the minimum in $f_s(T, V, N, \Theta)$ for given values of T, V, and N.

As described above, we consider the solid semiconductor to be composed of three components: ions in a diamond lattice, bond charges located midway between the instantaneous ionic positions, and the electron gas, comprised of all the valence electrons in the solid which are not in the bond charges.

For the phonon approximation, we will consider a Debye acoustic mode and an Einstein optical mode with frequencies given by

$$\begin{aligned}\hbar\omega_{\vec{q}\,\mathrm{ac}}&=k_B\Theta|\vec{q}|/q_D,\\ \hbar\omega_{\vec{q}\,\mathrm{op}}&=k_B\Theta,\end{aligned} \tag{8}$$

where Θ is the Debye temperature, k_B is Boltzmann's constant, and q_D is the radius of a sphere of the same volume as the Brillouin zone. In using this simple approximation for the phonon spectrum, we will approximate the Brillouin zone by a sphere of radius q_D throughout this work.

We describe the response of the electron gas to an external potential by Penn's dielectric function[29] corrected for electron exchange by the Hubbard exchange correction[17] similar to the work of Martin.[18] The bond charges are assumed to contain total charge $Z_b e$,[9] where

$$Z_b=2/\epsilon_{\vec{q}=0}. \tag{9}$$

Because of the volume dependence of $\epsilon_{\vec{q}}$, Z_b is a function of volume which makes an important contribution to the volume dependence of the free energy. Figure 1 shows Z_b as a function of volume for a small range of volumes considered in the study of Ge. The fact that Z_b increases with increasing volume and hence decreases with increasing pressure indicates that increased pressure moves electrons from the covalent bonds to the electron gas, as one would expect. The effective number of electrons in the electron gas is

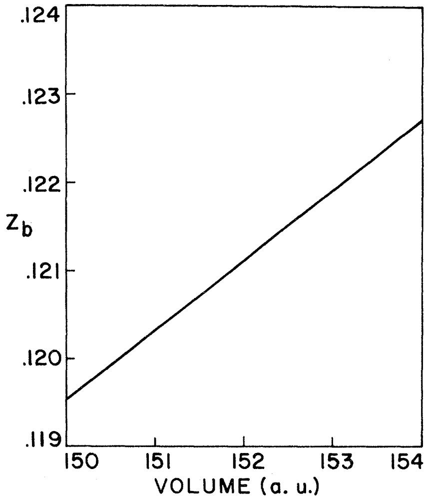

FIG. 1. Magnitude of the bond charge Z_b versus volume for volumes appropriate to germanium.

$(Z-2Z_b)N$, where Z is the valence ($Z=4$), and the factor 2 enters because there are two covalent bonding positions per ion. We found in preliminary studies of this model that neglecting the spatial extent of the covalent-bond charge distribution proved inadequate in the free-energy calculations. We have assumed a spherical charge distribution for the bond charges, as discussed below. Recent experimental studies of Ge and Si confirm the importance of considering the finite spatial extent of the bond charges, although they find (as expected) that these charge distributions are not really spherical.[13]

We calculate the function f_s of Eq. (6) as follows. First, we express the kinetic energy and entropy terms in f_s as

$$E_{0\,\mathrm{kin}} = E_{\mathrm{ph\,kin}} + E_{e\,\mathrm{kin}}, \tag{10}$$

and

$$S_0 = S_{\mathrm{ph}} + S_e, \tag{11}$$

where the subscripts ph and e refer, respectively, to the phonons and the electrons. We neglect the bond-charge kinetic energy and entropy since they comprise only a small fraction of the electron system and have very small mass, while their motion is essentially that of the ionic system.[13] In addition, $k_BT_m \ll E_F$ for the electron gas, where T_m is the melting temperature and E_F the Fermi energy, so we neglect the effect of finite temperatures on electron-gas contributions to f_s. In particular, we can take $S_e \cong 0$, and use the $T=0$ expression for E_{eg} (below) in all our calculations. In the three-component solid of our model, the potential energy will be

$$U = U_{ii} + U_{ie} + U_{ib} + U_{ee} + U_{eb} + U_{bb}, \tag{12}$$

where the subscripts i, e, and b refer, respectively, to the ions, electrons, and bond charges.

Since there is no ion-electron interaction in the reference system, $\langle U_{ee}\rangle_0$ is the potential energy of a free-electron gas (at $T=0$ K as discussed above). Then, we can combine this term with the electron kinetic energy to obtain the electron-gas energy:

$$E_{\mathrm{eg}} = E_{e\,\mathrm{kin}} + \langle U_{ee}\rangle_0 . \tag{13}$$

We use the Nozières and Pines[30] expression for the electron-gas energy (sum of kinetic, exchange, and correlation energies):

$$E_{\mathrm{eg}} = (Z-2Z_b)\frac{Ne^2}{2a_0}\left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} - 0.115 + 0.031\ln r_s\right), \tag{14}$$

where a_0 is the first Bohr radius and $\frac{4}{3}\pi r_s^3 a_0^3 = V/N$. The term $\langle U_{ie}\rangle_0$ represents the electron-ion interaction energy, including the change in the free-electron-gas energy due to the redistribution of electrons when the electron-ion interaction is turned on. This term is just the band-structure energy E_{bs}[31]:

$$E_{\mathrm{bs}} = \tfrac{1}{2}N\sum_{\vec{k}\neq 0}\frac{k^2V}{4\pi e^2}\left|u_{ie\,\vec{k}}\right|^2 \mathcal{S}(\vec{k})\left(\frac{1}{\epsilon_{\vec{k}}} - 1\right), \tag{15}$$

where $u_{ie\,\vec{k}}$ is the $\vec{k}$ Fourier component of the ion-electron interaction pseudopotential, $\mathcal{S}(\vec{k})$ is the ion-ion structure factor in the reference system, and $\epsilon_{\vec{k}}$ is the dielectric function described above. We take the effect of finite temperature into account through the temperature dependence of $\mathcal{S}(\vec{k})$. We have used the Ashcroft empty-core pseudopotential[32] for $u_{ie\,\vec{k}}$:

$$u_{ie\,\vec{k}} = -\frac{4\pi Ze^2}{k^2V}\cos r_c k, \tag{16}$$

where r_c is taken to be 0.83 a.u. for Ge and 0.74 a.u. for Si, as reported by Heine and Weaire.[33] The structure factor $\mathcal{S}(\vec{k})$ is defined for an arbitrary system by

$$\mathcal{S}(\vec{k}) = \frac{1}{N}\left\langle \sum_n \sum_{n'} e^{i\vec{k}\cdot(\vec{r}_n - \vec{r}_{n'})}\right\rangle_0, \tag{17}$$

where n and n' refer to ionic positions. We discuss $\mathcal{S}(\vec{k})$ more fully below.

