

Interstitialcy Model for Condensed Matter States of Face-Centered-Cubic Metals

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The special configuration and dynamics known for interstitialcies in face-centered-cubic metals are exploited to construct a model giving all the thermodynamic properties of crystalline, liquid, and amorphous states in a unified way. A large diaelastic softening of the shear modulus with defect concentration is derived. This leads to a softening of the interstitialcy formation energy, which, taken together with a large entropy contribution from the interstitialcy resonance modes, makes the model, which contains Lindemann's law, viable for quantitative calculations of thermodynamic properties.

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A considerable amount of detailed information about the configuration and dynamics of interstitials in face-centered-cubic metals, particularly copper, has become available in recent years. We use this to derive an interstitial-concentration-dependent Gibbs free energy, giving all the thermodynamic properties of crystalline, liquid (melts), and amorphous condensed matter states for these materials in a unified way. For the present purposes, we do not distinguish between amorphous and glassy states. We suppose crystalline properties to be given. Many of the properties of amorphous materials have already been rationalized in terms of a phenomenological two-level-system (TLS) tunneling model [1,2] but the question of the identity of the tunneling entity remains open. The TLS model supposes the existence of intrinsic, localized, two-level excitations strongly coupled to the lattice with energy differences Δ between levels with a nearly uniform density of states. This distribution may be supposed to arise from strain interactions [3] between tunneling systems at sufficiently high concentrations. The model does not account for a pronounced reduction of the shear modulus often observed [4,5]

It should be expected on topological grounds that monatomic condensed matter in stable mechanical equilibrium and metastable thermodynamic equilibrium configurations should consist of crystals containing intrinsic defects: vacancies, interstitials, dislocations or disclinations, or combinations of these. In fact, melting theories have been offered for each of vacancies [6], interstitial-vacancy Frenkel pairs [7], dislocations [8], and disclinations [9]. But dislocation energies are of the order of several eV per atomic length for common materials (for example, Cu) so that even the smallest stable loops would seem to have energies prohibitively high for generation by thermal activation. This difficulty becomes even more severe for disclinations. The properties of vacancies have been well studied in many materials. In particular, the ratio of formation entropy to volume is known to be insufficient to allow for catastrophic vacancy generation at the melting point [10]. Since these are the only intrinsic defects known from solid-state physics, we should then expect interstitials to be the source.

In an attempt to unify condensed matter states, Frenkel

[6] recognized the need for intrinsic defects and constructed a theory, but it was a theory for "holes," or vacancies. Lennard-Jones and Devonshire [7] gave a theory for point interstitials, in which atoms were supposed to jump thermally from normal lattice sites to interstitial sites. The defects in this case are in fact Frenkel pairs, leading, among other things, to homogeneous melting, contrary to the heterogeneous melting known from experiment [11,12]. Also, defect concentrations of the order of 50% inconsistent with observed volume changes are required, and the theory has not enjoyed general acceptance.

Stillinger and Weber [13] have made computer calculations using a potential which produces a bcc crystalline ground state. They find thermally excited states which are Frenkel pairs with the interstitial in a split configuration and a defect softening, or mean attraction between defects. They use these facts to construct a simple melting theory which shows that defect softening is basic to the fact that the solid-liquid transition found is thermodynamically first order.

In the earliest theoretical calculations [14] made for copper it was found that the interstitial has a higher formation and a lower migration energy than does a vacancy, but it was not possible to determine the stable interstitial equilibrium configuration. We now know [15,16] that the equilibrium configuration for an isolated interstitial atom, at least in Cu and Al, is not a pointlike interstitial with cubic symmetry as for a vacancy, but rather a linearlike extended dumbbell interstitialcy configuration (two atoms trying to occupy the same lattice site) with tetragonal symmetry. That is, the stable and saddle-point configurations are reversed for an interstitial atom from that for a vacancy. This has far-reaching consequences. In particular, the interstitialcy configuration has a strong coupling to external shear stress, low-frequency resonance modes [17], and an extended linear stringlike character which can lead to large entropy effects. It has been pointed out by Schober [18] that many features of low-temperature glass anomalies (low-frequency vibrations, relaxation processes, and general TLS behavior) are also observed in crystals after irradiation at doses much lower than those needed for amorphization.

