Quantum Thermodynamics of Defects in Solids

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A new method for the computation of thermodynamic properties of solid defects is introduced. The free energy of formation of a defect is written as a simple function of a universal crystalline free energy. Computed temperature variations of surface energies are found to be consistent with experiment. The source of the linear term in the low-temperature specific heat of defect materials is revealed. Computed magnitudes of the linear term are found to be in reasonable agreement with experiment for amorphous metals and nanocrystalline Pd.

There are many interesting thermodynamic properties of defects in solids which are quantum mechanical in nature. Examples which are addressed in this paper include the low-temperature specific heats of amorphous [1,2] and nanocrystalline solids [3] and the temperature dependence of surface energies [4,5]. Because solid defects are inherently complex at the atomic level, the usual Monte Carlo [6] or molecular dynamics [7] methods for computing defect thermodynamics are of necessity semiclassical in nature. Here a new method is proposed for the computation of quantum thermodynamic properties of solids as a function of the atomistic configuration of defects. We will see, among other things, that there is a common, simple explanation for the appearance of the linear term in the low-temperature specific heats of amorphous solids and nanocrystalline solids.

I will first derive an expression for $F_d(T)$, the Helmholtz free energy to form a defect in a crystal at temperature T. Thermodynamical properties of interest will then be calculated from $F_d(T)$, and results tested against experiment.

The approach taken in the derivation of $F_d(T)$ is a direct generalization to nonzero temperatures of the equivalent crystal theory [8]. Consider a single crystal at temperature T and volume per atom V_m. The subscript m refers to the minimum in Fig. 1. Now introduce a local defect into the crystal. The corresponding $F_d(T)$ is computed by perturbation theory, where the unperturbed system is taken to be a single crystal at temperature T and volume per atom V. The perturbation arises from the difference in ion core electronic potentials of the defect solid and the single crystal. By definition,

$$F_d(T) = F_c(T,V) + F_p(T,V) - F_c(T,V_m) , \qquad (1)$$

where $F_c(T,V)$ is the free energy of the single crystal and $F_p(T,V)$ is the sum of the perturbation series. Now we know that the introduction of the defect must raise the free energy of the crystal above the minimum in Fig. 1 (see, e.g., Ref. [9]). Thus there is a volume V such that

$$F_d(T) = F_c(T,V) - F_c(T,V_m) \qquad (2)$$

and

$$F_p(T,V) = 0 . \qquad (3)$$

The crystal with this volume V is called an equivalent crystal, since its free energy is equal or equivalent to that of the defect crystal. This complicated many-atom problem has now been formally reduced to the solution of one equation, Eq. (3), for one unknown, V. It remains to specify $F_c(T,V)$ and $F_p(T,V)$.

The crystalline free energy, $F_c(T,V)$, can be calculated from $P = -[\partial F(T,V)/\partial V]_T$, so that

$$F_c(T,V) = F_c(T,V_m) - \int_{V_m}^{V} P \, dV' , \qquad (4)$$

where P is the pressure. A knowledge of the equation of state, i.e., the P-V-T relation for the crystal, is all that is necessary to determine $F_c(T,V)$ via Eq. (4). Recently it has been discovered [10] that the equation of state (EOS) has a universal form for all classes of solids. Further, it has been found [11] that this universal EOS has a simple, analytic form:

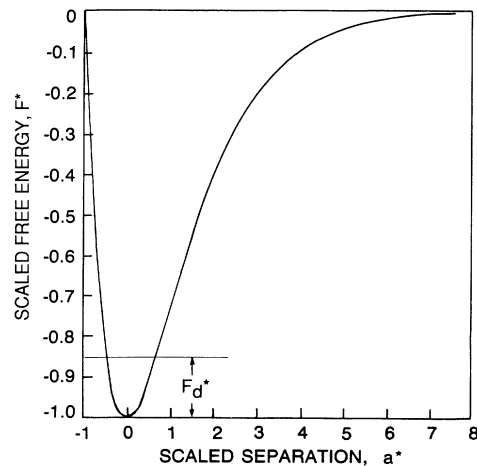$$P(T,X) = \frac{3B_m(T)}{X^2}(1-X)\exp[\eta_m(1-X)] , \qquad (5)$$

FIG. 1. Universal free energy function scaled as described in the text.

where $X \equiv [V/V_m(T)]^{1/3}$, $\eta_m(T) = \frac{1}{2}[(\partial B/\partial P)_T - 1]_m$, and B is the bulk modulus. A number of thermal properties of crystals have been accurately predicted [11] using Eq. (5) and input data only at a single (reference) temperature. These include the high-temperature isotherms, the temperature variation of the thermal expansion, $B_m(T)$, and $[\partial B/\partial P]_T$.