$\langle U_{ii}\rangle_0$ is the finite-temperature Madelung energy E_m for the ions in the diamond lattice, averaged over the reference system:

$$E_m = \tfrac{1}{2}N\sum_{\vec{k}\neq 0}\frac{4\pi Z^2e^2}{k^2V}\left[\mathcal{S}(\vec{k}) - 1\right]. \tag{18}$$

The other terms in Eq. (12) are U_{ib}, U_{eb}, and U_{bb}. We can express these contributions to f_s as follows:

$$\langle U_{ib}\rangle_0 \equiv E_{ib} = N\sum_{\vec{k}\neq 0} u_{ib\,\vec{k}}\,\mathcal{S}_{ib}(\vec{k}), \tag{19}$$

$$\langle U_{eb}\rangle_0 \equiv E_{eb} = N\sum_{\vec{k}\neq 0}\frac{k^2V}{4\pi e^2}u_{eb\,\vec{k}}\,u_{ie\,\vec{k}}\,\mathcal{S}_{ib}(\vec{k})\left(\frac{1}{\epsilon_{\vec{k}}} - 1\right), \tag{20}$$

and

$$\langle U_{bb}\rangle_0 \equiv E_{bb} = \tfrac{1}{2}N\sum_{\vec{k}\neq 0} u_{bb\,\vec{k}}\left[\mathcal{S}_{bb}(\vec{k}) - 2\right], \tag{21}$$

where the notation is analogous to that in Eqs. (15)–(18). We assume a spherical bond charge distribution, as mentioned above. We also assume that the bond charge distributions do not overlap with the ions or with each other, so $u_{bb\,\vec{k}}$ and $u_{ib\,\vec{k}}$ are simply Coulomb potentials:

$$u_{bb\,\vec{k}} = \frac{4\pi Z_b^2e^2}{Vk^2}, \tag{22}$$

$$u_{ib\,\vec{k}} = -\frac{4\pi ZZ_be^2}{Vk^2}. \tag{23}$$

The electron-gas–bond-charge interaction is not well understood at present. We have chosen to parameterize it as simply as possible by letting

$$u_{eb\,\vec{k}} = \frac{4\pi Ze^2}{Vk^3r_b}\sin r_b k, \tag{24}$$

where r_b is a free parameter in the theory. This form corresponds to putting all the bond charge in a spherical shell of radius r_b. While this charge distribution is not very physical, it nevertheless provides a simple means of inserting the finite size of the bond charges into our theory and including the resulting softer-than-bare Coulomb potential for $r < r_b$.

In Eqs. (14), (15), and (18)–(21), we have omitted the $\vec{k}=0$ components of E_{eg}, E_{bs}, E_m, E_{ib}, E_{eb}, and E_{bb}. These $\vec{k}=0$ Fourier components are separately infinite but have a finite sum which we call E_0:

$$\begin{aligned} E_0 = \frac{N^2}{V}\bigg[& \frac{1}{2}\int u_{ii}(\vec{r})\,d^3r + \tfrac{1}{2}(Z-2Z_b)^2\int u_{ee}(\vec{r})\,d^3r \\ & + 2\int u_{bb}(\vec{r})\,d^3r + (Z-2Z_b)\int u_{ie}(\vec{r})\,d^3r \\ & + 2(Z-2Z_b)\int u_{eb}(\vec{r})\,d^3r + 2\int u_{ib}(\vec{r})\,d^3r \bigg] \\ = {} & \frac{Ne^2}{2V}\left[(Z-2Z_b)Z\alpha_s - 2Z_b(Z-2Z_b)\alpha_s'\right], \end{aligned} \tag{25}$$

where

$$\alpha_s \equiv \frac{2}{Ze^2}\int\left(\frac{Ze^2}{r} + u_{ie}(\vec{r})\right)d^3r = 4\pi r_c^2 \tag{26}$$

and

$$\alpha_s' \equiv \frac{2}{Z_b e^2}\int\left(\frac{Z_b e^2}{r} - u_{eb}(\vec{r})\right)d^3r = \tfrac{4}{3}\pi r_b^2, \tag{27}$$

since we have assumed that $u_{ii}(\vec{r})$, $u_{ee}(\vec{r})$, $u_{bb}(\vec{r})$, and $u_{ib}(\vec{r})$ are all bare Coulomb potentials. Explicitly, we have taken

$$\begin{aligned} u_{ii}(\vec{r}) &= \frac{Z^2e^2}{r}, \quad u_{ee}(\vec{r}) = \frac{e^2}{r}, \\ u_{bb}(\vec{r}) &= \frac{Z_b^2e^2}{r}, \quad u_{ib}(\vec{r}) = -\frac{ZZ_be^2}{r}. \end{aligned} \tag{28}$$

The constants α_s and α_s' represent the spatial average of the difference of the potentials $u_{ie}(\vec{r})$ and $u_{eb}(\vec{r})$ with their corresponding bare Coulomb potentials. Positive or negative α_s and α_s' correspond to $u_{ie}(\vec{r})$ and $u_{eb}(\vec{r})$ less repulsive or more repulsive than the bare Coulomb potential. These constants relate to the long-wavelength limits ($\vec{k}\to 0$) of $u_{ie}(\vec{r})$ and $u_{eb}(\vec{r})$, while most local pseudopotentials are chosen to fit short-wavelength data. Because of this fact, we ignore the second equality in Eq. (26) and treat α_s as a free parameter which we use to fit the zero-pressure melting points. As mentioned above, r_b is a free parameter in this theory; we maintain $\alpha_s' = 4\pi r_b^3/3$, so α_s' is determined by r_b.

