PHYSICAL REVIEW B VOLUME 37, NUMBER 12 15 APRIL 1988-II

Temperature dependence of energy and entropy of formation of self-interstitials in Cu

P. N. Ram
Department of Physics, North-Eastern Hill University, Shillong 793 003, India

(Received 27 April 1987; revised manuscript received 26 October 1987)

The vibrational contribution to energy of formation of self-interstitials in fcc metals is investigated with the use of the Green's-function method. The vibrational contributions to the energy, entropy, and free energy of formation of ⟨100⟩-split interstitials have been calculated for the case of copper so as to discuss their temperature dependence. The vibrational contribution to the formation energy at low temperatures is ~0.045 eV. The variation in formation entropy at low temperatures is found to be more pronounced.

I. INTRODUCTION

The properties of self-interstitial atoms in metals continue to be interesting. For fcc metals, ⟨100⟩-split or "dumbbell" interstitial seems to be the most stable configuration as obtained by computer simulation[1–5] as well as different experimental studies.[6–13] One of the most important developments in this field has been the discovery of low-frequency resonant modes of self-interstitials.[9,14–17] These resonant modes are instrumental in explaining many physical properties of irradiated metals; particularly high interstitial mobility at low temperatures.[5,18,19] In a recent paper[20] we have presented a Green's-function theory for the formation entropy of defects in metals and applied it for the case of self-interstitials in copper—where the role of resonant modes was emphasized. In the present paper, we calculate the vibrational contribution to formation energy of the self-interstitials in Cu so as to discuss the temperature dependence of the formation energy. Further, the temperature dependence of the formation entropy and formation free energy is also discussed.

An understanding of the properties of self-interstitial atoms depends upon a knowledge of the thermodynamic parameters of the point defects: the energies and entropies which control their formation, migration, and association. Calculations of point-defect energies have almost exclusively been made for the static lattice and any effects of zero-point motion and thermal vibrations have been ignored. In contrast, the entropies are generally evaluated in the high-temperature limit. However, experimentally the defect parameters are usually measured at elevated temperatures. For example, the experimental measurements of diffusion coefficients in metals are usually analyzed in terms of a defect model in order to determine the diffusion mechanism. Quantitative analysis of the data results in numerical values for the thermodynamic parameters of the point defects. Though the equilibrium concentrations of self-interstitials at high temperatures are orders of magnitude smaller than the equilibrium vacancy concentration, an interstitial contribution to self-diffusion is possible because of the high mobilities of self-interstitials, and the observed curvature in the Arrhenius plot of the self-diffusion data in many metals including Cu may not be ascribed to divacancies only.[19] In any case, in order to understand the role of self-interstitials in diffusion the temperature dependence of the the defect parameters, i.e., formation energy and entropy, should be studied and as such, the evaluation of the temperature-dependent vibrational part of the formation energy, even if small, is worthwhile and interesting. Further, in the present case of self-interstitials, the occurrence of low-frequency resonance modes is expected to give a significant contribution to the thermodynamic quantities at low temperatures and consequently a more pronounced temperature effect may be obtained. The aim of the present work is, therefore, to study the temperature dependence of thermodynamic parameters of self-interstitials in Cu. In the calculation we use the results of dynamics of self-interstitials in Cu discussed in our earlier works.[21,22,20]

Incidentally, Leung and Stott[23] have discussed the temperature dependence of properties of vacancies in sodium and aluminum on the basis of the Gibbs-Bogoliubov variational principle for the Helmholtz free energy treating the perfect crystal in the Einstein model as a reference. The present method uses full phonon spectrum where change in the density of states is expressed in terms of a generalized phase shift which can be used for the evaluation of any thermodynamic property of the defect crystal.

In Sec. II, we sketch the necessary theoretical background where the formula for vibrational contribution to thermodynamic properties is given. Section III is devoted to the calculation of vibrational formation energy, entropy, and free energy of ⟨100⟩-dumbbell interstitials in Cu at different temperatures.