Combining Eqs. (4) and (5), we find

$$F_c(T,V) = F_c(T,V_m) + \Delta F(T)[F^*(a^*) + 1], \qquad (6)$$

where $\Delta F(T) = 9B_m V_m / \eta_m^2$, $a^* = \eta_m(T)(X - 1)$, and $F^*(a^*) = -(1 + a^*)e^{-a^*}$. We see then that there is a universal form for the free energy. The scaled functional $F^*(a^*)$ is plotted in Fig. 1, and one can see that it is the same as the universal scaled functional for the internal energy, $E^*(a^*)$, shown in Figs. 1-4 of Ref. [12]. At $T = 0$ K the free energy and the internal energy are identical, with $\Delta F(0) = \Delta E$ and $a^* = (r_{WS} - r_{WSM})/l$, where ΔE is the cohesive energy, r_{WS} is the Wigner-Seitz radius of equilibrium value r_{WSM}, and $l = [\Delta E/12\pi B_m r_{WSM}]^{1/2}$ is a scaling length. Combining Eqs. (2) and (6), we have

$$F_d(T) = \Delta F(T)[1 + F^*(a^*)]. \qquad (7)$$

An example value of $F_d(T)/\Delta F(T) \equiv F_d^*$ is shown in Fig. 1.

Next Eq. (7) will be applied to the prediction of the low-temperature specific heat, $c_v(T)$, for amorphous metals and nanocrystalline materials. For single crystals, the Debye continuum model has been a good approximation for the phonon specific heat. It predicts a low-temperature $c_v(T)$ proportional to T^3. For metals above the superconducting transition temperature T_c, there is also a linear electronic specific heat. However, a linear dependence on T has been discovered [1,13] for amorphous insulators. It was also found [2] that even below T_c there was a linear specific heat for amorphous metals. The linear $c_v(T)$ and other properties of amorphous materials have been successfully explained [14] in terms of localized two-level systems characterized by tunneling through a potential barrier. The microscopic origin of such localized states remains an unsolved problem [15], however.

Here the problem will be revisited via a different approach. First, the origin of the linear term will be revealed. The difference between the specific heat of a solid containing defects and the corresponding single crystal is by definition

$$\Delta c_v(T) = -T(\partial^2 F_d/\partial T^2)_V, \qquad (8)$$

since $c_v(T) \equiv -T(\partial^2 F/\partial T^2)_V$. To determine the form of $\Delta c_v(T)$ near $T = 0$ K, one would expand it in a Taylor series in T about $T = 0$ K. Of particular interest is the value of $-(\partial^2 F_d/\partial T^2)_V$ at $T = 0$ K, because that would be the coefficient of the linear term in T. From Eq. (7) we find that at $T = 0$ K

$$\left[\frac{\partial^2 F_d}{\partial T^2} \right]_V = \frac{d^2 \Delta F}{dT^2}[1 - (1 + a^*)e^{-a^*}]$$
$$+ \frac{\Delta F}{\eta_m} \frac{d^2 \eta_m}{dT^2} a^{*2} e^{-a^*}. \qquad (9)$$

In deriving Eq. (9), use has been made of the following crystalline properties [16,17] at $T = 0$ K: $dB_m/dT = 0$, $d\eta_m/dT \equiv 3/2(\partial/\partial T)_V(\partial B/\partial P)_T = 0$, $dV_m/dT = 0$, and $d^2 V_m/dT^2 = 0$. The last two equalities follow from the low-temperature behavior of the volume thermal expansion coefficient α due to lattice vibrations in a single crystal [17]: $\alpha \sim T^3$. Equation (9) can perhaps be made more transparent by looking at its leading term in the limit of small a^*:

$$(\partial^2 F_d/\partial T^2)_V = 9V_m(d^2 B_m/dT^2)(X - 1)^2/2 + \cdots. \qquad (10)$$