We obtain $E_{\text{ph kin}}$, S_{ph}, and $\mathcal{S}(\vec{k})$ using the phonon approximation. The first two of these can be written in the usual form:

$$E_{\text{ph kin}} = \frac{1}{2}\sum_{\vec{q},s}\hbar\omega_{\vec{q}s}(n_{\vec{q}s} + \tfrac{1}{2}) \tag{29}$$

and

$$S_{\text{ph}} = -k_B\sum_{\vec{q},s}\ln(1 - e^{-\beta\hbar\omega_{\vec{q}s}}) + \frac{1}{T}\sum_{\vec{q},s}\hbar\omega_{\vec{q}s}n_{\vec{q}s}, \tag{30}$$

where

$$n_{\vec{q}s} = (e^{\beta\hbar\omega_{\vec{q}s}} - 1)^{-1} \tag{31}$$

and the sum on s is over the six branches of the phonon spectrum. The structure factor $\mathcal{S}(\vec{k})$ is obtained as follows:

$$\mathcal{S}(\vec{k}) = \frac{1}{N}\sum_{ll'jj'} e^{i\vec{k}\cdot(\vec{R}_{lj}-\vec{R}_{l'j'})}\langle e^{i\vec{k}\cdot(\vec{u}_{lj}-\vec{u}_{l'j'})}\rangle_0, \tag{32}$$

where $\vec{R}_{lj}$ is the equilibrium position of the jth atom in the lth unit cell, and $\vec{u}_{lj}$ is its instantaneous displacement from equilibrium. Evaluation of the average in Eq. (32) for a harmonic crystal with n atoms per unit cell on n identical sublattices, having a center of inversion and assuming triply degenerate acoustic and optical branches, leads to

$$\begin{aligned} \mathcal{S}(\vec{k}) = \frac{1}{N}\sum_{ll'jj'} e^{i\vec{k}\cdot(\vec{R}_{lj}-\vec{R}_{l'j'})}\big[& \delta_{jj'}e^{-k^2\gamma_{l-l'}} \\ & + (1-\delta_{jj'})e^{-k^2\Lambda_{l-l'}^{jj'}}\big], \end{aligned} \tag{33}$$

where the Debye-Waller-type factors containing the effect of finite temperature are given by

$$\gamma_l \equiv \frac{\hbar n}{4MN}\sum_{\vec{q}}\left(\frac{2n_{\vec{q}\,\text{ac}}+1}{\omega_{\vec{q}\,\text{ac}}} + \frac{2n_{\vec{q}\,\text{op}}+1}{\omega_{\vec{q}\,\text{op}}}\right)(1 - \cos\vec{q}\cdot\vec{R}_l) \tag{34}$$

and

$$\begin{aligned} \Lambda_l^{jj'} \equiv \frac{\hbar n}{4MN}\sum_{\vec{q}}\bigg(& \frac{2n_{\vec{q}\,\text{ac}}+1}{\omega_{\vec{q}\,\text{ac}}}\left[1 - \cos\vec{q}\cdot(\vec{R}_l + \vec{\Delta}_{jj'})\right] \\ & + \frac{2n_{\vec{q}\,\text{op}}+1}{\omega_{\vec{q}\,\text{op}}}\left[1 + \cos\vec{q}\cdot(\vec{R}_l + \vec{\Delta}_{jj'})\right]\bigg), \end{aligned} \tag{35}$$

where $\vec{R}_l$ is the equilibrium position of the lth unit cell, and $\vec{\Delta}_{jj'}$ is the separation vector for atoms j and j' in the unit cell. The term γ_l results from interactions within a sublattice, while $\Lambda_l^{jj'}$ is due to interactions between sublattices. We use a "zero-phonon" approximation[34] to calculate $\mathcal{S}(\vec{k})$, putting

$$\gamma_l = 0 \text{ if } l = 0, \quad \gamma_l = \gamma_{2n} \text{ if } l \neq 0, \tag{36}$$

where γ_{2n} refers to γ_l evaluated for $\vec{R}_l$ equal to a second-neighbor separation (i.e., nearest neighbors on the same sublattice). We also let

$$\Lambda_l^{jj'} = \Lambda_{\text{nn}}, \tag{37}$$

where Λ_{nn} refers to $\Lambda_l^{jj'}$ evaluated for $\vec{R}_l + \vec{\Delta}_{jj'}$ equal to nearest-neighbor separation (between sublattices). This approximation will be satisfactory if the energies which depend on $\mathcal{S}(\vec{k})$ are dominated by contributions from $\vec{R}_{lj}$'s close to the first- and second-neighbor separations. The difficulty of this problem has led us to proceed with this approach as a first approximation even though the elementary state of our understanding of semiconductors does not allow its detailed justification. These approximations lead to

$$\mathcal{S}(\vec{k}) = \tfrac{1}{2}N\delta_{\vec{k},\vec{K}}[e^{-K^2\gamma_{2n}} + \cos(\vec{K}\cdot\vec{\Delta})e^{-K^2\Lambda_{nn}}] + 1 - e^{-k^2\gamma_{2n}}, \tag{38}$$

where $\vec{K}$ is a reciprocal-lattice vector and $\vec{\Delta}$ is the vector between the two atoms in the diamond unit cell.