II. THEORETICAL ASPECTS

When lattice defects are introduced in a crystal, the free energy of the crystal is increased. The increase due to a single point defect is called the Gibbs free energy of formation, G^F, of the defect. The free energy is decomposed into an enthalpy term and an entropy term according to the thermodynamical relation

$$G^F = H^F - TS^F , \tag{1}$$

where T is the absolute temperature. Here H^F, the formation enthalpy, represents the work done when a defect is created and S^F is the formation entropy. The enthalpy term can be expressed as

$$H^F = E^F + pV^F \;, \tag{2}$$

where E^F and V^F are formation energy and formation volume, respectively, and p is the pressure. The term pV^F is negligible at atmospheric pressure as the volume V^F is usually of the order of the volume of the unit cell in the crystal.

In the harmonic approximation, the internal energy of the crystal may be expressed as the sum of two terms,

$$E(T,V) = E_{\text{elastic}}(V) + E_{\text{vib}}(T) \;, \tag{3}$$

where E_{elastic} is the part of the energy referring to the static lattice and depends only on crystal volume, and E_{vib} is the vibrational part of the energy depending on temperature only. For the present our concern is the vibrational part of the formation energy. As thermodynamic quantities are expressed as averages over the total frequency spectrum of the crystal, the change in thermodynamic parameters is obtained in terms of the change in frequency spectrum.

The calculation of the change in density of states due to defects, $\Delta Z(\omega)$, has been discussed earlier.[20] The change for the single defect can be expressed as

$$\begin{aligned}\Delta Z(\omega) &= \frac{2\omega}{\pi}\operatorname{tr}\operatorname{Im}[\tilde{G}(\omega) - \tilde{G}^0(\omega)] \\ &= -\frac{1}{\pi}\frac{d}{d\omega}\operatorname{tr}\operatorname{Im}[\ln(D-\omega^2) - \ln(D^0-\omega^2)] \;,\end{aligned} \tag{4}$$

where $\tilde{G}(\omega) = (D-\omega^2)^{-1}$ is the mass-reduced Green's function and D is the dynamical matrix of the lattice. In terms of the usual lattice Green's function $G^0(\omega) = (\phi^0 - M^0\omega^2)^{-1}$, $\Delta Z(\omega)$ is expressed as

$$\Delta Z(\omega) = -\frac{1}{\pi}\frac{d}{d\omega}\operatorname{Im}\ln\tilde{D}(\omega) \tag{5}$$

with $\tilde{D}(\omega) = \det|G^0(\omega)(\phi - M\omega^2)|$, where ϕ (ϕ^0) and M (M^0) are the force constant matrix and mass, respectively, of the defect (ideal) crystal. Introducing the generalized phase shift as

$$\theta(\omega) = \tan^{-1}\left[\frac{-\operatorname{Im}\tilde{D}(\omega)}{\operatorname{Re}\tilde{D}(\omega)}\right] , \tag{6}$$

the change in density of states is

$$\Delta Z(\omega) = \frac{1}{\pi}\frac{d\theta(\omega)}{d\omega} \;. \tag{7}$$

The determinant $\tilde{D}(\omega)$ is restricted only to the perturbed region spanned by the defect and atoms directly affected by it.

The vibrational contribution to the internal energy is given by

$$E_{\text{vib}}(T) = \sum_{\alpha} \varepsilon(\omega_\alpha, T) \;, \tag{8}$$

with

$$\varepsilon(\omega_\alpha, T) = \hbar\omega_\alpha\left[\frac{1}{2} + \frac{1}{e^{\hbar\omega_\alpha/kT} - 1}\right] , \tag{9}$$

where ω_α are the eigenfrequencies of the lattice and k is the Boltzmann constant. Introducing the frequency spectrum

$$E_{\text{vib}} = \int_0^\infty \varepsilon(\omega, T) Z(\omega) d\omega \;, \tag{10}$$

the change in energy due to the presence of a single defect, i.e., formation energy is given by

$$\Delta E_{\text{vib}} = \int_0^\infty \varepsilon(\omega, T)\Delta Z(\omega) d\omega \;, \tag{11}$$

where $\Delta Z(\omega)$ is given by Eq. (7). In terms of the phase shift $\theta(\omega)$ the formation energy is

$$\Delta E_{\text{vib}} = \frac{1}{\pi}\int_0^\infty \varepsilon(\omega, T)\frac{d\theta}{d\omega} d\omega \;. \tag{12}$$

