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LETTER TO THE EDITOR

The solid–liquid interfacial tension of diamond-structure Si and Ge

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Abstract. We extend our previously developed Ginzburg–Landau theory for the solid–liquid interfaces of BCC elements to treat the diamond-structure elements Si and Ge. We use as an order parameter the amplitude of the [220] components of the density of solid. This order parameter is inserted into a simplified density-functional theory for the freezing of Si and Ge, and used to estimate explicitly the crystal–melt interfacial tensions.

Recently, we have developed a simple Ginzburg–Landau theory [1] for the solid–liquid interface of BCC elements. This theory gives good agreement with experiments for the BCC elements Na and Fe. The theory uses only one order parameter, the amplitudes of the [110] Fourier components of the density of solid. Since in the BCC structure there exist groups of three [110] reciprocal-lattice vectors summing to zero, the density-function expansion has terms that are cubic in the order parameter, and hence permits a first-order liquid–solid transition [2]. In contrast, for FCC structures, the cubic term is absent if the only order parameters are the Fourier components of the smallest reciprocal-lattice vector. In order to obtain the observed first-order transition, it is generally necessary to include at least two sets of Fourier components [3, 4].

In this Letter, we show that the diamond-structure elements Si and Ge, which are composed of two FCC sublattices, can be approximately treated within a single-order-parameter density-functional theory. The appropriate order parameter is the [220] Fourier component of the density of solid. The [220] reciprocal-lattice vectors, denoted K_{220} , are the third shortest in the diamond lattice, the shortest sets being the [111] and the [200]. However, in Si and Ge, the liquid structure factor $S(k)$ is larger at $k = K_{220}$ than at either K_{111} or K_{200} (see figures 1 and 2). This is consistent with the behaviour of the diamond lattice. The quantity analogous to $S(k)$ in the solid phase is $W_K = \sum_{\mathbf{K}} \cos(\mathbf{K} \cdot \mathbf{b}/2)^2$ where \mathbf{b} is a basis vector for the diamond lattice and the sum runs over all reciprocal-lattice vectors of a given length. W_{220} is larger than either W_{110} or W_{200} (which is, in fact, zero). Since there do exist sets of three [220] reciprocal-lattice vectors summing to zero, the theory permits a first-order phase transition for the diamond structure, in agreement with experiment. We use the theory, in conjunction with experimental data for the freezing of Si and Ge [5, 6], to estimate the liquid–solid interfacial tension, in reasonable agreement with available experiment.

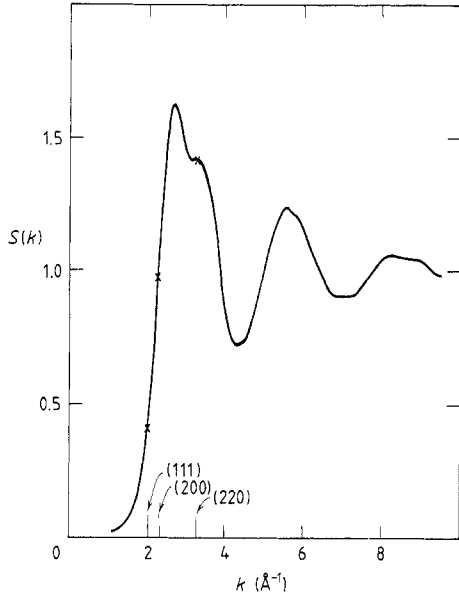


Figure 1. Experimental structure factor of Si at $T = 1460^\circ\text{C}$ and liquid mass density $\rho_l = 2.59\text{ g cm}^{-3}$ [5, 12].

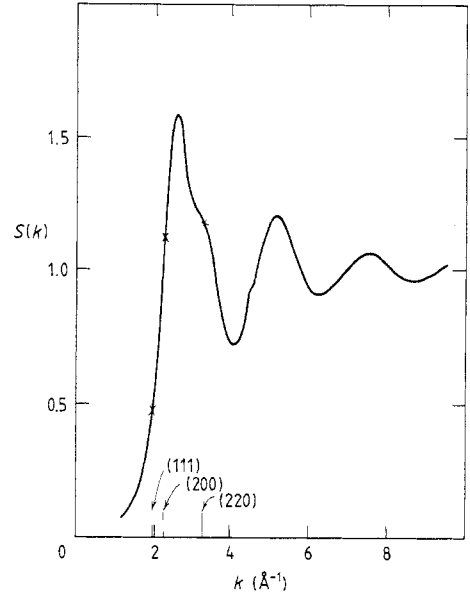


Figure 2. Experimental structure factor of Ge at $T = 980^\circ\text{C}$ and liquid mass density $\rho_l = 5.56\text{ g cm}^{-3}$ [5, 12].

