Role of Self-Interstitial Atoms on the High Temperature Properties of Metals

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(Received 22 December 1997)

Equilibrium concentrations of self-interstitial atoms and divacancies have been determined in Cu by molecular dynamics computer simulations using embedded atom potentials. Near the melting temperature these concentrations are both $\sim 10^{-6}$. Owing to the higher mobility of the interstitial atoms, however, they contribute more to diffusion. In perfect, or pulse-heated crystals, spontaneous Frenkel pair production results in even higher interstitial concentrations. [S0031-9007(98)06040-2]

It is well known that vacancies are the predominant point defect in metals at elevated temperatures. Most diffusion-mediated properties of metals are indeed explained with reasonable accuracy solely in terms of vacancy mechanisms [1]. Less attention, outside the field of radiation damage, is usually paid to the other point defect, the self-interstitial atom. The high mobility of this defect and its large relaxation volume and diaelastic effect, however, may give interstitials influence on the properties of metals far beyond what their concentrations might suggest. For example, the curvature observed in Arrhenius plots of self-diffusion is usually attributed to divacancies, but it has also been suggested for Cu and Pt that interstitial diffusion may be the underlying cause [2]. Recently, a broader interest in the properties of self-interstitial atoms has arisen in response to the Granato theory of melting, in which melting has been ascribed to a transition from a solid with a small concentration of interstitial atoms $\sim 10^{-5}$ (which is far larger than usually assumed), to one with a high concentration of ~ 0.09 [3]. Central to these questions about the influence of interstitial atoms on materials properties is therefore obtaining a reliable estimate of their equilibrium concentrations.

The hope for experimentally measuring interstitial concentrations is not promising, primarily because vacancies are always present in far greater numbers, dominating measurements. On the other hand, modern semiempirical interatomic potentials have been found to be rather reliable in predicting point defect properties in metals [4]. We have thus turned to computer simulations using molecular dynamics (MD) to calculate the concentration of interstitials and assess their influence on high-temperature properties. Using these methods we find that the concentration of interstitials at the melting temperature in metals like Cu is surprisingly high, $\sim 1 \times 10^{-6}$ at equilibrium and even higher during rapid heating, with implications for several aspects of material behavior.

The difficulty in calculating the equilibrium concentrations of point defects is that both the formation enthalpy and entropy of the defect must be known. We have approached this problem by simply counting the number of interstitials in a molecular dynamics simulation of Cu as a function of temperature [5]. The small concentra-

tion of interstitials at the melting temperatures (T_m), and the rather long time required for equilibration, several nanoseconds, unfortunately stretches the practical limits of such calculations, even when employing scalable MD algorithms which are optimized for parallel supercomputers. A vast savings in computational requirements was achieved, however, by exploiting the periodic boundary conditions of the computational cell in that no sources or sinks of point defects and no nucleation sites for melting are present. This condition cannot be experimentally realized, but it enables the cell to be superheated by $\sim 15\%$, and allows for far higher concentrations of defects than are otherwise possible. Without sources, moreover, point defects come into equilibrium by Frenkel pair generation, yielding equal concentrations of vacancies and interstitial atoms. Since the product of the interstitial and vacancy concentrations is constrained by the law of mass action to be constant, the equilibrium concentration of interstitial atoms, as we will show, is further enhanced by an order of magnitude relative to when sources are present. With the large levels of point defects thus produced, accurate enthalpies and entropies of formation could be obtained.

We chose Cu as a model system for our study since it is one of the few metals for which various properties of both interstitial and vacancy defects are known, and self-diffusion data are available up to the melting point. Defects are recognized in the simulations by counting the number of atoms in Wigner-Seitz cells drawn about each lattice point, with an empty cell interpreted to be a vacancy and one with two atoms an interstitial. Rapid quenches (20–50 ps) of several test simulation cells to 0 K showed that interstitials and vacancies which are separated by at least two lattice constants are stable in the sense that they still exist after the quench. We therefore count only such defects as real lattice defects. We shall see later, however, that unstable Frenkel defects are also present and that they too influence the high temperature properties of the material.