Using Eq. (38) for $\mathcal{S}(\vec{k})$, we can now rewrite those energies which depend on $\mathcal{S}(\vec{k})$. From Eqs. (15) and (18) we have

$$E_{bs} + E_m = \tfrac{1}{4}N^2 \sum_{\vec{K}\neq 0} U_{\vec{K}}[e^{-K^2\gamma_{2n}} + \cos(\vec{K}\cdot\vec{\Delta})e^{-K^2\Lambda_{nn}}]$$

$$-\tfrac{1}{2}N\sum_{\vec{k}\neq 0} U_{\vec{k}}\, e^{-k^2\gamma_{2n}} + \tfrac{1}{2}N\sum_{\vec{k}\neq 0} \frac{k^2V}{4\pi e^2}|u_{ie\,\vec{k}}|^2\left(\frac{1}{\epsilon_{\vec{k}}} - 1\right), \tag{39}$$

where

$$U_{\vec{k}} \equiv \frac{4\pi Z^2e^2}{Vk^2} + \frac{k^2V}{4\pi e^2}|u_{ie\,\vec{k}}|^2\left(\frac{1}{\epsilon_{\vec{k}}} - 1\right). \tag{40}$$

The energies E_{ib}, E_{eb}, and E_{bb} depend on ion-bond and bond-bond structure factors. These are calculated in a way similar to $\mathcal{S}(\vec{k})$, again assuming that $\mathcal{S}_{ib}(\vec{k})$ and $\mathcal{S}_{bb}(\vec{k})$ are dominated by nearest-neighbor effects. (In this case, we are assuming that the bonds are primarily correlated with their nearest-neighbor ions, as suggested by the evidence cited above which indicates that the bond charges are located midway between the instantaneous positions of their neighboring ions.) We obtain

$$\mathcal{S}_{ib}(\vec{k}) = \tfrac{1}{2}N e^{-K^2\Lambda_{nn}/4}\sum_{i=0}^{3}\cos(\tfrac{1}{2}\vec{K}\cdot\vec{a}_i)\,\delta_{\vec{k},\vec{K}}, \tag{41}$$

where $\vec{a}_i = \vec{\Delta} - \vec{\tau}_i$, and the $\vec{\tau}_i$ are the primitive lattice vectors for $i = 1, 2, 3$, while $\vec{\tau}_0 = 0$. This leads to

$$E_{ib} + E_{eb} = 2N\sum_{\vec{k}\neq 0} T_{\vec{K}}\cos(\tfrac{1}{2}\vec{K}\cdot\vec{\Delta})\, e^{-K^2\Lambda_{nn}/4}, \tag{42}$$

where

$$T_{\vec{k}} \equiv u_{ib\,\vec{k}} + \frac{k^2V}{4\pi e^2}u_{eb\,\vec{k}}u_{ie\,\vec{k}}\left(\frac{1}{\epsilon_{\vec{k}}} - 1\right). \tag{43}$$

Similarly, we obtain

$$\mathcal{S}_{bb}(\vec{k}) = N\left[1 + \frac{1}{2}\sum_{j=1}^{3}(\cos\tfrac{1}{2}\vec{K}\cdot\vec{\tau}_j + \cos\tfrac{1}{2}\vec{K}\cdot(\vec{\tau}_{j+1} - \vec{\tau}_j))\right]$$

$$\times e^{-K^2\gamma_{2n}/4}\,\delta_{\vec{k},\vec{K}} + 2 - 2e^{-k^2\gamma_{2n}/4}, \tag{44}$$

where $\vec{\tau}_4 \equiv \vec{\tau}_1$. Putting this into Eq. (21) gives

$$E_{bb} = \tfrac{1}{2}N^2\sum_{\vec{K}\neq 0} u_{bb\,\vec{K}}(1 + 3\cos\tfrac{1}{2}\vec{K}\cdot\vec{\tau}_1)e^{-K^2\gamma_{2n}/4}$$

$$-N\sum_{\vec{k}\neq 0} u_{bb\,\vec{k}}\, e^{-k^2\gamma_{2n}/4}. \tag{45}$$

Now all that remains is for us to put in the Einstein-Debye approximation to the phonon spectrum [Eq. (8)] which we have chosen to use. This results in the following expressions:

$$E_{\text{ph kin}} = \tfrac{3}{4}k_BT\,I(\Theta/T) + \tfrac{21}{32}k_B\Theta + \frac{3}{4}\frac{k_B\Theta}{e^{\Theta/T} - 1}, \tag{46}$$

$$-TS_{\text{ph}} = \tfrac{1}{2}k_BT\Big(6\ln(1 - e^{-\Theta/T})$$

$$-4I(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1}\Big), \tag{47}$$

$$\gamma_{2n} = \frac{\hbar^2}{4Mk_B\Theta}\left(3\frac{T}{\Theta}J(\Theta/T, R_{2n}) + \coth\frac{\Theta}{2T}\right), \tag{48}$$

and

$$\Lambda_{nn} = \frac{\hbar^2}{4Mk_B\Theta}\left(3\frac{T}{\Theta}J(\Theta/T, \Delta) + \coth\frac{\Theta}{2T}[1 + L(\Delta)]\right), \tag{49}$$

where

$$L(\Delta) \equiv \frac{2}{N}\sum_{\vec{q}}\cos\vec{q}\cdot\vec{\Delta} = -2(2/\pi)^3, \tag{50}$$

$$I(x) \equiv \frac{3}{x^3}\int_0^x \frac{t^3\,dt}{e^t - 1}, \tag{51}$$

and

$$J(x, y) \equiv \frac{1}{x}\int_0^x [t\coth(t/2)]\left(1 - \frac{\sin(tyq_D/x)}{tyq_D/x}\right)dx. \tag{52}$$

Using Eqs. (46)–(52) together with Eqs. (14), (25), (39), (42), and (45) gives us the expression for f_s:

$$f_s(T, V, N, \Theta) = E_{\text{ph kin}} + E_{eg} + (E_{bs} + E_m) + (E_{ib} + E_{eb})$$

$$+ E_{bb} + E_0 - TS_{\text{ph}}, \tag{53}$$

and hence the solid free energy $F_s(T, V, N)$ as described in Eq. (7).

Liquid state

We calculate the Helmholtz free energy of the liquid, $F_l(T, V, N)$, and the pressure

$$P = -\left(\frac{\partial F_l}{\partial V}\right)_{T,N}. \tag{54}$$

As with the solid, we obtain the Gibbs free energy $G_l(T, P, N)$ from these functions. We again use the Gibbs-Bogoliubov variational principle,[28] this time in its classical form since a classical approximation is valid for liquid Ge and Si near the melting curve. Proceeding as we did for the solid state, we can again write

$$F_l \leq f_l(T, V, N, \eta) \equiv E_{0\,\text{kin}} + \langle U\rangle_0 - TS_0, \tag{55}$$

where η is the hard-sphere packing fraction, as discussed below.

