Monovacancy and divacancy formation and migration in copper: A first-principles theory

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The formation and migration of monovacancies and divacancies in copper have been studied from first-principles in order to resolve the discrepancies between previously published experimental and theoretical data. The monovacancy and divacancy formation, migration and binding enthalpies as well as the formation volumes have been calculated in the framework of a plane-wave pseudopotential implementation of the density functional theory, with full structural relaxations included. The monovacancy and divacancy formation entropies have been estimated from experimental data by performing a least-squares analysis. We show that the complete set of first-principles data, taking into account the presence of both vacancies and divacancies as well as the temperature dependence of the formation enthalpies and entropies allow one to reproduce the Arrhenius plot of the total vacancy concentration and the diffusion coefficient, both in good agreement with the most accurate experiments.

I. INTRODUCTION

It is of vital importance to understand the formation of vacancies and divacancies in technologically important materials like copper due to their influence on such physical properties as diffusion,[1,2] electrical conductivity[3,4] and heat capacity.[4,5] Unfortunately, available experimental and theoretical values of the monovacancy and divacancy formation, migration and binding enthalpies as well as the formation entropies in copper exhibit remarkable disagreements. Experimental and theoretical estimates of these parameters, reported in a large body of publications, are collected in Table I.

For copper in its ground state face centered cubic (fcc) structure the most accurate to date experimental technique for the determination of the vacancy concentration is the differential dilatometry, often referred to as the absolute technique. The absolute technique makes use of the vacancy induced simultaneous change of the lattice constant, $\Delta a / a_0$ and the macroscopic length, $\Delta L / L_0$, of the sample measured as functions of temperature. Here L_0 and a_0 are the corresponding reference values at room temperature. If the concentration of thermally generated self-interstitials is negligible, which is reported to be true for copper,[4,6] then the total concentration of vacancies as a function temperature, T, is given by[6]

$$C_v(T) = 3\left(\frac{\Delta L(T)}{L_0} - \frac{\Delta a(T)}{a_0} \right). \tag{1}$$

The absolute technique is supposed to be highly accurate at temperatures close to the melting point. The concentration of monovacancies and divacancies are denoted as C_{1v} and C_{2v}, respectively, and they can be calculated from simple thermodynamics as

$$C_{1v}(T) = \exp\left(-\frac{H_{1v}^F}{k_B T} + \frac{S_{1v}^F}{k_B} \right), \tag{2}$$

and

$$C_{2v}(T) = 6 \exp\left(-\frac{H_{2v}^F}{k_B T} + \frac{S_{2v}^F}{k_B} \right). \tag{3}$$

In Eq. (2) and (3) H_{1v}^F is the monovacancy formation enthalpy, H_{2v}^F the divacancy formation enthalpy, S_{1v}^F the monovacancy formation entropy, S_{2v}^F the divacancy formation entropy and k_B the Boltzmann constant. Notice that H_{1v}^F, H_{2v}^F, S_{1v}^F and S_{2v}^F are usually supposed to be independent of temperature. Both monovacancies and divacancies contribute to the total concentration of vacancies (vacancy clusters that contain more than two atoms are expected to be of minor importance) and accordingly

$$C_v = C_{1v} + 2C_{2v}. \tag{4}$$

Hehenkamp *et al.*[6] used the absolute technique to determine the total vacancy concentration in copper as a function of temperature, however, they assumed the effect of divacancies to be small and therefore neglected the second term in Eq. (4). Thus their least-squares fit of experimental data to Eq. (4) only yielded values of H_{1v}^F and S_{1v}^F. The absolute technique was also applied in measurements by Simmons and Balluffi,[7] but they did not include divacancies into their analysis either.

Kluin[8] added more data points to the measurements of Hehenkamp *et al.*[6] and in his analysis, which accounts for the existence of divacancies, he chose $H_{1v}^F = 1.15$ eV as a fixed parameter. Later Neumann *et al.*[9] argued that $H_{1v}^F = 1.15$ eV was too large and that Kluin[8] consequently overestimated H_{2v}^F and S_{2v}^F. Neumann *et al.*[9] also pointed out that their parameter set resulted in an equally good fit to the experimental data used in Ref. 8.

TABLE I. A collection of experimental and theoretical vacancy parameters in copper. The values of parameters from Ref. 12 are all high temperature values, except the value of H_{1v}^F within parentheses.