We break the integral in Eq. (12) into two parts to give

$$\begin{aligned}\Delta E_{\text{vib}} = {}& \frac{1}{\pi}\int_0^{\omega_{\max}} \varepsilon(\omega, T)\frac{d\theta}{d\omega} d\omega \\ &+ \int_{\omega_{\max}}^\infty \varepsilon(\omega, T)\Delta Z(\omega) d\omega \;,\end{aligned} \tag{13}$$

where $\omega_{\max}$ is the maximum frequency of the lattice. Above the maximum frequency $\Delta Z(\omega)$ has a δ function at the possible localized mode frequencies ω_l and, therefore, the second part is integrated to give $\sum_l \varepsilon(\omega_l, T)$, while the first part is integrated by parts with the result

$$\Delta E_{\text{vib}} = -\frac{\hbar}{2\pi}\int_0^{\omega_{\max}} \theta(\omega)\left[\coth\left[\frac{\hbar\omega}{2kT}\right] - \left[\frac{\hbar\omega}{2kT}\right]\operatorname{cosech}^2\left[\frac{\hbar\omega}{2kT}\right]\right] d\omega + \frac{1}{\pi}\theta(\omega_{\max})\varepsilon(\omega_{\max}, T) + \sum_l \varepsilon(\omega_l, T) \;. \tag{14}$$

Though one atom from the surface enters the lattice to form the interstitial dumbbell, the number of surface atoms still remains invariant and there is a loss of energy corresponding to a bulk atom. Making allowance for such a loss of bulk atoms the vibrational contribution to formation energy is given by

$$\begin{aligned}E_{\text{vib}}^F = {}& -\frac{\hbar}{2\pi}\int_0^{\omega_{\max}} \theta(\omega)\left[\coth\left[\frac{\hbar\omega}{2kT}\right] - \left[\frac{\hbar\omega}{2kT}\right]\operatorname{cosech}^2\left[\frac{\hbar\omega}{2kT}\right]\right] d\omega \\ &+ \frac{1}{\pi}\theta(\omega_{\max})\varepsilon(\omega_{\max}, T) + \sum_l \varepsilon(\omega_l, T) - 3\int_0^{\omega_{\max}} \varepsilon(\omega, T) Z_x^0(\omega) d\omega \;,\end{aligned} \tag{15}$$

where $Z_x^0(\omega)$ is the frequency spectrum of the ideal lattice normalized to unity.

The vibrational contribution to formation entropy is found to be[20]

$$S_{\mathrm{vib}}^F=\frac{k}{\pi}\int_0^{\omega_{\max}}\frac{\theta(\omega)}{\omega}\left[\frac{\hbar\omega}{2kT}\right]^2\operatorname{cosech}^2\left[\frac{\hbar\omega}{2kT}\right]d\omega+\frac{1}{\pi}\theta(\omega_{\max})\sigma(\omega_{\max},T)+\sum_l\sigma(\omega_l,T)-3k\int_0^{\omega_{\max}}\sigma(\omega,T)Z_x^0(\omega)d\omega\ , \tag{16}$$

where

$$\sigma(\omega,T)=\frac{\hbar\omega/kT}{e^{\hbar\omega/kT}-1}-\ln(1-e^{-\hbar\omega/kT})\ . \tag{17}$$

It may be noted that the important quantity in the determination of the vibrational contribution to formation energy and entropy is the phase shift $\theta(\omega)$ which contains the relevant dynamics of the defect crystal.