From Eqs. (8)-(10), $\Delta c_v(T)$ will contain a linear term in T provided $a^* \neq 0$ or, equivalently, $V \neq V_m$ and $X \neq 1$. Thus any defect in the single crystal would introduce a linear T dependence in $\Delta c_v(T)$, since any defect would require [9] that $V \neq V_m$ and therefore $a^* \neq 0$ (see Fig. 1). This suggests why it has been found experimentally that a linear T dependence in $c_v(T)$ can arise from a broad variety of sources, e.g., amorphous structure, nanocrystalline structure, impurities, and vacancy distributions due to, say, neutron irradiation.

The source of the linear term in the specific heat can thus be understood simply. Now I wish to go further and estimate the magnitude of the linear term. This will require an approximate form for $\Delta c_v(T)$, as suggested by Eq. (10):

$$\Delta c_v(T) \approx -T \frac{\Delta E}{B_m(0)} F_d^*(a^*) \frac{d^2 B_m(T)}{dT^2}. \qquad (11)$$

The coefficient of the linear term in $c_v(T)$ at low temperatures is given by the coefficient of T in Eq. (11) evaluated at $T = 0$ K.

The first application of Eq. (11) will be to amorphous metals. Amorphous metals are thought [18] to be in a random close-packed structure. Fortunately, there are radial distribution function data obtained by electron diffraction [19,20] for amorphous Ni, Co, Ag, and Au. Nearest-neighbor approximations can provide rather accurate total energies, as can be seen from Table V of Ref. [8] for the example of surface energies. The data (from Ref. [20] as tabulated in Tables I and II of Ref. [19]) indicate approximately twelve nearest neighbors and a nearest-neighbor distance which is of the order of 0.01 Å larger than that for the single-crystal structure. Thus the defect, which is by definition the difference between the amorphous and crystalline structures, takes the form in a nearest-neighbor approximation of a lowering of the crystalline atomic volume. In this case the equivalent-crystal atomic volume and the observed defect atomic volume are identical [note only the first term of Eq. (20) of Ref. [8]

survives]. This allows for a particularly simple computation of a^*. The experimental values of twelve nearest neighbors and 0.01 Å increase in nearest-neighbor distance will now be used to estimate a^* for all four metals. The scaled parameter a^* is given immediately [8] by $a^* = \sqrt{2}(3/16\pi)^{1/3}(0.01)/l$. Fortunately, there are good data [21–25] for $B_m(T)$ near $T = 0$ K which allowed computation of $d^2 B_m(T)/dT^2$ by numerical differentiation. Now we are prepared to evaluate the right-hand side of Eq. (11) at $T = 0$ K, which yields the coefficient a of the linear term aT in $c_v(T)$. The results are shown in Table I. The authors of Refs. [19,20] report no $c_v(T)$ data, but there are data [2,26] taken for a number of different metals below the superconducting transition temperature (to eliminate the electronic contribution). The computed values $1.0 \le a \le 2.0$ μJ/g K^2 listed in Table I are surprisingly close to all values measured [2,26] for a variety of metals, which are of order 1 μJ/g K^2.

The second application is to nanocrystalline materials [3,27]. These materials are polycrystals with crystallite sizes of only a few nanometers. This leads to a significant grain boundary component to the material. Since this grain boundary material has a lower density than that of the single crystal, $V \neq V_m$, $a^* \neq 0$, and $X \neq 1$. Thus from Eqs. (9) and (10), one would expect a linear term in $\Delta c_v(T)$ at low T. This is in fact the case, with the measured [3,28] value for nanocrystalline Pd being $a = 410$ μJ/g K^2. These data are the specific heat of nanocrystalline Pd minus the specific heat of single-crystal Pd, consistent with Eqs. (7)–(11). Presumably this difference essentially eliminates the (smaller) electronic contribution to $c_v(T)$. Note this value of 410 μJ/g K^2 is 2 orders of magnitude larger than those values reported for amorphous metals [2,26]. To attempt to understand the origin of that large difference, the magnitude of a will now be estimated for nanocrystalline Pd. First, data for $B_m(T)$ for Pd from Ref. [25] is numerically differentiated, yielding $d^2 B_m/dT^2$. Second, since only a fraction A_G of the material is the grain-boundary component, the right-hand side of Eq. (11) is multiplied by A_G. Finally, we need to estimate a^* from the atomic structure. Now the local atomic structure of grain-boundary material in nanocrys-