	Experiment	Previous calculations
H_{1v}^F(eV)	1.03 (Ref. 9), 1.19±0.03 (Ref. 6), 1.17±0.11 (Ref. 7), 1.03 (Ref. 10), 1.03 (Ref. 11), 1.15 (Ref. 8)	1.13 (Ref. 13),[a] 1.33 (Ref. 14),[b] 1.2332 (1.09) (Ref. 12),[c] 1.27[d] (Ref. 16)[e]
H_{2v}^F(eV)	1.826 (Ref. 9), 1.94 (Ref. 10), 1.86 (Ref. 11), 2.15±0.10 (Ref. 8)	2.3252 (Ref. 12), 2.37 (Ref. 16)
H_{2v}^B(eV)	0.234 (Ref. 9), 0.12 (Ref. 10), 0.20 (Ref. 11), 0.15±0.10 (Ref. 8)	0.096 (Ref. 14), 0.17 (Ref. 16), 0.076 (Ref. 15)[f]
H_{1v}^M(eV)	1.024 (Ref. 9), 1.06 (Ref. 10), 1.06 (Ref. 11)	0.77[d] (Ref. 16)
H_{2v}^M(eV)	0.64 (Ref. 9), 0.64 (Ref. 10), 0.64 (Ref. 11)	0.26 (Ref. 16)
Ω_0(Å³)	11.9 (Ref. 5)	11 (Ref. 14)
S_{1v}^F/k_B	1.08 (Ref. 9), 3.0±0.03 (Ref. 6), 1.5±0.5[g] (Ref. 7), 0.3 (Ref. 10), 1.4 (Ref. 11), 2.5 (Ref. 8)	1.4214 (Ref. 12), 2.3±0.2 (Ref. 16)
S_{2v}^F/k_B	5.0 (Ref. 9), 2.6 (Ref. 10), 4.9 (Ref. 11), 6.7±1.0 (Ref. 8)	2.8395 (Ref. 12), 5±1 (Ref. 16)

[a]Full-potential KKR, GGA.
[b]LDA+ASA+M.
[c]Pair potentials.
[d]The potential was fitted to this value.
[e]Embedded atom method.
[f]Full-potential KKR, LDA.
[g]Fixed value estimated from theory.

In Ref. 9 Neumann *et al.* analyzed the data of Hehenkamp *et al.*[6] with the effect of divacancies included. Neumann *et al.*[9] fitted H_{1v}^F, H_{2v}^F, S_{1v}^F and S_{2v}^F to experimental data. The results were $S_{1v}^F/k_B=2.1\pm0.8$, $H_{1v}^F=1.11\pm0.06$ eV, $S_{2v}^F/k_B=12_{-12}^{+19}$ eV and $H_{2v}^F=2.67\pm2.26$ eV. The standard deviation from the experimental data was $\sigma=0.126$. These results are hardly useful, due to the large error bars, especially for H_{2v}^F. From these results it is also impossible to give a fair estimate of the divacancy binding energy,

$$H_{2v}^B = 2H_{1v}^F - H_{2v}^F, \qquad (5)$$

and therefore it is difficult to conclude whether the interaction between nearest neighbour vacancies is attractive or repulsive. In order to improve the accuracy, Neumann *et al.*[9] used an approach where two of the parameters were deduced from experimental data of the temperature dependence of the diffusion coefficient, D.[9] D can be calculated as

$$D(T) = D_{1v}^0 \exp\left(\frac{-Q_{1v}}{k_B T}\right) + D_{2v}^0 \exp\left(\frac{-Q_{2v}}{k_B T}\right). \qquad (6)$$

In Eq. (6),

$$Q_{1v} = H_{1v}^F + H_{1v}^M \qquad (7)$$

and

$$Q_{2v} = H_{2v}^F + H_{2v}^M, \qquad (8)$$

where H_{1v}^M and H_{2v}^M are the monovacancy and divacancy migration enthalpies, respectively. D_{1v}^0 and D_{2v}^0 are the preexponential factors and are assumed to be constant. Neumann *et al.*[9] estimated $D_{1v}^0=0.131\times10^{-4}$ m² s⁻¹, Q_{1v}

$=2.054$ eV, $D_{2v}^0=4.56\times10^{-4}$ m² s⁻¹ and $Q_{2v}=2.466$ eV from diffusion data. In order to calculate H_{1v}^M and H_{2v}^F, the values $H_{1v}^M=1.03$ eV and $H_{2v}^M=0.64$ eV had to be obtained from previous experiments. The vacancy formation entropies could then be derived from the enthalpies and the vacancy concentration data. The accuracy of these estimates is partly determined by the accuracy of the vacancy concentration measurement and partly by the error in Q_{1v}, Q_{2v}, H_{1v}^F and H_{2v}^M, which may not be negligible.