An alternative formulation using local representation of the total frequency spectrum can be employed to evaluate the change in thermodynamical quantities.[24] The total spectrum of the lattice can be expressed as the sum of the local frequency spectra of all the atoms in the lattice[22,25]

$$Z(\omega)=\sum_{m,i}Z_i^m(\omega)\ , \tag{18}$$

where

$$Z_i^m(\omega)=\frac{2\omega M^m}{\pi}\mathrm{Im}G_{ii}^{mm}(\omega) \tag{19}$$

is the local frequency spectrum of the atom m; $G_{ii}^{mm}(\omega)$ being the same site Green's function. Thus in terms of the local frequency spectrum of the defect, the energy and entropy of formation can be expressed as

$$E_{\mathrm{vib}}^F=\int_0^\infty[Z^d(\omega)-Z^0(\omega)]\varepsilon(\omega,T)d\omega\ , \tag{20}$$

$$S_{\mathrm{vib}}^F=\int_0^\infty[Z^d(\omega)-Z^0(\omega)]\sigma(\omega,T)d\omega\ , \tag{21}$$

where Z^d (Z^0) is the local frequency spectrum of the defect atom (a host atom). For the present case of dumbbell interstitials, the local spectrum of the defect is described by the resonant and localized modes alone and almost negligible contribution comes from the eigenfrequencies of the perfect lattice[21,22] and therefore, expressions (20) and (21) are especially suitable for the limiting cases of the low and high temperatures. For example, at very low temperatures

$$\varepsilon(\omega,T)\rightarrow\frac{\hbar\omega}{2},\quad kT\ll\hbar\omega \tag{22}$$

and only zero-point motion of the atoms contributes to the energy; as a consequence, low-temperature E_{vib}^F is dominated by the localized mode frequencies and contributions of low-frequency modes are not important. Of course with increasing temperatures the resonant mode contribution should be significant as a result of thermal vibrations. In the high-temperature limit the contributions of both the terms in Eq. (20) are of the order of $3kT$ and E_{vib}^F is vanishingly small.

III. ⟨100⟩-SPLIT INTERSTITIAL IN CU

The vibration of ⟨100⟩-split interstitials has been discussed in some detail previously.[21,22] The defect is described by an assumed vacancy at the origin and two interstitials at $(0,0,\pm d)$, where $2d=0.5a$ is the distance between the dumbbell atoms; a is the lattice constant. A nearest-neighbor defect model with central and noncentral force constants between dumbbell atoms $(f_\parallel,f_\perp)$, between a dumbbell atom and its nearest neighbors $(F_\parallel,F_\perp)$, and zero force between the assumed vacancy and neighbors has been employed. The force constants to be used in the calculation are those obtained by Zeller[26] in computer simulation:

$$\begin{aligned}&f_\parallel=8.14f_\parallel,\quad f_\perp=-0.66f_\parallel^0\ ,\\&F_\parallel=5.55f_\parallel^0,\quad F_\perp=-0.30f_\parallel^0\ ,\end{aligned} \tag{23}$$

TABLE I. Temperature dependence of energy, entropy, and free energy of formation of self-interstitials in Cu.

T (K)	E_{vib}^F (eV)	S_{vib}^F/k	E^F (eV)	S^F/k	ΔF (eV)
5	0.0386	0.0070	2.2075	3.0070	2.2062
25	0.0402	1.1374	2.2091	4.1374	2.2002
65	0.0451	2.6259	2.2140	5.6259	2.1825
100	0.0425	2.2872	2.2114	5.2872	2.1659
200	0.0294	1.2162	2.1983	4.2162	2.1257
400	0.0164	0.6613	2.1853	3.6613	2.0592
600	0.0112	0.5371	2.1801	3.5371	1.9973
800	0.0086	0.4921	2.1775	3.4921	1.9369
1000	0.0069	0.4711	2.1758	3.4711	1.8768
1200	0.0059	0.4598	2.1748	3.4598	1.8172
1355	0.0053	0.4543	2.1742	3.4543	1.7710