The embedded atom method (EAM) potential used to describe interactions between atoms [6] was tested with respect to a wide range of vacancy and interstitial properties (see Table I). The defect formation enthalpies and relaxation volumes were obtained using a 0 K relaxation

TABLE I. Defect properties obtained in the present work, and experimental values where ones are available. The statistical uncertainty is given only for quantities for which it is significant compared to the number of digits given. The subscript v denotes the vacancy, $2v$ the divacancy, and i the interstitial. The relaxation volumes ΔV are given in units of the volume per atom in the lattice $\Omega = 11.8$ Å^3.

Quantity	Present work	Experiment
ΔV_v	$-0.23\,\Omega$	$-0.25 \pm 0.05\,\Omega$ [7]
H_v^f	1.27 eV[a]	1.28 ± 0.05 eV [7]
S_v^f	$(2.3 \pm 0.2)k$	$2.35k$ [1]
H_v^m	0.77 eV[a]	0.70 ± 0.02 eV [7]
$w_{0,v}$	510 ± 10 jumps/ps	
ΔV_{2v}	$0.46\,\Omega$	
H_{2v}^f	2.37 eV	
S_{2v}^f	$(5 \pm 1)k$	
H_{2v}^m	0.26 eV	
$w_{0,2v}$	10.0 ± 0.2 jumps/ps	
ΔV_i	$2.0\,\Omega$	$1.55 \pm 0.20\,\Omega$ [7]
H_i^f	3.2 eV	$2.8 - 4.2$ eV [7]
S_i^f	$(15 \pm 2)k$	
H_i^m	0.081 eV	0.117 eV [7]
$w_{0,i}$	7.6 ± 0.3 jumps/ps	
$d\ln C_{44}/dc_i$	-31	-31 [8]
$d\ln C'/dc_i$	-11	-15 [8]
$d\ln B/dc_i$	-2	0 ± 1 [8]
T_{melt}	1295 ± 5	1356

[a]Potential fitted to this property.

and the migration properties by simulating the migration of single defects (see below). The formation entropies were obtained from the high-temperature runs in large cells described below. Of particular note is excellent agreement with experiment of the dependence of the elastic moduli on interstitial concentration, $d\ln C_{ij}/dc_i$ [8], as the large change in the shear modulus, C_{44}, is central to the Granato theory. The melting point was obtained from simulating a liquid and solid in equilibrium. Our EAM potential reproduces most experimental values to within about 10%. We also found that the low-temperature formation and migration enthalpies were consistent with the equilibrium concentrations and diffusion coefficients obtained in the high-temperature runs of large systems, showing that equilibrium was indeed established in the high-temperature simulations.

We feel the overall accuracy of the potential gives a good description of a Cu-like fcc metal, if not precisely Cu. Since there is nothing special about the Cu diffusion properties compared to similar metals, the qualitative results can be expected to have bearing on other fcc metals as well. Test simulations of Frenkel pair concentrations in Cu and Au (at a few selected temperatures) with other EAM potentials [9] confirmed this expectation. For the other Cu potential we obtained the same Frenkel pair concentrations within the uncertainties as in

our main Cu simulations. In Au simulated with the experimental vacancy concentration we obtained interstitial concentrations of roughly one-tenth the vacancy concentration slightly above the melting temperature.

We use the following notation in our study. The jump rate w and equilibrium concentration c of one defect type are written [10]

$$w = Z\nu e^{S^m/k} e^{-H^m/kT}, \qquad (1)$$

$$c = g e^{S^f/k} e^{-H^f/kT}, \qquad (2)$$

where Z and g are geometrical factors, ν is a lattice vibration rate, and k is Boltzmann's constant. H^m and H^f are the defect formation and migration enthalpy, and S^f and S^m the formation and migration entropies, respectively. The self-diffusion due to a single defect type is $D = \frac{1}{6} r^2 f c w$, where r is the jump distance in the lattice and f is the jump correlation factor [10]. For convenience, we introduce the term $w_0 = Z\nu \exp(S^m/k)$.