The vacancy parameters reported in Refs. 10 and 11 are also presented in Table I, though it should be stressed that these measurements are not considered to be as accurate as the measurements in Ref. 6.

Theoretical studies of vacancies in copper may be divided into two groups. The first group comprises studies based on first-principles approaches while the second group relies on semi-empirical methods with one or more parameters fitted to experiment. The recent theoretical results are compiled in Table I, and one may notice that the disagreement among them is rather dramatic. The reasons behind such a disagreement lie in the different techniques (first-principles or semi-empirical) and in different approximations within similar first-principles approaches [i.e., whether the local density approximation (LDA) or the generalized gradient approximation (GGA) was used; whether relaxations were taking into account or not, etc.].

In particular, Hoshino *et al.*[13] obtained a value of H_{1v}^F from a first-principles full-potential Korringa-Kohn-Rostoker method (FP-KKR) with the exchange and correlation described by the generalized gradient approximation (GGA). Korzhavyi *et al.*[14] included a correction for the charge deple-

tion around vacancies to the atomic-sphere approximation (ASA), a first-principles method which was denoted ASA +M, and calculated H_{1v}^F, H_{2v}^B, Ω_{1v}^F and Ω_{2v}^F within the local density approximation (LDA) to the exchange and correlation energy. Table I also contains results from studies by Klemradt et al.[15] (FP-KKR, LDA). Notice that relaxations were taken into account by Hoshino et al.[13] but they were neglected by Korzhavyi et al.[14] and Klemradt et al.[15] It is important to emphasize that neither of the previous first-principles studies reports a complete set of vacancy parameters for copper.

On the other hand such sets were obtained within semi-empirical methods, in particular by Nordlund and Averback,[16] who applied the embedded atom method (EAM), and by Sandberg and Grimvall,[12] who used a pair potential approximation to calculate high temperature values of H_{1v}^F, H_{2v}^F, Ω_{1v}^F, Ω_{2v}^F, S_{1v}^F and S_{2v}^F. In both these works relaxations were taken into account. We especially notice the publication by Sandberg and Grimvall,[12] who pointed out the importance of the temperature dependence of the vacancy formation enthalpies and entropies at temperatures close to the melting point and attributed it to the anharmonic vibrations. Based on their findings Sandberg and Grimvall also concluded that the effect of divacancies is negligible in copper. We notice, however, that the latter conclusion, which is rather crucial, is still based on the technique making use of parameters fitted to experiment. Therefore a re-check based on an accurate first-principles approach would be desirable.

Here we present the results of first-principles calculations of H_{1v}^F, H_{2v}^F, H_{2v}^B, H_{1v}^M and H_{2v}^M that can be directly compared to experimental results and available theoretical data. To the best of our knowledge this is the first investigation that reports a complete set of vacancy parameters for copper based on accurate first-principles methods. S_{1v}^F and S_{2v}^F are very cumbersome to calculate directly from first-principles and therefore we try to adopt the experimental approach, in which entropies are obtained from a least-squares analysis of the experimental data of C_v. Further, we incorporate temperature dependences of H_{1v}^F, H_{2v}^F, S_{1v}^F and S_{2v}^F, obtained in Ref. 12. In addition to S_{1v}^F and S_{2v}^F the model that is used to interpret the experimental data of C_v, i.e., Eqs. (2)–(4), include H_{1v}^F and H_{2v}^F which are known from our theoretical calculations. The same idea can be used to estimate the pre-exponential factors in Eq. (6), which describe the self-diffusion coefficient. This enables us to produce the Arrhenius plots of the temperature dependences of the total vacancy concentration and the self-diffusion coefficient and compare them to experimental results. In experimental analysis of vacancy properties the formation and migration enthalpies must also be obtained indirectly from C_v and D. However, according to the above reasoning, a theoretical calculation could also be used as a tool to reduce the number of free parameters that needs to be estimated from a limited amount of experimental data.