tals is not well understood. Wagner [27] has modeled the grain-boundary material as a single crystal of the ground-state structure but having a nearest-neighbor distance larger than the ground-state value. This neglects entirely bond-angle distortions. Let us examine his model within the context of equivalent crystal theory [8]. In Eq. (20) of Ref. [8], the total energy is divided into four terms. The influence of bond-angle distortion is felt primarily through terms two, three, and four, which are all zero in Wagner's Model. Table IV of Ref. [8] shows that, at least for the example of surface energies, the first term dominates the total energy of the defect in metals. This suggests that the model of Wagner [27] may be adequate for a rough estimate of the magnitude of a, and so we will adopt it here. As noted in the preceding example, in this case the equivalent-crystal atomic volume and the defect atomic volume are identical. The characteristics A_G and V/V_m of the grain-boundary component will depend on the method of preparation, so it is important to have characterized the particular material of interest. Here one can follow Wagner [27], who estimates $A_G = 0.30$ and $V/V_m = (r_{WS}/r_{WSM})^3 = 1.30$ for the grain-boundary material of the nanocrystalline Pd of Ref. [3]. These values yield $a = 390$ μJ/g K^2, which is perhaps fortuitously close to the measured value. The main point is that the computed and measured $\Delta c_v(T)$ values are over 100 times the amorphous metal values. This can be simply explained as follows. $V/V_m = 1.30$ corresponds to a nearest-neighbor-distance increase in the Pd grain-boundary material of 0.25 Å. Earlier, data [19,20] for amorphous metals were discussed which indicated an increase of nearest-neighbor distance for those materials of the order 0.01 Å. Since near $a^* = 0$, $1 + F_d^*(a^*) \approx a^{*2}/2$, then $A_G F^*(a^*)$ is ≈ 190 times larger for the nanocrystalline Pd of Ref. [3] than for the corresponding amorphous metal value. This is roughly consistent with the ratio of Δc_v's shown in Table I.

Finally, an approximate form of Eq. (7) for $F_d(T)$ is proposed for the purpose of performing simple computations of free energies of defects in solids. In doing this, we require that our approximations be consistent with those of Eq. (11) for $\Delta c_v(T)$:

$$F_d(T) \approx \Delta E \frac{B_m(T)}{B_m(0)} F_d^*(a^*). \qquad (12)$$

Note that according to Eq. (12), as $T \to 0$ K, $(\partial F_d/\partial T)_V \to 0$, as it must according to the third law of thermodynamics. A further test can be found in the T dependence of the surface energy $\sigma(T)$. By definition, $\sigma(T)$ is $F_d(T)$ per unit surface area formed. Thus with the exception of those surface phase transitions for which a^* changes significantly, Eq. (12) suggests that

$$\sigma(T) \approx B_m(T)\sigma(0)/B_m(0). \qquad (13)$$

This is consistent with data collected by Wawra [29] for a broad range of materials. In fact, Wawra [4] has as-

TABLE I. Linear term aT in the low-temperature specific heats computed as described in the text.

Metal	$-d^2 B_m/dT^2$ (10^6 dyn/cm^{2}K^2)	a (10^{-6} J/g K^2)
a-Ni	2.5[a]	2.0
a-Au	3.7[b]	1.0
a-Ag	3.1[b]	1.6
a-Co	2.1[c]	1.7
nc-Pd	6.0[d]	390

[a]Reference [22].   [c]Reference [24].
[b]Reference [23].   [d]Reference [25].

sumed a relation consistent with Eq. (13), as deduced empirically from the aforementioned data. Wawra's results for $\sigma(T)$ based on Eq. (13) and his measurements of $B_m(T)$ are in reasonable agreement with measurements of others [30].

In conclusion, a new method for computing the quantum thermodynamic properties of solid defects has been introduced. It is a simple, semiempirical method which is based on the equivalent-crystal approach. A universal form for the free energy of a crystal was discovered, and the free energy to form a defect was shown to be a simple function of the universal form. The predicted temperature dependence of the surface energies were found to be consistent with experiment. The source of a linear term in the low-T specific heat of amorphous materials and nanocrystalline materials was found simply. Magnitudes of computed linear terms in the specific heats of amorphous metals and nanocrystalline Pd were found to be in reasonable agreement with experiment.