We suppose that the volume (V_0), bulk modulus (B_0), shear modulus (G_0), and their pressure derivatives (B' and G'), evaluated for the static lattice (no thermal or zero-point vibrations), are given, and the Helmholtz free energy $\tilde{F} = \tilde{F}(V, \varepsilon)$, where ε is the shear strain, can be expressed in terms of these parameters. For high temperatures, using a quasiharmonic Einstein approximation for the vibrational free energy, we then have the free energy of the perfect crystal F_p given by

$$F_p = \tilde{F}(V, \varepsilon) + 3NkT \ln[\hbar \omega_E(V)/kT].$$

For the change in the free energy δF of the crystal containing n defects, where $c = n/N$, we must add (1) the work F_w necessary to create a concentration c of interstitialcies, (2) the change δF_v of the vibrational free energy resulting from the change in the frequency spectrum, and (3) a configurational free energy F_c given by $F_c = -T\Delta S_c = -Tnk[1 + \ln z N/n]$. The latter term differs from the usual small- c expression for the configurational entropy only by the factor z , put in to take account of the fact that the interstitialcy can be oriented along any of z directions ($z = 3$ for fcc lattices).

We require F_w to be given in terms of the independent variables and assume that this dependence can be expressed in the form $\delta f_w/\delta c = \alpha_1 G \Omega + \alpha_2 B \Omega$, where $f = \delta F/N$, Ω is the volume per atom, and α_1 and α_2 are constants presumed to be the same for the same crystal structure. This is the principal assumption of the present work. We further expect that $\alpha_2/\alpha_1 \ll 1$ (and find $\alpha_2/\alpha_1 \approx 0.03$ later in a fitting procedure for Cu). This means that the work is mainly that of a shear deformation, as supposed by many [19–22]. Support for this form also comes from computer calculations using the embedded-atom method of Johnson [23], who finds that defect energies have negligible dependence on the cohesive energy, vary only slightly with the bulk modulus, but are linearly proportional to the average shear modulus. For a concentration c of interstitials, f_w becomes

$$f_w = \int_0^c [\alpha_1 G \Omega + \alpha_2 B \Omega] dc. \quad (1)$$

The vibrational frequency spectrum of fcc crystals containing isolated interstitialcies has been described in detail by Dederichs *et al.* [17]. They find both low-frequency resonance modes and high-frequency local modes. The results depend a bit on the interatomic potential chosen. The dumbbell displacements are aligned in $\langle 100 \rangle$ directions and are strongly coupled to atoms in the close-packed $\langle 110 \rangle$ directions, so that the configuration consists of a $\langle 100 \rangle$ dumbbell extended with appreciable displacement chains for several atoms along $\langle 110 \rangle$ directions. For the present high-temperature approximate calculation, we replace the lattice frequencies by the single Einstein frequency ω_E , the resonance modes by a single ω_R , and the local modes by a single ω_L . There are five resonant and six local modes for each interstitialcy. Since the resonance and local modes come at the expense of the lattice

modes, the change in the free energy per particle becomes

$$f = f_w - kTc \{5 \ln \omega_E/\omega_R + 6 \ln \omega_E/\omega_L + (1 + \ln z/c)\}. \quad (2)$$

Supposing that the shear strain dependence of B may be neglected, the shear modulus G is obtained from its definition $G \equiv (\partial^2 F/\partial \varepsilon^2)/N\Omega_0$, with Eqs. (1) and (2), to be

$$G(V, \varepsilon, c) = \tilde{G}(V, \varepsilon) + \alpha_1 \int_0^c (\partial^2 G/d\varepsilon^2)(\Omega/\Omega_0) dc, \quad (3)$$

or $\partial G/\partial c = \alpha_1(\Omega/\Omega_0)\partial^2 G/\partial \varepsilon^2$. The shear modulus in a crystal along planes separated by a distance d must be periodic in displacements b , which repeat the lattice structure. Assuming the simplest periodic even function, we take

$$G = G(V, c) \cos 2\pi x/b = G \cos 2\pi d\varepsilon/b,$$

where $\varepsilon = x/d$. Then $\partial^2 G/\partial \varepsilon^2 = -\beta G$, where $\beta = 4\pi^2 d^2/b^2$. As a first approximation, taking $\Omega/\Omega_0 \approx 1$, this leads to

$$G = \tilde{G}(V, \varepsilon) \exp(-\alpha_1 \beta c) \quad (4)$$

for the concentration dependence of the shear modulus.

The result, Eq. (4), is basic for what follows. It describes a large diaelastic softening of the shear modulus and of the free energy with defect concentration. For $d \sim b$, $\alpha_1 \sim 1$, $\beta \approx 4\pi^2 \sim 40$, so that a concentration of a few percent of interstitialcies should greatly reduce the shear modulus. The only material for which the diaelastic effect for interstitialcies is known for all elastic constants is copper, for which the values $d(\ln C_{ij})/dc = -31$, -15 , and 0 have been measured for C_{44} , $C' = (C_{11} - C_{12})/2$, and B , respectively, at low concentrations [15].