The layout of this paper will be as follows. In Sec. II the computational details are described, Section III contains the results and finally our conclusions are presented in Sec. IV.

II. METHOD OF CALCULATION

Our calculations are based on a plane-wave pseudopotential implementation of the density functional theory with the exchange and correlation described by the generalized gradient approximation (GGA),[17–19] which reproduces bulk properties of copper, such as the equilibrium lattice parameter and bulk modulus, in very good agreement with experiment. In Ref. 20 Carling et al. showed that the GGA fails to reproduce vacancy formation enthalpies in aluminum due to correlation effects near electronic edges and introduced an empirical correction for this deficiency. This effect is expected to be of less importance in copper since the $3d$ valence electrons in copper are more localized than the sp valence electrons in aluminum, which reduces the electronic edges around vacancies. Nevertheless, the test showed that the agreement with experiment is slightly improved when the correction is taken into account. Therefore we incorporated this correction into our calculations.

A. Supercell calculations

The vacancy parameters were calculated by using a supercell with a constant number of lattice sites. A fcc based supercell containing 48 lattice sites was considered to yield sufficiently accurate and converged results. In order to justify this choice H_{1v}^F, H_{2v}^F, H_{2v}^B and H_{1v}^M were calculated for a supercell containing 64 sites. The divacancy formation volume was calculated to be 17.3 Å^3 for the 64 site supercell and 17.9 Å^3 for the 48 site supercell. Since the enthalpies of the two cases differ by at most 0.08 eV, which is at least better than experimental accuracy, we conclude that the results are converged already for a supercell with 48 sites. Calculations of formation enthalpies on a smaller supercell with 32 sites differs by at most 0.04 eV from the 48 site case and thus provide further support for the above conclusion. For H_{2v}^B there is a rather large relative uncertainty, which follows from the fact that H_{2v}^B is calculated as a difference between two big numbers which are of the same magnitude. However this parameter is not used to produce the Arrhenius plots and plays only a minor role for the present study. Therefore no attempts to further improve the convergence was made. Another way to determine whether the results have converged, is to study the relaxation of atoms in different coordination shells around vacancies. For the vacancy systems that are studied in this paper the relaxations are rather small already in the first coordination shell (as expected, the displacements are larger for the systems with a migrating atom) and display a substantial reduction in the second shell. Further, the relaxations fall off, indicating that the convergence with respect to the size of the supercell is fast and a 48 site supercell ought to suffice.

Let N be the number of lattice sites of the supercell and $E(N_v, \Omega_{N_v})$ the total energy of the supercell with $N - N_v$ atoms and N_v vacancies at a relaxed unit cell volume of Ω_{N_v} that corresponds to an external pressure p. For a system where the number of atoms is kept constant while the number of vacancies is allowed to change, H_{1v}^F and H_{2v}^F can be calculated as

$$H_{1v}^F = E(1, \Omega_1) - \frac{N-1}{N} E(0, \Omega_0) + p(N\Omega_1 - (N-1)\Omega_0)$$

(9)

and

$$H_{2v}^F = E(2, \Omega_2) - \frac{N-2}{N} E(0, \Omega_0) + p(N\Omega_2 - (N-2)\Omega_0). \tag{10}$$

In this paper all calculations are done for zero pressure and in this case $H_{1v}^F = E_{1v}^F$ and $H_{2v}^F = E_{2v}^F$. The monovacancy and divacancy formation volumes are given by

$$\Omega_{1v}^F = N\Omega_1 - (N-1)\Omega_0 \tag{11}$$

and

$$\Omega_{2v}^F = N\Omega_2 - (N-2)\Omega_0. \tag{12}$$

The migration enthalpy for monovacancies and divacancies can be expressed as

$$H_{1v}^M = H_{1v}^{F,S} - H_{1v}^{F,G} \tag{13}$$

and

$$H_{2v}^M = H_{2v}^{F,S} - H_{2v}^{F,G}. \tag{14}$$

In Eq. (13) and (14) the superscript S refers to the saddle point position of the migrating atom and the superscript G refers to the ground-state position. For the monovacancy case a simple symmetry argument implies that the saddle point must be located half-way between the vacancy and the migrating atom. Similarly, for the divacancy system the saddle point should be located at the center of the triangle formed by the two vacancies and the lattice site of the migrating atom. These conclusions were, in particular, confirmed by calculations by Tajima *et al.*[21] H_{2v}^B is defined in Eq. (5) and this definition implies that positive values of H_{2v}^B correspond to attraction between vacancies.