The migration enthalpies H^m and preexponential factors w_0 of each defect type were obtained by determining their jump rates in small simulation cells over long time periods. For the vacancy and divacancy we followed the position of the defect itself to obtain the jump rates. Since interstitial migration is complex and very rapid at high temperatures, it is difficult to distinguish successive independent jumps. We therefore *defined* the number of interstitial jumps to be $N = R^2/r^2 f_i$, where R^2 is the total atom displacement in a cell with a migrating interstitial, r the nearest-neighbor distance, and $f_i = 0.44$ the correlation factor for interstitial migration in fcc metals [10]. The use of this value for f_i does not necessarily correspond to the migration at high temperatures, but the description is sufficient for our discussion of self-diffusion presented later. The migration results are illustrated in Fig. 1.
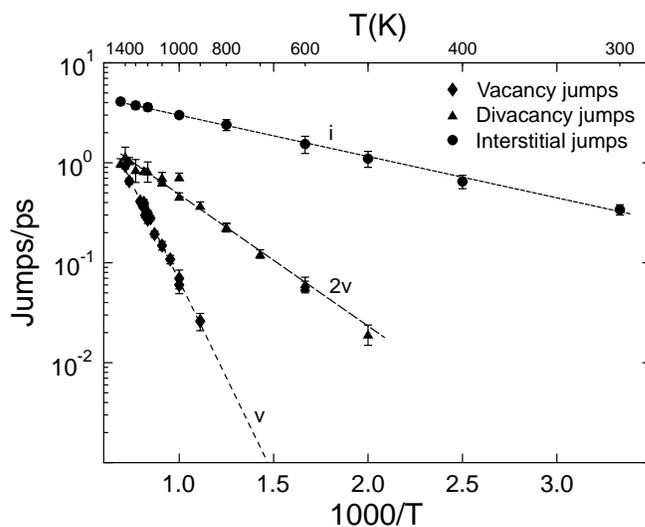

FIG. 1. Jump rates of intrinsic defects in copper. The interstitial migration is derived from the total atom displacement and does not necessarily correspond to uncorrelated independent jumps (see text).

To obtain the formation entropy and equilibrium concentration of vacancies we simulated a system of 250 000 Cu atoms with about equally large liquid and solid parts in equilibrium at the melting point. This simulation was run for ~3 ns, which was long enough for equilibration. The liquid acted as a source and sink for defects. The simulations gave an equilibrium vacancy concentration of $11 \pm 1 \times 10^{-5}$, yielding $S_v^f = (2.3 \pm 0.2)k$. At the beginning of the same run, we inserted ten interstitials in the crystalline zone. All interstitials vanished from the crystalline zone within 1 ns, and no interstitials were seen to reenter it, giving an upper limit of $c_i(T_m) \lesssim 10^{-6}$ for the interstitial concentration.

A more precise determination of the interstitial concentration was obtained by simulating perfect crystalline Cu arranged in periodic cubic cells containing 32 000 or 131 000 atoms. Each of the simulations was carried out until an equilibrium value of the examined quantity was obtained, requiring times between 0.5 and 2.5 ns. Because of the large computational cost of these simulations, the number of temperatures used remained limited. Some of the simulations involved initially defect-free single-crystalline Cu, others Cu containing the equilibrium number of vacancies (since the potential accurately reproduces S_v^f and H_v^f, our vacancy concentrations correspond closely to the experimental ones). We denote the former kind of simulated copper Cu$_{\text{perf}}$ and the latter Cu$_{\text{vac}}$. The use of periodic crystalline simulation cells allowed the significant advantage of superheating alluded to earlier, with temperatures as high as $T_m/T = 0.85$ possible without melting the cell. It is noteworthy that this degree of superheating agrees remarkably well with the Granato theory which predicts that the solid Cu phase is no longer metastable above $1.15 T_m$ [3].

