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Formation entropy and the diffusion constant for vacancies in Cu and α-Fe

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The formation entropy of single vacancies and divacancies and the frequency factors entering in the diffusion constants are calculated for Cu and α-Fe based on a pair-potential approach. For Cu a Morse and a Born-Mayer potential have been employed, for α-Fe the potential of Chang and Graham. The calculations have been performed by a determinant method and partly also by the Green's-function method. The effects of the long-range displacements have been carefully estimated and are very important. For the Morse potential the formation entropy is $2.3k$ for a single and $4.0k$ for the divacancy in Cu, whereas the temperature-independent part of the diffusion constant is 0.12 and 3.7 cm^2/sec, respectively. For α-Fe, the Chang-Graham potential leads to a formation entropy of $2.1k$ and to a diffusion constant of 0.16 cm^2/sec for single vacancies.

I. INTRODUCTION

In thermal equilibrium, the concentration c_1 for single vacancies is given by

$$c_1 = e^{S_1/k} e^{-H_1/kT} ,$$

where S_1 is the formation entropy and H_1 is the formation enthalpy. Experimentally it is very difficult to determine the formation entropy since, e.g., at 1000 K an error of 0.1 eV in H_1 gives rise to an error of $0.7k$ in S_1. Previous theoretical calculations are listed below and give widely diverging results ranging, e.g., for Cu from about $0.49k$ to $3.1k$. Thus an accurate theoretical calculation of S_1 is highly desirable. As most of the previous theoretical attempts, our approach is also based on the assumption of a pair-potential interaction. However, we will strictly avoid all additional assumptions. Our aim is to compare the theoretical results with new experimental measurements[1-5] in order to see if a pair-potential approach gives a reasonable description of the dynamical behavior of a vacancy.

Previous calculations of the entropy of formation of vacancies in copper include the following. In 1955 Huntington, Shirn, and Wajda[6] used an Einstein approximation for the 12 nearest neighbors and obtained 1.47 for S/k (ratio of entropy of formation to Boltzmann's constant). In 1964 Schottky, Seeger, and Schmidt[7] fitted the coupling parameters to experimental data and using the frequencies from the group of the 12 nearest neighbors obtained 0.49. Both of these authors used, in addition, elastic and surface corrections. In 1969 Wynblatt[8] used an Einstein approximation for about 700 atoms to obtain 1.67, McLellan[9] used only elastic theory with a spherical cavity to obtain 2.7 and Dobrzynski[10] obtained 1.5 using a determinant method but without relaxation. In 1972 Burton[11] used the frequencies from the first six shells (86 atoms) but employed no elastic or surface correction to obtain 3.1 for the Morse potential.

With so many varied results it was felt desirable to repeat the calculation, making use of the frequency distribution from as large a group of atoms as possible (about 150–400), to use a Morse potential which fits the energy of formation of single vacancies and to use elastic and surface corrections where necessary.

Section II deals with the basic theory connecting the theoretical and experimental quantities, Sec. III covers the calculations based on a determinant method, Sec. IV the Green's-function method, and Sec. V considers the comparison with experimental results.

II. THEORY

At given temperature T and pressure p the concentration $c_1(T,p)$ of single vacancies in a crystal is given by

$$c_1 = e^{-G_1/kT} = e^{S_1/k} e^{-H_1/kT} \approx e^{S_1/k} e^{-E_1/kT} . \tag{1}$$

Here $G_1(T,p) = H_1 - S_1 T$ is the Gibb's free energy of formation, S_1 is the formation entropy, and H_1 the enthalpy of formation, which for normal pressures can be well approximated by the formation energy E_1, since the difference $H_1 - E_1 = p\Delta V$ is small (ΔV is the formation volume).

The corresponding formula for divacancies $c_2(p,T)$ is

$$c_2(p,T) = \tfrac{1}{2} z e^{S_2/k} e^{-E_2/kT} . \tag{2}$$

The factor $\frac{1}{2}z$ gives the number of divacancies per lattice site (z is the number of nearest neighbors). Only two vacancies on nearest-neighbor sites (in bcc: second-nearest-neighbor sites) are considered as a "divacancy."

The entropy S of an arbitrary crystal can be calculated, e.g., from the free energy F by $S = -(\partial F/\partial T)_V$. It consists of a vibrational part S^v and a smaller electronic part S^e (see below).

In the harmonic theory the vibrational part is a sum of single-oscillation contributions[12]

$$S^V = k \sum_\alpha \left(-\ln(1 - e^{-\hbar\omega_\alpha/kT}) + \frac{\hbar\omega_\alpha/kT}{e^{\hbar\omega_\alpha/kT} - 1} \right), \quad (3)$$

where ω_α represents the eigenfrequencies of the system.