B. k-point sampling

For the supercell with 48 sites, k-point grids of 40, 40, 80, 128 and 256 irreducible k points were used for the bulk, the monovacancy, the divacancy, the monovacancy migration and the divacancy migration calculations. The k points were generated by a Monkhorst-Pack routine $(8 \times 8 \times 8)$[22] and the different number of k points is due to different irreducible wedges of the corresponding Brilluoin zones. A k-point grid of 75 points (Monkhorst-Pack $10 \times 10 \times 10$) produced a decrease of the monovacancy formation energy by $\approx 1.5\%$ (unrelaxed values) and thus the result can be considered to be well converged for 40 k points. The increase of the number of k points that were used for the divacancy, the monovacancy migration and the divacancy migration calculations ensured that these results were also well converged.

C. Relaxations

When vacancies are introduced the lattice structure and the cell volume, i.e. the lattice constant, relax, though these effects are known to be rather small for metals like copper crystallizing in close-packed structures.

In the structural relaxation the positions of the atoms were allowed to change. A conjugate-gradient algorithm was used. For the calculations of H_{1v}^M and H_{2v}^M all atoms, except the migrating atom itself, were allowed to relax into positions that correspond to a local energy minimum. For all other structural relaxation calculations all atoms were allowed to relax.

Volume relaxation was done by calculating the total energy for three different lattice constants about the equilibrium bulk value and then determining the minimum of a parabolic curve that was fitted to the three energy values. This minimum was taken as the equilibrium lattice constant of the system.

Full relaxation was performed by calculating the total energies for three lattice constants about the equilibrium value, of which the middle value, closest to equilibrium, was structurally relaxed. The other two values were obtained by using the relaxed structure of the middle value. Ideally the last two values should also be structurally relaxed but, since the error due to this simplification was estimated to be rather small (forces were found to be negligible for all atoms) and the gain in performance was considerable, this simplification was accepted.

D. Estimation of entropies

S_{1v}^F and S_{2v}^F were estimated by performing a nonlinear least-squares fit of Eq. (4) to the total vacancy concentration data in Ref. 6. In Eq. (4) our first-principles values of the enthalpies were used. The least-squares analysis was done both with and without weights. The weights account for the uncertainties of the measurements at low temperatures. The standard deviations of the experimental points from the fitted equation, as well as the standard deviations of S_{1v}^F and S_{2v}^F, were calculated.

E. Temperature dependences of formation enthalpies and entropies

Temperature dependences of the formation enthalpies and entropies were taking from Sandberg and Grimvall,[12] with our first-principles values of the formation enthalpies used as the $T = 0$ K reference points. For the formation entropies the low temperature values were used as fitting parameters.

III. RESULTS

A. Bulk properties

The lattice constant and the bulk modulus were calculated for copper in the fcc structure and the results agreed well with the experimental data from Refs. 5 and 23 and the first-principles calculations in Ref. 13. We calculated the lattice constant to be 3.64 Å and the bulk modulus to be 143 GPa. The experimental reference values are 3.62 Å[5] and 138 GPa.[23]

B. Vacancy properties

In Table II the vacancy parameters from our first-principles calculations at $T = 0$ K are shown, both with and without relaxations, and Table I contains results from previously published calculations.

TABLE II. Present results for the vacancy parameters of copper at low temperature. Values within parentheses include the correction for the correlation effect near electronic edges (see the text).