We use the hard-sphere liquid with packing fraction η as the reference system for the solid. We then minimize f_l with respect to η to obtain the best approximation to $F_l(T, V, N)$ (and hence to G_l). We define η in terms of the hard-sphere radius R as $\eta = \frac{4}{3}\pi R^3 N/V$.

As described above, we consider the liquid state of these group-IV elements to be a simple metallic liquid composed of ions and an electron gas. So the calculation of G_l is essentially that of Stroud and Ashcroft.[1] We calculate the function f_l of Eq. (55) as follows. First we express the kinetic energy and entropy terms in f_l as

$$E_{0\,\mathrm{kin}} = E_{\mathrm{hc\,kin}} + E_{e\,\mathrm{kin}} \tag{56}$$

and

$$S_0 = S_{\mathrm{hc}} + S_e\,, \tag{57}$$

where the subscripts hc and e refer, respectively, to the hard-core liquid and the electron gas. As in the solid, we can neglect S_e and finite-temperature effects in the electron-gas energy. The potential energy for our model is

$$U = U_{ii} + U_{ie} + U_{ee}\,. \tag{58}$$

As for the solid,

$$E_{\mathrm{eg}} = E_{e\,\mathrm{kin}} + \langle U_{ee}\rangle_0\,, \tag{59}$$

which is still given by Eq. (14). The term $\langle U_{ie}\rangle_0$ is again the band-structure energy E_{bs}, which is of the same form as Eq. (15) with $\mathcal{S}(\vec{k}) = \mathcal{S}_{\mathrm{hc}}(k)$ and $\epsilon_{\vec{k}}$ the modified Hubbard interpolation form,[17] as used by Ashcroft and Langreth[35] and by Stroud and Ashcroft.[1] We again use the Ashcroft empty-core pseudopotential[32] with the same values of r_c.

The term $\langle U_{ii}\rangle_0$ is the Madelung energy E_m averaged in the hard-sphere reference system. It is again of the form of Eq. (18) with $\mathcal{S}(\vec{k}) = \mathcal{S}_{\mathrm{hc}}(k)$. E_0 is the sum of the $\vec{k} = 0$ Fourier components of E_{eg}, E_{bs}, and E_m. It has the form

$$E_0 = \frac{Z^2 e^2 N}{2V}\,\alpha_l\,, \tag{60}$$

where α_l is not taken to be $4\pi r_c^2$ as would be calculated from the definition of E_0, but, as in the solid, α_l is a free parameter which is used to fit the zero-pressure melting curve. We do not take $\alpha_l = \alpha_s$ because of the great difference between the solid and the liquid: The solid is a semiconductor, while the liquid is metallic.

The properties of the hard-core liquid which are needed for this approach to the liquid free energy are obtained as follows: $E_{\mathrm{hc\,kin}}$ is just the ideal-gas energy,

$$E_{\mathrm{hc\,kin}} = \tfrac{3}{2} N k_B T\,. \tag{61}$$

To find S_{hc}, we follow the work of Lebowitz *et al.*[36] and obtain

$$\frac{S_{\mathrm{hc}}}{Nk_B} = \frac{S_{\mathrm{gas}}}{Nk_B} + \ln(1-\eta) - \frac{6\eta}{1-\eta} - \frac{9\eta^2}{2(1-\eta)^2} + \frac{1-\eta^3}{(1-\eta)^3}\,, \tag{62}$$

where

$$\frac{S_{\mathrm{gas}}}{Nk_B} = \tfrac{3}{2} + \ln\left[\frac{V}{N}\left(\frac{Mk_BT}{2\pi\hbar^2}\right)^{3/2}\right]. \tag{63}$$

As stated above, we use the Percus-Yevick approximation[24] to obtain $\mathcal{S}_{\mathrm{hc}}(k)$. This result was obtained by Ashcroft and Lekner.[25] Jones[37] has shown that E_m can be evaluated exactly by considering the Laplace transform of the hard-core two-body correlation function $g(r)$ obtained from the Percus-Yevick equation. Jones derives

$$E_m = -\,2\pi\rho Z^2 e^2 N \left(\frac{6\eta}{\pi\rho}\right)^{2/3} \frac{\frac{1}{2} - \eta/10 + \eta^2/20}{1+2\eta}\,; \tag{64}$$

where an error[38] has been corrected in the reported results of Jones by changing the minus sign in front of $(\eta^2/20)$ to a plus sign.

Using Eqs. (14), (15), and (60)–(64) together with the expression for $\mathcal{S}_{\mathrm{hc}}(k)$ gives us an expression for f_l:

$$f_l(T, V, N, \eta) = E_{\mathrm{hc\,kin}} + E_{\mathrm{eg}} + E_{\mathrm{bs}} + E_m + E_0 - TS_{\mathrm{hc}}\,, \tag{65}$$

and hence the free energy $F_l(T, V, N)$ as described in Eq. (55).

CALCULATIONS AND RESULTS FOR Ge AND Si

For the calculations we used atomic units (a.u.) where

$$\hbar = m_e = e = 1\,. \tag{66}$$

Most results will be quoted in this system. All the calculations were performed on the IBM 7030 at Brigham Young University. About three hours of cpu time were required for the calculation of a single point on the melting curve of Ge or Si. The calculation time for a point on the solid Gibbs-free-energy isotherms increases with a decrease in temperature. This calculation time is not temperature dependent for the liquid in our calculations near the

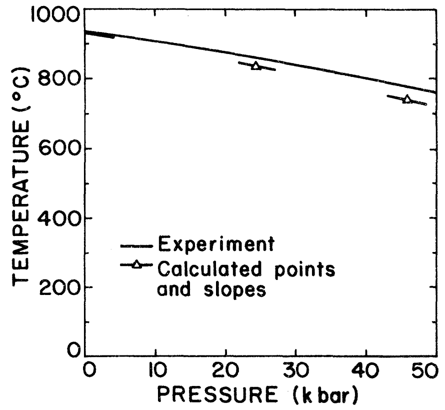

FIG. 2. Experimental and theoretical melting curves for germanium.

TABLE I. Theoretical melting curve for germanium.