The basis of our approach is a density functional formalism [7–9], according to which the grand free energy Ω is expressed as a functional of the singlet atomic number density, $n(\mathbf{x})$:

$$\Omega = \Omega[n(\mathbf{x})]. \quad (1)$$

For a bulk solid or a bulk liquid, $n(\mathbf{x})$ can be written

$$n(\mathbf{x}) = n_l \left(1 + \eta + \sum_n u_n \exp(i\mathbf{K}_n \cdot \mathbf{x}) \right) \quad (2)$$

where n_l is the liquid number density, the \mathbf{K}_n are the reciprocal-lattice vectors of the solid phase, and the amplitudes η and u_n are constants in the uniform solid phase, zero in the liquid phase. If there is a planar interface between solid and liquid perpendicular to the z axis, then the amplitudes η and u_n are z -dependent and we have

$$n(z) = n_l \left(1 + \eta(z) + \sum_n u_n(z) \exp(i\mathbf{K}_n \cdot \mathbf{x}) \right). \quad (3)$$

In order to calculate the solid–liquid interfacial tension of diamond-structure Si and Ge at melting, we take u_{220} as the principal order parameter and express the grand free energy difference per unit surface area, $\Delta\omega = \omega_{\text{sol}} - \omega_{\text{liq}}$, in the form of a Ginzburg–Landau expansion, as described in detail in [1]. The form of the expansion is

$$\Delta\omega = (n_l k_B T / 2) \int_{-\infty}^{+\infty} [a_2 u_{220}^2(z) - a_3 u_{220}^3(z) + a'_4 u_{220}^4(z) + b (du_{220}/dz)^2] dz \quad (4)$$

where the coefficients a_2 , a_3 , a'_4 , and b can be related to properties of the bulk liquid, and of the liquid–solid transition [1]. Since the structure coefficient $\cos(\mathbf{K}_{220} \cdot \mathbf{b}/2)$ equals

Table 1. Input experimental data for Si and Ge. The columns are the lattice constant a_0 , liquid number density n_l , fractional density increase η on freezing, measured structure factor $S(K_{220})$ [13], measured temperature derivative $[dS(k)/dT]_{T=\tau_m}$ for k at the main peak of the $S(k)$ [5], entropy change Δs [14] per atom on melting, melting temperature T_m .

Element	a_0 (Å)	n_l (Å ⁻³)	η	$S(K_{220})$	$10^4 dS(k)/dT$ (K ⁻¹)	$\Delta s/k_B$	T_m (K)
Si	5.431	0.05553	-0.101	1.409	—	3.61	1683
Ge	5.657	0.04612	-0.047	1.184	~2.4	3.15	1210

unity for all twelve [220] reciprocal-lattice vectors, the formalism of [1] yields the following expressions for the coefficients a_2 and b :

$$a_2 = 12/S(K_{220}) \quad (5)$$

$$b = -(1/2)C''(K_{220}) \sum_{\hat{\mathbf{K}}} (\hat{\mathbf{K}}_{220} \cdot \hat{\mathbf{z}}) = -2C''(K_{220}) \quad (6)$$

where $S(k)$ is the liquid structure factor, $C(k)$ is the direct correlation function defined by

$$S(k) = 1/[1 - C(k)] \quad (7)$$

and $C''(k) = d^2C/dk^2$. Similarly, from the melting condition $\Delta\omega = 0$ and the extremal condition $\partial\Delta\omega/\partial u_{220} = 0$, we obtain the coefficients a_3 and the bulk order parameter u_{220} in the solid phase:

$$a_3 = (2a_2 a'_4)^{1/2} \quad (8)$$

$$u_{220} = (a_2/a'_4)^{1/2}. \quad (9)$$

The remaining coefficients a_3 and a'_4 can be determined by requiring that the density-functional expansion correctly reproduces both the observed increase in entropy Δs on melting, and the observed temperature derivative of the structure factor, $dS(k)/dT$, at the melting temperature [1], namely,

$$\Delta s = \frac{1}{2} T_m u_{220}^2 (da_2/dT)_{T=\tau_m}. \quad (10)$$

Given the coefficients appearing in (4), the surface tension and surface profile are obtained by minimising the free-energy functional with respect to the $u_{220}(z)$. This can be done analytically with the results

$$\tau = (n_l k_B T_m / 6) u_{220}^2 (a_2 b)^{1/2} \quad (11)$$

$$u_{220}(z) = u_{220} [1 + \tanh(\alpha z)] \quad (12)$$

where $\alpha = [a_2/(4b)]^{1/2}$. The interfacial width w can be estimated by using the 10–90 width of the profile $u_{220}(z)$ with

$$w = 2.2/\alpha. \quad (13)$$

To apply this theory to Si and Ge, we require experimental information about their melting properties [6, 10, 11]. These data are listed in table 1. For Ge, the experimental measurement of $dS(k)/dT$ is only for k at the main peak of the structure factor $S(k)$ [5]. It is reasonable to assume that such value is invariant approximately for the k around the main peak of $S(k)$. For Si, no experimental data for $dS(k)/dT$ are available; we