	No relaxation	Full relaxation
H_{1v}^F(eV)	1.07 (1.13)	0.976 (1.04)
H_{2v}^F(eV)	2.10 (2.22)	1.89 (2.01)
H_{2v}^B(eV)	0.0335	0.0620
H_{1v}^M(eV)	1.16	0.718
H_{2v}^M(eV)	0.752	0.472
Ω_0(Å^3)	12.1	12.1
S_{1v}^F/k_B	1.41 (2.12)	0.347 (1.05)
S_{2v}^F/k_B	7.40 (8.05)	5.93 (6.76)

The difference between fully relaxed and unrelaxed results are rather small and do not qualitatively change the physical picture. Though, in the models for C_{1v} [Eq. (2)], C_{2v} [Eq. (3)] and D [Eq. (6)] the vacancy parameters are found in exponential expressions and thus we argue that the relaxed values should be used when trying to interpret experiments. Especially at high temperature rather small differences in the vacancy parameters can affect C_v and D significantly. We notice that the structural relaxations influence the vacancy parameters more than the volume relaxations.

Both our fully relaxed and unrelaxed values of H_{1v}^F agree well with the experimental results in Refs. 9–11. As expected our value is smaller than the experimental estimates that do not take the existence of divacancies into account.[6,7] It is evident that all theoretical values of H_{1v}^F in Table I (Refs. 12–14 and 16) are larger than both our fully relaxed and unrelaxed values of H_{1v}^F. The main difference between our value and the value in Ref. 13 is due to different estimations of the relaxation effects. In this context it is of interest to note that the bulk properties that are predicted in Ref. 13 are almost identical to ours. In Ref. 14 Korzhavyi *et al.* did not include structural relaxations, but argued that this effect was small. However, according to our results, structural relaxations decrease the value of H_{1v}^F by 0.09 eV, i.e. by about 8%. This relaxation effect is larger than the effect estimated in Ref. 13. The other computational references (Refs. 12, 13, and 16) included structural relaxations. For H_{2v}^F the agreement between our fully relaxed value and the experimental results of Refs. 9–11 is good, however in this case our estimate is larger than the experimental estimates. The value of H_{2v}^F that was calculated in Ref. 12 is somewhat larger than ours.

The experimental estimates of H_{2v}^B in Refs. 9–11 are up to four times larger than the fully relaxed value in this paper, though the agreement is better with the first-principles results in Refs. 14 and 15. In Ref. 15 relaxations were not included and the authors argued that the relaxation contribution to the interaction should be small. Since H_{2v}^B is calculated as a difference between two big numbers that are of the same magnitude there might be a rather large relative uncertainty. Still, the experimental estimates are rather high. The analysis employed by Neumann *et al.* in Ref. 9 to find H_{1v}^M, H_{2v}^F and H_{2v}^B was described in the Introduction. Neumann *et al.*[9] made use
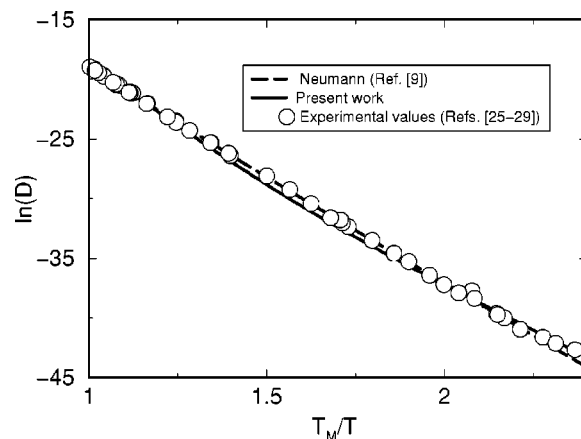

FIG. 1. Arrhenius plot of the diffusion coefficient D. T_M is the melting temperature of copper and is equal to 1357.77 K.