In the classical limit of high temperatures S^v approaches

$$S^v \approx k \sum_\alpha \left[1 + \ln(kT/\hbar\omega_\alpha) \right]. \quad (4)$$

By the formation of the vacancy, the atom at the vacancy site is transferred to the surface. Thus both the perfect crystal and the crystal with a vacancy contain the same number of atoms. The formation entropy $S_1 = S^v(\text{vac}) - S^v(\text{perfect})$ is then, in the classical limit,

$$S_1 = k \sum_{\alpha=1}^{3N} \ln \frac{\omega_\alpha^0}{\omega_\alpha} = \frac{k}{2} \sum_{\alpha=1}^{3N} \ln \frac{(\omega_\alpha^0)^2}{\omega_\alpha^2} = \frac{k}{2} \ln \left(\frac{\prod_{\alpha=1}^{3N} (\omega_\alpha^0)^2}{\prod_{\alpha=1}^{3N} \omega_\alpha^2} \right), \quad (5)$$

where ω_α refers to the $3N$ eigenfrequencies in the defect lattice and ω_α^0 to those of the ideal lattice. Thus for a vacancy one expects $S_1 > 0$, since the general effect should be a softening of the lattice (i.e., $\omega_\alpha < \omega_\alpha^0$).

A. Equivalent representations

The frequencies ω_α^2 are the eigenvalues of the dynamical matrix D, similarly $M\omega_\alpha^2$ are the eigenvalues of the coupling matrix ϕ (M is the atomic mass). We can therefore give different expressions for S_1 in terms of ϕ which are quite useful for the numerical analysis. Using the relation between the product of the eigenvalues and the determinant of a matrix

$$\prod_{\alpha=1}^{3N} M\omega_\alpha^2 = \det\phi, \quad (6)$$

and the relation between the sum of the eigenvalues and the trace of a matrix

$$\sum_{\alpha=1}^{3N} f(\omega_\alpha^2) = \mathrm{Tr} f(\phi), \quad (7)$$

where f represents some function of the eigenvalues, we obtain the following equivalent expressions for S_1 (or S_2)

$$S_1 = \tfrac{1}{2} k \ln(\det\phi^0/\det\phi) = \tfrac{1}{2} k \, \mathrm{Tr}(\ln\phi^0 - \ln\phi). \quad (8)$$

The determinant expression will be used in Sec. III for a numerical calculation of S_1.

Another very useful expression can be gained by introducing the total frequency spectra $Z(\omega)$ and $Z^0(\omega)$ of the defect and ideal lattice:

$$S_1 = k \int d\omega \ln\omega \left[Z^0(\omega) - Z(\omega) \right], \quad (9)$$

with

$$Z(\omega) = \sum_{\alpha=1}^{3N} \delta(\omega - \omega_\alpha) = 2\omega \sum_{\alpha=1}^{3N} \delta(\omega^2 - \omega_\alpha^2) \equiv 2\omega M \, \mathrm{Tr}\, \delta(M\omega^2 - \phi). \quad (10)$$

The corresponding expression holds also for $Z^0(\omega)$. By performing the trace in a local representation, we can write $Z(\omega)$ as a sum of local spectra $z_i^m(\omega)$

$$Z(\omega) = \sum_{mi} z_i^m(\omega),$$

with

$$z_i^m(\omega) = 2\omega M \langle mi | \delta(M\omega^2 - \phi) | mi \rangle = \sum_{\alpha=1}^{3N} |u_i^m(\alpha)|^2 \delta(\omega - \omega_\alpha). \quad (11)$$

$z_i^m(\omega)$ describes the local vibrational behavior of atom m for vibrations in direction i and is directly related to the Green's function of Sec. IV. It is a normalized spectrum, essentially the total frequency spectrum, but each contribution $\delta(\omega - \omega_\alpha)$ is weighted by the square of the amplitude $u_i^m(\alpha) = \langle mi | \alpha \rangle$ of atom m for the direction i.

Since both the ideal and the defect crystal contain the same number of atoms we can write (9) in the form

$$S_1 = k \int d\omega \ln\omega \sum_{i,\, m\,(\neq 0)} \left[z_i^{0m}(\omega) - z_i^m(\omega) \right]. \quad (12)$$

The transfer of the vacancy atom to the surface does not mean that the number of surface atoms has been increased, since this atom is incorporated preferentially in a step or kink at the surface, so that a former "surface atom" below this atom belongs now to the "bulk." Thus both the ideal as well as the defect crystallite have the same number of surface and bulk atoms. Therefore we can in the above equation make the transition to an infinite crystal by summing over all m

with the exception of the term $m=0$. Essential contributions to the sum arise only for atoms near to the vacancy, since for large distances $z_i^m(\omega) \approx z_i^{0m}(\omega)$.