The change in Gibbs free energy \mathcal{G} is obtained from F by $\mathcal{G} = F + pV$. At constant pressure, all the frequencies change as a result of the concentration-induced volume change, adding a term $3NkT \ln \omega_E(V)/\omega_E(V_0)$. Also we may expect ω_R to be reduced. On the other hand, for large concentrations, the stringlike extensions of the interstitialcy may be inhibited, or "pinned" by neighboring interstitialcies. A quantitative calculation of these effects would be difficult and lengthy. For the time being, we bypass these important considerations with a very crude estimate. If the interstitialcy chain were to be replaced by an elastic string of length L pinned by an interstitial, then we would expect the frequency $\omega_R = 2\pi v/L = (2\pi v/L_0)(1 + \alpha_1 \beta c)$, where v is the sound velocity, to be doubled when $\beta c \sim 1$. We will simply use a linear interpolation formula with $\omega_R = \omega_{R0}(1 + \lambda \alpha_1 \beta c)$ and expect $\lambda < 1$. (A fitting later for Cu gives $\lambda \sim 0.2$.) But, also, these strings have higher modes of oscillation. Again we approximate this effect by assuming that harmonics exist as in a string, so that $\ln \omega_E/\omega_R$ in Eq. (2) is replaced by $\sum_1^{y'} \ln(y'/m)$, where m is an integer, $y' = v/(1 + \lambda \beta c)$, and $v = \omega_E/\omega_R$. The sum is well approximated over the range of interest by $0.87y' - 1.05$.

Using $V = \partial \mathcal{G} / \partial p$ and $\omega_E(V) / \omega_E(V_0) = (V_0/V)^\nu$, the (normalized) Gibbs free-energy difference y is then given as a function of (normalized) concentration x for different (normalized) temperatures t by

$$y = x \left[(1-q) \left(\frac{1-e^{-x}}{x} \right) + q \right] - tx \left\{ 6a\gamma \left[\gamma - \frac{1}{3} \right] \frac{G_0}{B} \left[(1-q) \left(\frac{1-e^{-x}}{x} \right) + q \right] + \frac{4.35\nu}{1+ax} + \ln \frac{b}{x} - 4.25 \right\}, \quad (5)$$

where $y = [\delta \mathcal{G}(1-q)\beta] / NG_0V_0$, $x = a_1\beta c$, $t = kT/aG\Omega$, $t' = T/T_m$, and where we have defined a by $a_1GV + a_2BV = aGV$, $1-q = a_1/a$, $a = \lambda/a(1-q)$, and $b = za(1-q)\beta(\omega_E/\omega_L)^6$. In Eq. (5), G' has been replaced by a shear Grüneisen gamma γ with $G' = (2\gamma + \frac{1}{3})G/B$ [10].

The six parameters (α_1 , α_2 , β , ν , λ , and ω_L/ω_E) have been fitted to copper, for which the most data are available, by the following procedure. For a range of assumed values of ν near that estimated theoretically [17] and determined experimentally [15], the requirement that the interstitiality concentration be at least an order of magnitude less than the vacancy concentration [24] just below T_m is imposed. This allows $\alpha = 1$, for $2G = C_{44} + C'$, and the formation energy of the isolated interstitiality is $\alpha G_0\Omega_0 = 3.94$ eV. This is also in good agreement with stored energy measurements [25]. ω_L/ω_E was taken to be 1.73 from theory [17]. No general solution to the equations is found for $\beta < 30$, and a trial value of 35 has been chosen. Then fitting the measured entropy change of $1.15k$ at the melting temperature T_m determines $q = q(\nu)$, $\lambda(\nu)$, and $x(\nu)$. Choosing $\nu = 5.3 \pm 7\%$ leads to values of $\lambda = 0.206 \pm 10\%$, $q = 0.075 \pm 22\%$, and $x = 3.0 \pm 17\%$, so that $c(T_m) = 0.0927 \pm 17\%$. With this choice of parameters, the results shown in Fig. 1 are obtained. These parameters may be expected to change slightly as more and improved data become available.

Three distinct regimes are found by setting $d(\delta \mathcal{G})/dc = 0$. For low enough temperatures only one solution $C_1(T)$ is obtained which gives the equilibrium interstitial-

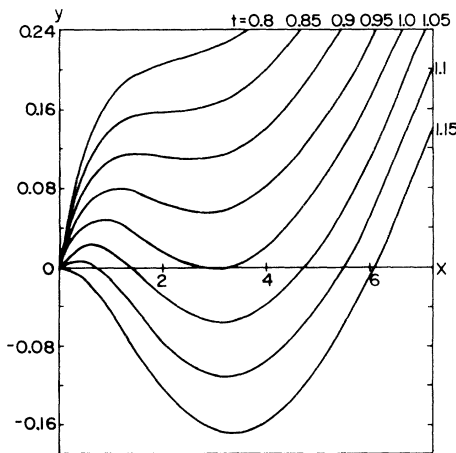


FIG. 1. The (normalized) Gibbs free-energy difference y as a function of the (normalized) interstitiality concentration x for different temperatures t . The temperature is normalized to the melting temperature. The parameters are chosen for copper.