of experimental values of Q_{1v}, Q_{2v}, H_{1v}^F and H_{2v}^M. Both the value of H_{1v}^M and H_{2v}^M that we have calculated are somewhat smaller than the corresponding values in Ref. 9. Though, the ratio of H_{1v}^M and H_{2v}^M is similar for our values and the values of Neumann *et al.*[9]. This is also true for a comparison with the values in Refs. 10 and 11, but the results deduced by Nordlund and Averback[16] from an embedded atom method differ by almost a factor two. If our estimate of H_{1v}^M is used in the same manner as in the analysis of Ref. 9, it follows from Eq. (7) that H_{1v}^F would increase, which would contradict our result for H_{1v}^F. Similarly our value of H_{1v}^F would produce an even larger value of H_{1v}^M, which once again does not agree with our results. This indicates that the discrepancy between our results and the results of Neumann *et al.*[9] can be attributed to H_{1v}^M, H_{2v}^M, Q_{1v} and Q_{2v}, which in Ref. 9 were obtained from the two-exponential fit of the diffusion coefficient. If Q_{1v} and Q_{2v} are re-calculated with our fully relaxed parameter values, $Q_{1v}=1.69(1.75)$ and $Q_{2v}=2.36(2.48)$ according to Eq. (7) and (8). The values within parentheses include the correction for the correlation effect near electronic edges. In Ref. 24, $Q_{1v}=2.05\pm0.02$ and $Q_{2v}=2.46\pm0.12$ are reported as experimental estimates and thus our value of Q_{2v} is in agreement with experiments, in contrast to Q_{1v}. In Fig. 1 two Arrhenius plots of the diffusion coefficient D, given by Eq. (6), are presented. One of the plots employs the parameters that were used by Neumann *et al.*[9] and the other employs our first-principles values of Q_{1v} and Q_{2v} together with D_{1v}^0 and D_{2v}^0 calculated from a least-squares analysis. Experimental data are also displayed in Fig. 1.[25–29] The figure shows that our values of Q_{1v} and Q_{2v} are in agreement with diffusion data. It should be stressed that our plot was obtained with only two fitting parameters compared to four in the experimental plot.

The vacancy formation volume of monovacancies and divacancies were calculated to be 10.3 Å^3(0.851Ω_0) and 17.9 Å^3(1.48Ω_0), respectively, with full relaxations included. These values agree reasonably well with those in Refs. 12 and 14.

The experimental and theoretical low temperature values of S_{1v}^F and S_{2v}^F in Table I are rather dispersed and our fully relaxed estimates lie in the same range. The standard devia-
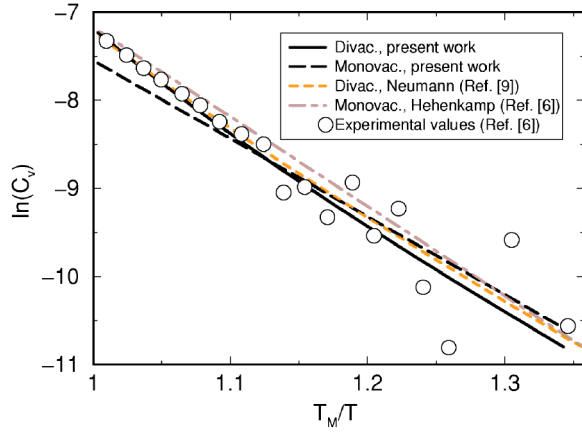
FIG. 2. (Color online) Arrhenius plot of the total vacancy concentration C_v.
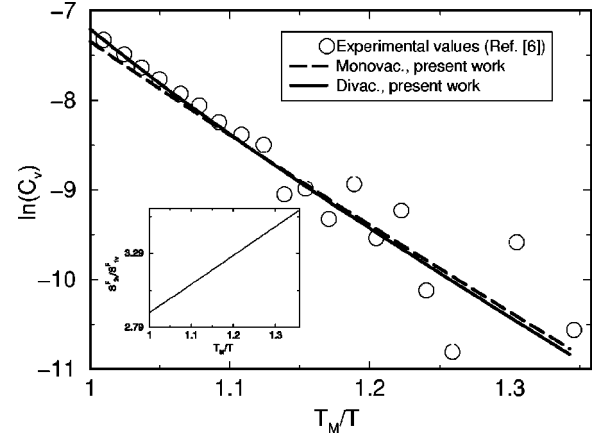

FIG. 3. Arrhenius plot of the total vacancy concentration C_v. The present work includes temperature dependent formation enthalpies and entropies. The inset shows the ratio of S_{2v}^F and S_{1v}^F.