The defect concentration results are illustrated in Fig. 2 for both Cu$_{\text{vac}}$ and Cu$_{\text{perf}}$. For Cu$_{\text{perf}}$ the vacancy and interstitial concentrations are, of course, equal. Since the Frenkel pair concentration can be written

$$C_{\text{FP}} = g_i^{1/2} e^{(S_i^f + S_v^f)/2k} e^{-(H_i^f + H_v^f)/2kT} \quad (3)$$

the interstitial formation entropy and enthalpy can be obtained from the concentration data after subtracting the separately determined vacancy quantities. For the entropy we obtain $S_i^f = (15 \pm 2)k$. This large value of S_i^f is a necessary condition in the Granato theory of melting, but heretofore was largely unknown (Granato estimated a value between $10k$ and $20k$ [3]). It is noteworthy that the value $15k$ compares closely with the experimentally determined value of $S_i^f = (16 \pm 2)k$ obtained for solid krypton using lattice parameter measurements [11]. Recent *ab initio* MD simulations also indicate that the fcc dumbbell can have a high formation entropy due to local vibrational models [12], but this work does not give a value for the entropy. Finally we note that the same value of S_i^f is obtained in Cu$_{\text{vac}}$, although the uncertainties in
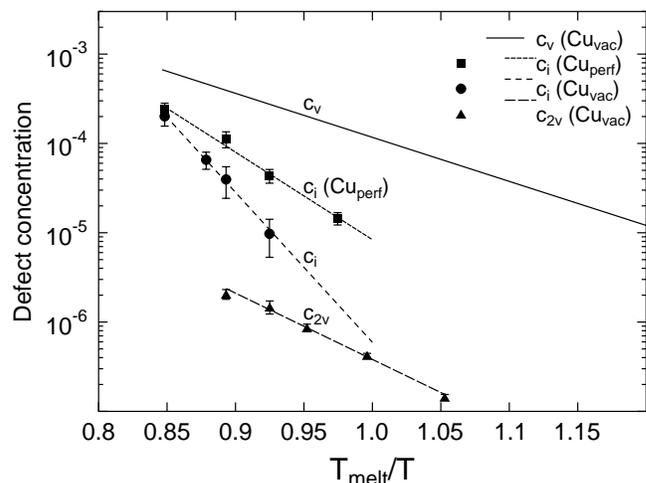

FIG. 2. Concentrations of vacancies (c_v), divacancies (c_{2v}), and interstitials (c_i) in defect-free single-crystalline copper Cu$_{\text{perf}}$ and copper containing the equilibrium vacancy concentration Cu$_{\text{vac}}$. The concentration of vacancies in Cu$_{\text{vac}}$ is shown for comparison with the interstitial and divacancy concentrations obtained from our simulations.

these calculations are greater owing to the far smaller concentrations of interstitials.

Obtaining good statistical averages of the number of divacancies [13] directly in Cu$_{\text{vac}}$ was not possible. Since the divacancy concentration is proportional to c_v^2 [1], we instead determined the divacancy concentration at any given temperature by increasing the vacancy concentration beyond the equilibrium number to obtain $c_{2v}(c_v)$. By fitting a parabolic function to the divacancy concentrations for high values of c_v, we could then extrapolate the divacancy concentration to the lower equilibrium values of c_v. Using Eq. (2) and $g_{2v} = 6$ we obtained a divacancy formation entropy of $(5 \pm 1)k$. The small divacancy concentration, which is similar to that of interstitials at T_m, agrees well with recent experiments [14].