Table 2. Calculated results for Si and Ge. The columns are the coefficients a_2 , $[da_2/dT]_{T=\tau_m}$, b [12], the theoretical and experimental [15] liquid–solid surface tension τ_{th} and τ_{ex} , and the interfacial width w .

Element	a_2	$10^3 da_2/dT$ (K ⁻¹)	$10^{16} b$ (cm ²)	τ_{th} (dyn cm ⁻¹)	τ_{ex} (dyn cm ⁻¹)	w (Å)
Si	8.571	~1.4	~0.80	167	—	1.34
Ge	10.14	~2.0	~2.8	176	181 [15]	2.31

therefore determine this derivative by conjecturing that the quantities $T_m(da_2/dT)_{T=\tau_m}$ are equal at the melting temperatures T_m for Si and Ge. To calculate the coefficient b , we use $C(k)$ of the dual-hard-sphere model developed in [12]. This model gives a very good fit to the experimental structure factor $S(k)$ of liquid Si and Ge for $k \leq 2k_F$, where k_F is the Fermi wavevector of the free-electron gas corresponding to the liquid metal. The coefficients a_2 , da_2/dT , b , as well as the calculated and measured liquid–solid surface tensions τ_{th} and τ_{ex} are listed in table 2. Direct measurements of the liquid–solid surface tensions for Si and Ge are unavailable; the quoted experimental value for Ge is an indirect estimate of [11], obtained by measuring the supercooling limits of small droplets of purified liquid and deducing a surface tension from crystal–melt nucleation theory. Agreement between theory and indirect measurement data of Ge is quite reasonable, considering the simplicity of our assumptions and taking into account the substantial uncertainty of the measurements and the theory. It is generally expected that the surface tension of Si is slightly larger than the surface tension of Ge. We believe that our slightly smaller surface tension for Si is due partly to inaccuracies in calculating the quantity $T_m(da_2/dT)_{T=\tau_m}$ and coefficient b . The surface widths we obtain are too narrow. Although there are no experimental measurements of surface widths to compare with, a few atomic layers for the surface widths are expected. We believe the calculated narrow widths are due to the very small value of $|C''(K_{110})|$ (about one order of magnitude smaller than those of the simple metals) obtained from the dual-hard-sphere model, since $C(k)$ of this model is obtained by interpolating experimental data and thus the values $C''(k)$ at the shoulder are very sensitive to the fitting algorithm. Of course, the use of a Ginzburg–Landau theory with only one order parameter for the diamond structure also produces inaccuracies.

Note that our estimates are based on the assumption of an isotropic surface tension. In the case of BCC metals, several theories give an orientation dependence of order 1% [1, 4]. While this dependence is probably larger for the diamond-structure elements, it may still be small enough for the isotropic assumption to be adequate. Note also that, although the density change on melting does not appear explicitly in our theory, it is still included indirectly by the device of fitting the coefficient a'_4 to melting data, as explained in [1]. This is clearly important for Si and Ge, in which there is a considerable expansion on freezing.

The order parameter we use corresponds to the shoulder on the liquid structure factor of Si and Ge. The presence of the shoulder could be interpreted as meaning that the liquid is ‘trying’ to form a diamond-structure solid. The large increase in volume on freezing apparently occurs because it is required in order for the [220] reciprocal-lattice vectors to line up with the shoulder. There is considerable evidence that the shoulder is due to residual liquid-state effects of three-body forces that stabilise the diamond structure [16]. We have exploited the presence of the shoulder to estimate the surface

tension using a few bulk properties of the elements. For more quantitative accuracy, we can include more order parameters and carry out free-energy expansion to higher power in the order parameters. If so, the effect of all density fluctuations, as it occurs in the fluid phase, through observed $C(k)$ and other higher-order correlation functions, will be included exactly. Here, we simply exhibit the grand free energy explicitly only as a function of the dominant order parameter. Obviously, such mean-field theory cannot account for roughening, and to our knowledge, there is no report on the roughening temperature of Si and Ge. Nevertheless, it is unlikely that the roughening effect will influence the surface free energy much [17], even if the roughening temperature of Si and Ge is close to the melting temperature.

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