T (K)	P (kbar)	V_s (a.u./ion)	V_l (a.u./ion)	$10^4 S_s$ (a.u./ion)	$10^4 S_l$ (a.u./ion)	$(dT/dP)_m$ (K/kbar)
1210	0.0	154.10	143.80	0.27543	0.36546	−3.89
1110	24.4	150.96	138.93	0.26558	0.35399	−4.63
1010	45.8	148.34	134.98	0.25521	0.34189	−5.24

melting curve.

The melting curve was obtained from the intersection of Gibbs-free-energy isotherms for the solid and liquid, giving the melting pressure for the temperature being considered. The slope of the melting curve at each calculated point was determined from the Clausius-Clapeyron equation using the values of S_s, S_l, V_s, and V_l produced in the free-energy calculation.

Three variable parameters needed to be chosen in applying the theory discussed above. These were chosen as follows: (i) The parameter α_l was chosen to make the theoretical volume match the experimental volume of the liquid at the atmospheric-pressure melting point. (ii) The parameters α_s and α_s' ($=\frac{4}{3}\pi r_b^2$) were chosen to fit the atmospheric-pressure melting point and the experimental volume of the solid at that point. We used the following values in determining these parameters: For Ge, $T_m = 1210$ K, $V_l = 143.8$ a.u./ion, and $V_s = 154.1$ a.u./ion. For Si, $T_m = 1683$ K. $V_l = 117.6$ a.u./ion, and $V_s = 138.0$ a.u./ion. Since these parameters completely determine the atmospheric-pressure melting point and volumes, the theory determines the slope of the melting curve at atmospheric pressure only through the calculated entropies determined by Θ and η, whose values come from the variational procedure we have followed.

We show the calculated points and slopes for the melting curve of Ge in Fig. 2, along with the experimental melting curve.[39] We show the parameters of the melting curve in Table I and the contributions to the Gibbs free energies in Tables II and III. The parameters of the model are

$$\alpha_l = 12.513293, \quad \alpha_s = 14.246481, \quad \alpha_s' = 16.734604.$$

This value for α_s' gives $r_b = 1.9987727$, which is about the same size as the nearest-neighbor distance. Recent experiments[13] indicate that the bond charges do have a finite size; however, it is not yet possible to say experimentally whether the above value is reasonable (in fact, it looks a little large). The fact that α_s' is positive is consistent with our assumption of a finite-size bond charge distribution and an electron-bond charge interaction which is less repulsive than the bare Coulomb interaction for close approach. It is also interesting to note that α_l and α_s are significantly differ-

TABLE II. Contributions to the theoretical Gibbs free energies for the solid phase of germanium along isotherms near melting.

T (K)	V (a.u./ion)	G (a.u./ion)	$10^4 P$ (a.u.)	$10^4 S$ (a.u./ion)	Θ (K)
1210	154.1	−4.2211875	0.0	0.27542533	214.19644
1110	151.5	−4.2082599	0.67122	0.26590777	217.25009
	151.1	−4.2064912	0.78826	0.26566564	217.80594
	150.7	−4.2047102	0.90642	0.26542271	218.36506
1010	147.8	−4.1898987	1.7279	0.25487459	222.09645
	147.3	−4.1875432	1.8877	0.25456112	222.83287
	146.8	−4.1851668	2.0495	0.25424635	223.57484

E_0 (a.u./ion)	$10\,E_{eg}$ (a.u./ion)	$E_{bs}+E_{eb}+E_{ib}+E_{bb}$ (a.u./ion)	E_m (a.u./ion)	$10\,E_{bb}$ (a.u./ion)	$10^2 E_{\text{ph kin}}$ (a.u./ion)
0.64415102	−0.69171249	−0.79376434	−3.9748360	−0.20584819	0.57595440
0.65677674	−0.63452419	−0.78573346	−4.0017900	−0.20060880	0.52859961
0.65875802	−0.62553862	−0.78495116	−4.0054520	−0.19974901	0.52860650
0.66074980	−0.61650246	−0.78416718	−4.0091266	−0.19889059	0.52861345
0.67551499	−0.54942761	−0.77554447	−4.0395353	−0.19307117	0.48129899
0.67811979	−0.53757905	−0.77455730	−4.0442561	−0.19200936	0.48130924
0.68074250	−0.52564452	−0.77356753	−4.0489981	−0.19094965	0.48131961

TABLE III. Contributions to the theoretical Gibbs free energies for the liquid phase of germanium along isotherms near melting.

T (K)	V (a. u./ion)	G (a. u./ion)	$10^4 P$ (a. u.)	$10^4 S$ (a. u./ion)	η	E_0 (a. u./ion)	$10 E_{eg}$ (a. u./ion)	E_{bs} (a. u./ion)	E_m (a. u./ion)
1210	143.8	−4.221 187 5	0.0	0.365 46	0.3526	0.696 149 85	−0.259 400 85	−0.781 234 55	−4.071 689 7
1110	140.0	−4.208 865 5	0.614 50	0.355 01	0.3660	0.715 045 33	−0.155 223 76	−0.743 949 42	−4.138 908 3
	139.6	−4.207 744 0	0.694 66	0.354 67	0.3666	0.717 094 21	−0.143 934 66	−0.741 869 30	−4.144 177 5
	139.2	−4.206 632 1	0.774 54	0.354 28	0.3673	0.719 154 79	−0.132 582 46	−0.739 579 41	−4.149 678 5
1010	134.8	−4.191 889 3	1.5968	0.341 64	0.3835	0.742 628 70	−0.003 366 01	−0.697 488 16	−4.228 510 0
	134.2	−4.190 118 6	1.7285	0.340 81	0.3850	0.745 948 93	+0.014 894 41	−0.693 322 32	−4.237 806 7
	133.6	−4.188 310 6	1.8635	0.340 02	0.3864	0.749 298 99	+0.033 314 63	−0.689 367 67	−4.246 925 2

ent, as we expected initially due to the metallic nature of the liquid. The number of points actually calculated on the melting curve was limited by the large amount of computation required per point, as mentioned above.