tion of the experimental data in Ref. 6 from our unweightened least-squares fit is approximately $\sigma = 0.350$ and the standard deviations of our estimated entropies are $\sigma_{S_{1v}^F/k_B} = 0.149$ and $\sigma_{S_{2v}^F/k_B} = 0.846$. A weighted fit, with weights ranging from 1 to 1/8, that takes the uncertainties of the measurements at low temperature into account do no alter any of the results significantly. In Fig. 2 the Arrhenius plots of the experimental vacancy concentration data in Ref. 6 and Eq. (4) with our unweightened low temperature parameter estimations as well as the parameters that were used by Neumann *et al.* in Ref. 9 are shown. For comparison Fig. 2 also includes Eq. (2), with just monovacancy enthalpy and a least-squares fitted low temperature value of S_{1v}^F/k_B (=1.32 with the correlation correction at electronic edges included) as well as the parameters that were used by Hehenkamp *et al.* in Ref. 6. Both two-parameter sets result in good fits. As one could expect the one-parameter fits are not as good as the two-parameter fits. This is especially true in the high temperature region where the contribution from divacancies are traditionally expected to be important. We observe, however, that our least-squares values of S_{1v}^F and S_{2v}^F differ by approximately a factor 17, which seems to be a fairly large value. If the correction for the correlation effect near electronic edges is accounted for the ratio is reduced to about 6. S_{1v}^F and S_{2v}^F correspond to the change in vibrational entropy and from a very simple picture (Einstein model) one would rather expect S_{2v}^F to be roughly twice as large as S_{1v}^F. Thus our calculated low temperature enthalpies, which are, in line with usual experimental approaches, assumed to be constant (i.e., temperature independent) indicate that the fitting procedure normally used by experimentalists to obtain vacancy formation entropies is not completely adequate. This was also pointed out by Sandberg and Grimvall[12] who argued that the upward curvature of the Arrhenius plot of the vacancy concentration at temperatures close to the melting point, which has usually been attributed to the formation of divacancies, is mainly caused by anharmonicity in the lattice vibrations.[12] The anharmonicity causes the enthalpies and entropies to be temperature dependent. We notice that if one assumes enthalpies and entropies to be temperature independent, a somewhat remarkable relation between S_{1v}^F and S_{2v}^F is obtained. The

results of our calculations taking into account the temperature dependencies of H_{1v}^F, H_{2v}^F, S_{1v}^F, and S_{2v}^F, together with the experimental Arrhenius plot are presented in Fig. 3. We notice that a proper relation between high temperature S_{1v}^F and S_{2v}^F is restored (see the insert of Fig. 3). On the other hand, one may see that even with all temperature dependencies incorporated into first-principles calculations, both vacancies and divacancies are important to reproduce the Arrhenius plot in the best agreement with experiment. We emphasize that this issue may need further investigation. In particular, a first-principles molecular dynamics study of sufficiently big supercells would be of interest. With the current computer power development it may become feasible in the near future.

IV. CONCLUSIONS

The bulk lattice constant (a), bulk modulus (B), low temperature H_{1v}^F, H_{2v}^F, H_{2v}^B, H_{1v}^M and H_{2v}^M have been calculated directly from first-principles. Full relaxations were included in the calculations and reduce the enthalpies somewhat compared to the unrelaxed case. The effect is most important for the migration enthalpies. The knowledge of these parameters enabled us to obtain S_{1v}^F and S_{2v}^F from a nonlinear least-squares fit to experimental values of the vacancy concentration in a very simple way. This allowed us to produce an Arrhenius plot of the temperature dependences of the total vacancy concentration and by a similar approach we could also obtain the temperature dependence of the self-diffusion coefficient. Both results are in good agreement with experiments due to Neumann *et al.*[9] Our results for H_{1v}^F and H_{2v}^F agree fairly well with experimental data and especially with the recent estimates of Neumann *et al.*[9] However H_{1v}^M, H_{2v}^M and above all H_{2v}^B differ from the values given by Neumann *et al.* in Ref. 9. Neumann *et al.* calculate H_{1v}^M by relating it to diffusion parameters and other enthalpies, a procedure which may be associated with several uncertainty factors. This is a possible explanation for the disagreement. The same argument holds for H_{2v}^B, but one must also remember that this parameter is sensitive to uncertainties of H_{1v}^F and H_{2v}^F. We

also notice that our fitted values of low temperature S_{1v}^F and S_{2v}^F differ notably and this suggests that the least-squares fitting procedure is to some extent deficient, which we attribute to the ignorance of any temperature dependence of entropies and enthalpies. When this temperature dependence is included in our calculations, the proper relation between S_{1v}^F and S_{2v}^F is restored. We suggest that for an accurate theoretical description of the vacancy properties of copper one needs to take into account both vacancies and divacancies, and to incorporate the temperature dependencies of H_{1v}^F, H_{2v}^F, S_{1v}^F, and S_{2v}^F into calculations.

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