[1] See, e.g., D. G. Cahill, J. R. Olson, Henry E. Fischer, S. K. Watson, R. B. Stephens, R. H. Tait, T. Ashworth, and R. O. Pohl, Phys. Rev. B 44, 12226 (1991), and references therein.

[2] For a review of amorphous metal results, see H. v. Lohneysen, Phys. Rep. 79, 161 (1981).

[3] R. Birringer, Mater. Sci. Eng. A 117, 33 (1989).

[4] H. Wawra, Z. Metallk. 66, 395 (1975); 66, 492 (1975).

[5] W. R. Tyson and W. A. Miller, Surf. Sci. 62, 267 (1977).

[6] Monte Carlo Methods in Statistical Physics, edited by K. Binder (Springer-Verlag, New York, 1979).

[7] Computer Simulation in Materials Science, edited by R. J. Arsenault, J. R. Beeler, Jr., and D. M. Esterling (American Society of Metals, Metals Park, OH, 1988).

[8] J. R. Smith, T. Perry, A. Banerjea, J. Ferrante, and G. Bozzolo, Phys. Rev. B 44, 6444 (1991).

[9] K. Huang, Statistical Mechanics (Wiley, New York, 1963), p. 24.

[10] P. Vinet, J. H. Rose, J. Ferrante, and J. R. Smith, J. Phys. Condens. Matter 1, 1941 (1989).

[11] P. Vinet, J. R. Smith, J. Ferrante, and J. H. Rose, Phys. Rev. B 35, 1945 (1987).

[12] A. Banerjea and J. R. Smith, Phys. Rev. B 37, 6632 (1988).

[13] R. C. Zeller and R. O. Pohl, Phys. Rev. B 4, 2029 (1971).

[14] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1972). A two-level tunneling model was also proposed by W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).

[15] J. L. Black, Phys. Rev. B 17, 2740 (1978).

[16] Richard A. Swalin, Thermodynamics of Solids (Wiley, New York, 1972), 2nd ed.

[17] N. W. Ashcroft and N. D. Mermin, Solid State Physics (Holt, Rinehart, and Winston, New York, 1976), p. 493.

[18] Richard Zallen, The Physics of Amorphous Solids (Wiley, New York, 1983).

[19] For a review, see G. S. Cargill III, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1975), p. 227.

[20] L. B. Davies and P. J. Grundy, J. Non-Cryst. Solids 11, 179 (1972); Phys. Status Solidi (A) 8, 189 (1971).

[21] For a review, see G. Simmons and H. Wang, Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook (MIT Press, Cambridge, 1971).

[22] G. A. Alers, J. R. Neighbours, and H. Sato, J. Phys. Chem. Solids 13, 40 (1960).

[23] J. R. Neighbours and G. A. Alers, Phys. Rev. 111, 707 (1958).

[24] E. D. Fisher and D. Dever, Trans. Metall. Soc. AIME 239, 48 (1967).

[25] J. A. Rayne, Phys. Rev. 118, 1545 (1960). Scatter in the data complicated the calculation of d^2B_m/dT^2.

[26] G. Flinspach, C. Surgers, and H. v. Lohneysen, J. Phys. Condens. Matter 2, 4559 (1990), and references therein.

[27] M. Wagner, Phys. Rev. B 45, 635 (1992); see also M. R. Fitzsimmons, J. A. Eastman, M. Muller-Stach, and G. Wallner, Phys. Rev. B 44, 2452 (1991).

[28] Data for Δc_p in Ref. [3] are presented as approximately linear in T over the range $\approx 0 \le T \le 300$ K. It is presumed that $\Delta c_v \approx \Delta c_p$ for $T \le 20$ K.

[29] See Fig. 1 of H. H. Wawra, Materialprufung 14, 413 (1972); Acta Phys. Chem. 19, 41 (1973).

[30] H. Udin, A. J. Shaler, and John Wulff, Trans. AIME 185, 186 (1949). See also the calculations of W. R. Tyson and W. A. Miller, Surf. Sci. 62, 267 (1977); and W. R. Tyson, Can. Met. Quart. 14, 307 (1975).