The good agreement we obtain with experiment is, of course, to some extent due to the fact that we have three free parameters. However, preliminary studies of the model with $r_b = 0$, α_s' free, indicated that the form of the interactions is of great importance in producing the results shown here. Both the difficulty of this problem and the relative infancy of the theories of semiconductors and of liquids (compared to the theory of simple metals, for example) required that we make serious approximations and compensate for some fundamental gaps in the present understanding of these systems by the introduction of adjustable parameters. Even with these parameters, the results we obtain lead us to conclude that our model calculation is an appropriate first step toward a truly fundamental theory of melting in the group-IV semiconductors.

We show the calculated points and slopes for the melting curve of Si in Fig. 3, along with the experimental melting curve.[40] We show the parameters of the melting curve in Table IV and the contributions to the Gibbs free energies in Tables V and VI. The parameters of the model are

$$\alpha_l = 9.858\,820\,5, \quad \alpha_s = 12.546\,878, \quad \alpha_s' = 18.298\,653.$$

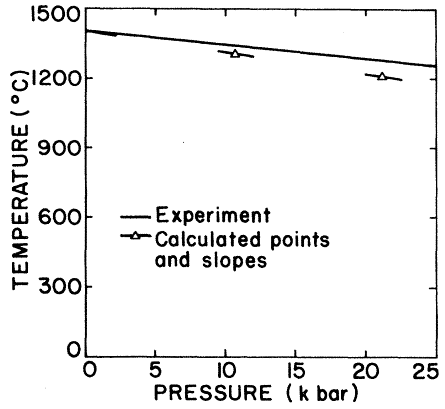

FIG. 3. Experimental and theoretical melting curves for silicon.

This value for α_s' gives $r_b = 2.090\,091\,3$.

Since there is a greater proportion of electrons involved in the covalent bonds in Si than in Ge, the results become more sensitive to our crude approximations to the covalent-bonded solid, and the deviation from the experimental curve is somewhat greater for Si than for Ge.

On both the Ge and the Si melting curves, the slopes determined from the Clausius-Clapeyron equation match an interpolation through the calculated points very well. This fact is due to the variational procedure which was used to calculate Θ. The procedure used in this work approximately preserves the thermodynamic self-consistency requirement that

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S. \tag{67}$$

As noted above, this requirement is not as well satisfied in earlier work.

CONCLUSIONS

We find that a model of Ge and Si in which the solid phase is composed of ions, an electron gas,

TABLE IV. Theoretical melting curve for silicon.

T (K)	P (kbar)	V_s (a. u./ion)	V_l (a. u./ion)	$10^4 S_s$ (a. u./ion)	$10^4 S_l$ (a. u./ion)	$(dT/dP)_m$ (K/kbar)
1683	0.0	138.00	117.60	0.253 96	0.327 66	−9.41
1583	10.7	136.96	116.16	0.247 74	0.321 14	−9.63
1483	21.2	135.97	114.79	0.241 16	0.314 14	−9.87

TABLE V. Contributions to the theoretical Gibbs free energies for the solid phase of silicon along isotherms near melting.

T (K)	V (a.u./ion)	G (a.u./ion)	10^4P (a.u.)	10^4S (a.u./ion)	Θ (K)
1683	138.0	−4.539 962 5	0.0	0.253 955 22	373.698 15
1583	137.2	−4.533 797 3	0.266 62	0.247 871 02	374.825 58
	136.8	−4.531 564 1	0.429 83	0.247 658 71	375.667 33
	136.4	−4.529 313 3	0.594 80	0.247 445 39	376.515 04
1483	136.4	−4.527 618 7	0.540 65	0.241 393 94	376.026 22
	136.0	−4.525 353 4	0.707 18	0.241 179 61	376.879 20
	135.6	−4.523 070 0	0.875 54	0.240 964 23	377.738 28

E_0 (a.u./ion)	$10E_{eg}$ (a.u./ion)	$E_{bs}+E_{eb}+E_{tb}+E_{bb}$ (a.u./ion)	E_m (a.u./ion)	$10E_{bb}$ (a.u./ion)	$10^2E_{ph\,kin}$ (a.u./ion)
0.583 186 99	−0.400 710 58	−0.937 322 99	−4.111 035 3	−0.406 110 73	0.802 056 59
0.587 364 94	−0.379 568 50	−0.932 577 50	−4.122 595 4	−0.402 977 34	0.754 738 70
0.589 472 57	−0.368 896 59	−0.931 621 43	−4.126 748 8	−0.401 102 56	0.754 751 31
0.591 592 66	−0.358 157 23	−0.930 661 92	−4.130 918 5	−0.399 230 88	0.754 764 05
0.591 592 66	−0.358 157 23	−0.927 813 05	−4.134 232 8	−0.399 862 52	0.707 446 57
0.593 725 51	−0.347 348 91	−0.926 855 35	−4.138 414 0	−0.397 989 84	0.707 460 25
0.595 871 14	−0.336 471 60	−0.925 894 18	−4.142 611 8	−0.396 120 21	0.707 474 07

and localized covalent bonds, and in which the liquid phase is a simple metal, gives a negative-slope melting curve which agrees well with experiment. The basic source of the negative-slope melting curve seems to be the presence of the covalent bonds which stabilizes the relatively open diamond crystal structure in these elements. This relatively open diamond structure has a sufficiently large volume per ion that the liquid phase, which is a random but more closely packed system, is able to be more dense than the solid. In the course of this investigation we have tried to isolate the effect of the diamond crystal structure from other effects leading to the negative-slope melting curve. In particular, we have done a brief calculation in which we impose the diamond crystal structure on a simple metal very much like the model for metallic sodium used by Stroud and Ashcroft.[1] That calculation indicates that at a very large negative pressure (~ − 100 kbar) a diamond-structure phase could be stable in this simple metal, and the melting curve, under those circumstances, would have a negative slope. It is, of course, the presence of covalent bonding in the diamond-structure semiconductors which lowers the Gibbs free energy of this phase so that the diamond structure is stable at positive pressures. So both the diamond structure and the covalent bonds play critically important roles in producing the negative-slope melting phenomenon.

The separation of the electronic system in the semiconductors into electrons in a gas and electrons in the covalent bonds is, of course, an arbitrary one. The work of Bennemann,[14,15] Harrison,[41] and especially the recent work of Herbert[10] point the way to a microscopic theory of covalent bonding in solids. Much work remains to be done in this area, however, and we are satisfied that the results of other investigations mentioned above,

TABLE VI. Contributions to the theoretical Gibbs free energies for the liquid phase of silicon along isotherms near melting.