where $f_{\parallel}^{0}$ is the nearest-neighbor central force constant in the ideal lattice. In the calculation of the lattice Green's functions a modified Gilat-Raubenheimer method[27] was followed. The necessary phonon data were obtained from a sixth-neighbor axially symmetric model based on neutron scattering measurements of the dispersion curve.[28] After using the force constants given in Eq. (23) and the lattice Green's functions, the phase shift $\theta(\omega)$ is obtained. The phase shift is a continuous function of ω except for the jump discontinuities at the localized mode frequencies. A similar strong but continuous increase occurs at resonant frequencies. There are seven localized modes in addition to three well-known resonant modes of E_g, A_{2u} and E_u symmetry occurring at 1.1, 1.6, and 2.3 THz, respectively.[21,22]

Utilizing phase shift and the density of states of the ideal lattice, the vibrational contribution to the formation energy and formation entropy are easily calculated. To obtain the total energy and entropy of formation, one has to add the volume-dependent part to the respective vibrational parts. For formation entropy the volume contribution (image term) has already been evaluated and is equal to $3.0k$.[20] As regards the formation energy, extensive calculations using computer simulation have been carried out.[1–5,29–32] The typical values for fcc metals are 3–4 eV. In a recent elastic calculation Kornblit[33] has obtained a value 2.1680 eV for the formation energy for Cu. We have used this value of E_{elastic}^{F} to obtain the total formation energy. This choice seems to be in line with the reported experimental value 2.2 eV.[19] The choice of E_{elastic}^{F} has no special significance because our interest for the present is the temperature dependence of E^F. The values of formation energy and entropy, along with their vibrational parts, are presented in Table I for a number of temperatures below the melting point (1356 K). The table also contains the free energy of formation $\Delta F = E^F - TS^F$.

It is observed that the free energy of formation ΔF varies more or less linearly with temperature—decreasing with rising temperature. As expected, the vibrational energy and entropy of formation decreases with increasing temperature, attaining constant values at high temperatures, except at low temperatures where they initially increase giving maximum values at 65 K. The low-temperature variation is more pronounced in the case of formation entropy. The behavior of formation entropy is well understood if we keep in mind the fact that at low temperatures only low-frequency vibrational modes are effective so that the occurrence of low-lying resonant modes of self-interstitials leads to significant contribution to S_{vib}^{F}. Evidently, while discussing the point-defect properties, the temperature dependence of thermodynamic parameters must be taken into account, especially at low temperatures. Thus, for instance, in the evaluation of the possible contribution of self-interstitials to self-diffusion in metals at low temperatures, the used parameters E^F and S^F ought to be temperature dependent. As a matter of fact, with a maximum value of 0.045 eV for E_{vib}^{F} at 65 K and corresponding formation entropy $5.62k$, a correction factor, $e^{-(E_{\text{vib}}^{F} - T\Delta S)/kT}$ $(=2.782\times 10^{-3})$, with $\Delta S = S^F(T) - S^F$ is introduced in the diffusion constant $D_1 \sim e^{(S^F+S^m)/k} e^{-(E^F+E^m)/kT}$; E^m and S^m are energy and entropy of migration. Consequently, D_1 should be 2–3 orders of magnitude smaller than the estimated value using temperature-independent E^F and S^F. However, it must be remarked that this has no immediate practical importance for the present case of copper, since the measurements are generally at higher temperatures where the vibrational effects are inconsequential for the formation energy.

ACKNOWLEDGMENTS

The author is thankful to Bal K. Agrawal for his constant encouragement. Financial assistance from the Council of Scientific and Industrial Research, New Delhi, is gratefully acknowledged.

---

[1] J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. **120**, 1229 (1960).

[2] A. Seeger, E. Mann, and R. V. Jan, J. Phys. Chem. Solids **23**, 639 (1962).