The results of these simulations have several implications for the high-temperature properties of solid metals. It supports the long-held assumption that Frenkel pair production during rapid heating of high-quality crystals provides the most rapid path back to equilibrium defect concentration [15]. Note that the production rate of Frenkel pairs in Cu near T_m is $\sim 4\pi r/\Omega D_i c_i^2$, or ~ 500 atom fraction/s (r is the interstitial-vacancy recombination radius). Similarly, fast heat pulses of metal surfaces could act as a generator of Frenkel pairs with equal numbers of interstitials and vacancies flowing into the bulk. Small defects observed experimentally during rapid heating of nearly perfect crystals may well be explained by this mechanism [16].

We also studied how the presence of self-interstitials in the cell affects self-diffusion (see Fig. 3). In Cu$_{\text{perf}}$ self-diffusion presumably derives entirely from the Frenkel pairs, with the rapidly migrating interstitial dominating the diffusion process. Comparison of the data for
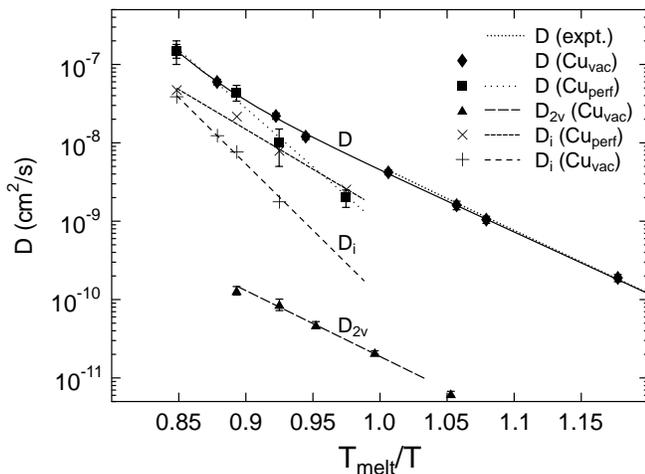
FIG. 3. Self-diffusion in defect-free single-crystalline copper Cu_{perf} and copper containing the equilibrium vacancy concentration Cu_{vac}. Except for the experimental diffusion $D(expt)$, the lines are exponential fits to the data, in some cases extrapolated down to the melting point.

self-diffusion in Cu_{perf}, with the estimate $D = D_i c_i$ (crosses in Fig. 3), shows this behavior at temperatures below $T_m/T \sim 0.96$ K, but not above, where the self-diffusion is higher than expected. Detailed analysis of the self-diffusion in Cu_{perf} at the highest temperature treated, $T_m/T = 0.85$, indicated that diffusion becomes enhanced by short-lived, unstable Frenkel pairs separated by less than $2a_0$. These close Frenkel pairs caused rearrangements of five or more atoms before annihilating. This diffusion, while not previously observed at equilibrium in fcc metals, was reported in simulations of Na and fluorites [17,18] and described as a cycle of replacement jumps initiated by the creation of an unstable Frenkel pair.

The self-diffusion coefficient of Cu_{vac} calculated here agrees well with experiments up to the melting point (see Fig. 3), providing confidence in the reliability of the potential. Around and above the melting point the self-diffusion exhibits clear curvature. This curvature, which is also observed in experiments, is usually attributed to divacancies [1]. Our calculations show, however, that the contribution from interstitial atoms is ~ 7 times larger than that of divacancies at T_m, and about the correct magnitude to explain the curvature in the experimental data. As in Cu_{perf}, we found that unstable Frenkel pairs contribute significantly to the extra self-diffusion at the highest temperatures, and at least a little at and below the melting temperature, but we cannot presently give a statistically significant value for their relative contribution to the total diffusion.

To summarize, we have obtained defect concentrations and the self-diffusion in copper from molecular dynamics computer simulations. The results indicate that the concentration of interstitial atoms is higher than previously assumed and that interstitial atoms are more likely than divacancies to explain the curvature in Arrhenius plots of diffusion in Cu. We showed that spontaneous Frenkel

pair generation in Cu is large and that it could possibly have a strong influence on rapidly heated metals. The high interstitial concentration and the maximum allowable superheating both find good agreement with the recent model proposed by Granato to explain thermodynamical properties of liquids and solids.

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