T (K)	V (a.u./ion)	G (a.u./ion)	10^4P (a.u.)	10^4S (a.u./ion)	η
1683	117.6	−4.539 962 4	0.0	0.327 661 42	0.3571
1583	116.5	−4.533 745 1	0.253 78	0.321 521 42	0.3642
	116.1	−4.532 224 2	0.384 48	0.321 076 38	0.3650
	115.7	−4.530 678 7	0.518 18	0.320 672 01	0.3657
1483	115.7	−4.528 722 7	0.412 38	0.315 179 00	0.3713
	115.3	−4.527 177 5	0.546 15	0.314 722 59	0.3721
	114.9	−4.525 619 6	0.681 63	0.314 264 57	0.3729

E_0 (a.u./ion)	$10E_{eg}$ (a.u./ion)	E_{bs} (a.u./ion)	E_m (a.u./ion)
0.670 668 03	0.591 601 25	−0.857 384 85	−4.365 254 6
0.677 000 55	0.635 416 59	−0.837 759 09	−4.396 107 3
0.679 332 99	0.651 547 13	−0.834 828 35	−4.403 040 3
0.681 681 59	0.667 785 19	−0.832 134 03	−4.409 757 1
0.681 681 59	0.667 785 19	−0.819 556 70	−4.422 700 7
0.684 046 53	0.684 131 77	−0.816 679 77	−4.429 625 5
0.686 427 87	0.700 587 29	−0.813 807 60	−4.436 569 4

which have divided the electrons into bonding electrons and free electrons, as well as the results of the present investigation, support this approach to the theory of the solid semiconductor.

ACKNOWLEDGMENT

We wish to acknowledge helpful discussions with Professor David Stroud.

---

[*] Work supported in part by Brigham Young University, Research Division, Provo, Utah 84602.

[†] Present address: Amoco Production Co., P.O. Box 50879, New Orleans, LA 70150.

[1] D. Stroud and N. W. Ashcroft, Phys. Rev. B 5, 371 (1972).

[2] Hilary D. Jones, Phys. Rev. A 8, 3215 (1973).

[3] G. Tamman, *Kristallisieren and Schmelzen* (Verlag von J. A. Barth, Leipzig, 1903).

[4] F. A. Lindemann, Z. Phys. 11, 609 (1910).

[5] W. G. Hoover and M. Ross, Contemp. Phys. 12, 339 (1971).

[6] J. S. Rowlinson, Nature 213, 440 (1967).

[7] S. M. Stishov, Usp. Fiz. Nauk 96, 467 (1968) [Sov. Phys-Usp. 11, 816 (1969)].

[8] J. A. Van Vechten, Phys. Rev. B 7, 1479 (1973).

[9] J. C. Phillips, Phys. Rev. 166, 832 (1968).

[10] D. C. Herbert, J. Phys. C 7, 669 (1974).

[11] R. Brill, Acta Cryst. 13, 275 (1960).

[12] H. Hattori, H. Kuriyama, T. Katagawa, and N. Kato, J. Phys. Soc. Jap. 20, 988 (1965).

[13] J. B. Roberto, B. W. Batterman, and D. T. Keating, Phys. Rev. B 9, 2590 (1974).

[14] K. H. Bennemann, Phys. Rev. 133, A1045 (1964).

[15] K. H. Bennemann, Phys. Rev. 139, A482 (1965).

[16] V. Heine and R. O. Jones, J. Phys. C 2, 719 (1969).

[17] J. Hubbard, Proc. R. Soc. A 243, 336 (1958).

[18] R. M. Martin, Phys. Rev. 186, 871 (1969).

[19] G. Nelin, Phys. Rev. B 10, 4331 (1974).

[20] M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).

[21] G. Nelin and G. Nilsson, Phys. Rev. B 10, 612 (1974).

[22] T. H. K. Barron, *Lattice Dynamics, Proceedings of an International Conference in Copenhagen* (Pergamon, New York, 1965), p. 247.

[23] V. M. Glazov, S. N. Ch'zhezskaya, and N. N. Glagoleva, *Liquid Semiconductors* (Plenum, New York, 1969), pp. 57 and 58.

[24] J. K. Percus and G. J. Yevick, Phys. Rev. 110, 1 (1958).

[25] N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966).

[26] Yu. G. Poltavtsev, Kristallografiya 16, 456 (1971) [Sov. Phys.-Cryst. 16, 387 (1971)].

[27] V. H. Hendus, Z. Naturforsch. A 2, 505 (1947).

[28] R. P. Feynmann, *Statistical Mechanics* (Benjamin, New York, 1972), p. 67; H. Falk, Am. J. Phys. 38, 858 (1970).

[29] D. R. Penn, Phys. Rev. 128, 2093 (1962); see also G. Srinivasan, Phys. Rev. 178, 1244 (1969).

[30] P. Nozières and D. Pines, Phys. Rev. 111, 442 (1958).

[31] This expression was derived in the same way as Eq. (10) of Ref. 1 above.

[32] N. W. Ashcroft, Phys. Lett. 23, 48 (1966).

[33] V. Heine and D. Weaire, Solid State Phys. 24, 249 (1970) (see p. 419).

[34] See, for example, C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), Chap. 19.

[35] N. W. Ashcroft and D. C. Langreth, Phys. Rev. 159, 500 (1967).

[36] J. L. Lebowitz, E. Helfand, and E. Praestgaard, J. Chem. Phys. 43, 774 (1965).

[37] H. D. Jones, J. Chem. Phys. 55, 2640 (1971).

[38] M. Ross and D. Seale, Phys. Rev. A 9, 396 (1974).

[39] S. N. Vaidya, J. Akella, and G. C. Kennedy, J. Phys. Chem. Solids 30, 1411 (1969); see also Ref. 40, below.

[40] J. F. Cannon, J. Phys. Chem. Ref. Data 3, 781 (1974).

[41] W. A. Harrison, Phys. Rev. B 8, 4487 (1973); see also, W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966), pp. 210–229.