[3] R. A. Johnson, J. Phys. F **3**, 295 (1973).

[4] A. Scholz and C. Lehmann, Phys. Rev. B **6**, 813 (1972).

[5] P. H. Dederichs, C. Lehmann, H. R. Schober, A. Scholz, and R. Zeller, J. Nucl. Mater. **69/70**, 176 (1978).

[6] P. Ehrhart, H. G. Haubold, and W. Schilling, Adv. Solid State Phys. **XIV**, 87 (1974).

[7] H. G. Haubold, in *Proceedings of the Conference on Foundamental Aspects of Radiation Damage in Metals, Gatlinburg, 1975*, edited by M. T. Robinson and F. W. Young, Jr. (U.S. Department of Commerce, Springfeld, Virginia, 1976), p. 268.

[8] P. Ehrhart, J. Nucl. Mater. **69/70**, 200 (1978).

[9] J. Holder, A. V. Granato, and L. E. Rehn, Phys. Rev. Lett. **32**, 1053 (1974).

[10] L. E. Rehn, J. Holder, A. V. Granato, R. R. Coltman, and F. W. Young, Jr., Phys. Rev. B **10**, 349 (1974).

[11] J. Holder, A. V. Granato, L. E. Rehn, Phys. Rev. B **10**, 363 (1974).

[12] K. H. Robrock and W. Schilling, J. Phys. F **6**, 303 (1976).

[13] V. Spiric, L. E. Rehn, K. H. Robrock, and W. Schilling, Phys. Rev. B **15**, 677 (1977).

[14] P. H. Dederichs, C. Lehmann, and A. Scholz, Phys. Rev. Lett. **31**, 1130 (1973).

[15] R. F. Wood and M. Mostoller, Phys. Rev. Lett. **35**, 45 (1975).

[16] H. R. Schober, V. K. Tewary, and P. H. Dederichs, Z. Phys. B **21**, 255 (1975).

[17] R. M. Nicklow, R. R. Coltman, F. W. Young, Jr., and R. F. Wood, Phys. Rev. Lett. **35**, 1444 (1975).

[18] F. W. Young, Jr., J. Nucl. Mater. **69/70**, 310 (1978).

[19] W. Schilling, J. Nucl. Mater. **69/70**, 465 (1978).

[20] P. N. Ram, Phys. Rev. B **30**, 6146 (1984).

[21] P. N. Ram and P. H. Dederichs, Z. Phys. B **42**, 57 (1981).

[22] P. N. Ram and P. H. Dederichs, Kernforschungsanlage Jülich

Report No. Jul 1725 1981 (unpublished).

[23] C. H. Leung and M. J. Stott, J. Phys. F 7, 1651 (1977).

[24] R. D. Hatcher, R. Zeller and P. H. Dederichs, Phys. Rev. B **19**, 5083 (1979).

[25] P. H. Dederichs and R. Zeller, in *Point Defects in Metals II,* Vol. 87 of *Springer Tracts in Modern Physics,* edited by G. Hohler and E. A. Niekisch (Springer, Berlin, 1979).

[26] R. Zeller (private communication).

[27] G. Gilat and L. J. Raubenheimer, Phys. Rev. **144**, 390 (1966).

[28] R. M. Nickow, G. Gilat, H. G. Smith, L. J. Raubenheimer, and M. K. Wilkinson, Phys. Rev. **164**, 972 (1967).

[29] R. A. Johnson and E. Brown, Phys. Rev. **127**, 446 (1962).

[30] M. Doyama and R. M. J. Cotterell, in *Lattice Defects and their Interactions,* edited by R. R. Hasiguti (Gordon and Breach, New York, 1966), p. 79.

[31] H. R. Schober, J. Phys. F **7**, 1127 (1977).

[32] K. M. Miller, Phys. Status Solidi B **98**, 387 (1980).

[33] L. Kornblit, Phys. Rev. B **22**, 1866 (1980).