cy concentration in the crystal depending exponentially on temperature with the isolated interstitiality formation enthalpy as the activation energy. For temperatures near the melting temperature, there are three solutions, C_1 , C_2 , and C_3 . We interpret $C_3(T)$ as the equilibrium liquid state, with C_2 the concentration at which $\delta \mathcal{G}$ has a maximum. For high enough temperatures, $C_3(T)$ is the only equilibrium stable state. We interpret frozen-in concentrations C_3^0 to represent amorphous states. One sees from Fig. 1 that there is a possible supercooling range of about 15% below T_m . An improved approximation for Eq. (4) would increase this somewhat. This may be compared with a measured [26] range of 17% for 15 to 50 μm Cu droplets. The predicted superheating range is smaller. The asymmetric and inhomogeneous nature of melting is to be understood from the fact that interstitial generation is nucleated at surfaces, dislocations, or other shear strain centers.

For temperatures just below T_m , the model predicts $C_1 \sim 3 \times 10^{-5}$ so that a shear modulus softening of $\sim 10^{-3}$ occurs. With currently available ultrasonic sensitivities of $\sim 10^{-6}$ for velocity changes, it should be possible to detect this effect to an accuracy sufficient to determine the magnitude, activation enthalpy, and entropy for isolated interstitialities. There are currently no measurements of the interstitiality entropy available, and enthalpies are available for only a few materials by subtraction of vacancy contributions from stored energy measurements of irradiated materials. Ultrasonic measurements may provide both a test of one prediction of the model and values for interstitiality activation enthalpies and entropies.

It is to be noted that melting occurs at the temperature T_m where $\delta \mathcal{G}$ and $\delta \mathcal{G}/dc = 0$ [y and $dy/dx = 0$ in Eq. (5)]. This gives a relation between T_m and the isolated interstitiality formation enthalpy $H_f = \alpha G_0\Omega_0$ which is equivalent to Lindemann's [27] melting criterion, $T_m \propto m\theta^2 \times \Omega^{2/3}$, where θ is the Debye θ and m is the atomic mass, found by supposing that melting occurs when atomic vibrational displacements reach a critical value. When note is taken of the fact that θ is dominated by shear distortions (two pure shear waves and a longitudinal wave which also has a large shear component), so that $\theta^2 \sim G\Omega^{1/3}/m$, one obtains $T_m \propto G\Omega$. Some minor deviations are to be expected if some of the parameters, for example G_0/B_0 , vary from one material to another in the same structure class. Further, the physical basis ($\delta \mathcal{G} = 0$) is on sounder ground than that of the original Lindemann criterion, and also one obtains here the proportionality constant in Lindemann's law. Using the fit to copper, we

have $H_F = \alpha G_0 \Omega = 33.7kT_m$. Although only data for Cu have been fitted here, the existence of an effective Lindemann law gives confidence that fits may be achieved for a wide range of materials. The extent to which the model can be extended to other materials will be the subject of further investigation, but we note here that split interstitial configurations are also found in hcp and bcc structures [17], and it should be possible to include compounds within the same formalism by including suitable additional terms in the free energy. More details and comparisons with experimental data, discussion of low-temperature behavior, and kinetics of the model will be published elsewhere.

In summary, a large diaelastic softening is predicted for crystals containing interstitialcies. The thermodynamic properties, and their discontinuities at the melting point, can be computed as functions of temperature, pressure, shear strain, and concentration. The thermodynamic properties are obtained regarding liquids as crystals containing a few percent of interstitialcies (9.3% for Cu at T_m) in thermal equilibrium ($\partial\delta S/\partial c = 0$), while amorphous materials result for a fixed concentration c_0 of frozen-in interstitialcies. The concentration c_0 depends on the method of preparation of the material. The existence of equivalent dumbbell orientations leads to the low-temperature properties expected for a TLS tunneling model. The tunneling entity is the interstitialcy configuration. The model appears to be viable, giving results which are analytic and quantitative, while providing a unified view of condensed matter states.

Salient features of the model are that the interstitialcy configuration is extended, strongly coupled to shear stress, with low-frequency resonance modes providing an unusually large entropy per defect. The shear modulus G carries the burden of providing the volume, shear strain, and concentration dependence needed for a thermodynamic treatment. Such an approach avoids many of the difficult technical problems involved in computer calculations of finding and using suitable many-body potentials. The crystalline elastic constants already contain this information, have often already been calculated from first principles in solid-state physics, and in any case are readily available from ultrasonic measurements with even higher accuracy.

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