B. Electronic contributions

In addition to the vibrational entropy we also have an electronic contribution which can, e.g., be calculated from the electronic specific heat, varying as $c_V(T) \cong \gamma T$ for metals. Thus

$$S^e = \int_0^T \frac{c_V(T)}{T} dT = \gamma T , \quad \gamma = k \tfrac{1}{3}\pi^2 n(E_F) . \tag{13}$$

Since γ is determined by the total density of states $n(E_F)$ at the Fermi energy, the electronic contribution ΔS_1^e to the formation energy S_1 is therefore given by the change $\Delta n(E_F)$ of the density of states

$$\Delta S_1^e = k \tfrac{1}{3}\pi^2 \Delta n(E_F) kT . \tag{14}$$

Due to the smallness of the electronic specific heat, this term is much smaller than the vibrational contribution. In the free-electron approximation $[n(E_F) = \frac{3}{2} N/E_F]$, the change $\Delta n(E_F)$ can be directly related to the larger volume $V+\Delta V$ available for the electrons in the defect crystal. Then

$$\Delta S_1^e = k \tfrac{1}{3}\pi^2 (kT/E_F)(\Delta V/V_c) ,$$

since

$$\Delta n(E_F) = (1/E_F)(\Delta V/V_c) , \tag{15}$$

(V_c is the volume of an elementary cell).

Assuming, e.g., $E_F \approx 7$ eV (Cu), $kT = 1300$ K, $\Delta V \approx 1 V_c$, we obtain a very small value of $\Delta S_1^e \approx 0.05k$. Considerably larger values can only be expected for materials with a large density of states at the Fermi energy, e.g., transition metals, where $n(E_F)$ can be more than an order of magnitude larger than the free-electron value.

C. Einstein approximation

A rather quick, first-order approximation to the formation entropy can be obtained by the Einstein approximation: The $3N$ eigenfrequencies ω_α^2 are calculated by allowing each atom m to vibrate by fixing its neighbors. The three eigenfrequencies of atom m are then obtained by diagonalizing the 3×3 matrix ϕ_{ij}^{mm}.

For a nearest-neighbor model, in a fcc crystal with a longitudinal force constant $f_\parallel$ and a transversal one $f_\perp$, we have the following situation: In the ideal lattice all Einstein frequencies for the different atoms and the different directions are equal, $M(\omega_E^0)^2 = 4f_\parallel + 8f_\perp$, whereas in the defect lattice only the Einstein frequencies of the nearest neighbors of the vacancy are changed. The eigenfrequency for a vibration of the neighboring atom towards the vacancy is

$$M\omega_\parallel^2 = 3f_\parallel + 8f_\perp , \tag{16}$$

whereas the two other eigenfrequencies for motions perpendicular to this direction are degenerate and given by

$$M\omega_\perp^2 = 4f_\parallel + 7f_\perp . \tag{17}$$

Note that for motions towards the vacancy the missing longitudinal spring leads to the value $3f_\parallel$ instead of $4f_\parallel$, whereas for perpendicular motions the missing tangential spring $f_\perp$ leads to $7f_\perp$ instead of $8f_\perp$ for the ideal crystal. By inserting these results for the 12 nearest neighbors into the product expressions for the entropy, we obtain

$$S_1^E = \frac{k}{2} 12 \ln \frac{(4f_\parallel + 8f_\perp)^3}{(3f_\parallel + 8f_\perp)(4f_\parallel + 7f_\perp)^2} . \tag{18}$$

For $f_\perp = 0$ this gives $S_1^E = 6k \ln\frac{4}{3} = 1.73k$ whereas for $f_\perp = -0.1 f_\parallel$ one obtains $S_1^E = 1.98k$. Stripp and Kirkwood[29] using a method requiring that the change in the frequencies be small obtain a value of $1.5k$ for S_1. This same value could be obtained for $f_\perp = 0$ from the above by expanding the ln terms assuming $(\omega_E - \omega_E^0)/\omega_E^0$ to be small.

This calculation can also be performed for the case of a divacancy and yields for $f_\perp = 0$ the value $S_2^E = 3.22k$, i.e., a binding entropy of $(2 \times 1.73 - 3.22)k = 0.24k$. These estimates give about the correct values for the entropies, as is confirmed by more realistic models and exact numerical calculations in the following Sections.

D. Effect of static displacements

The static displacements of the vacancy seriously complicate the calculation of the formation entropy since they lead to a long-range change of the coupling matrix $\phi = \phi^0 + \Delta\phi$. The total displacement field $\vec{s} = \vec{s}^\infty + \vec{s}^I$ can be split up into a field $\vec{s}^\infty$ in an infinite crystal, which varies as $1/R^2$ for large distances, and into an image field $\vec{s}^I$, which allows for a force-free surface. Since all image fields of the different vacancies superimpose to yield a homogeneous expansion, their contribution Δs_1^I to the formation entropy is determined by the volume change ΔV^I due to the image forces

$$\Delta V^I = \tfrac{2}{3}(1-2\nu)/(1-\nu)\Delta V_{\text{total}} \tag{19}$$

(ν is the Poisson number). For Cu, $\Delta V^I \approx \frac{1}{3}\Delta V_{\text{total}}$, since $\nu \approx \frac{1}{3}$. Therefore,

$$\Delta S_1^I = \left(\frac{\partial S}{\partial V}\right)_T \Delta V^I = K\alpha \Delta V^I , \tag{20}$$

where we have used the thermodynamic relation[6]

$$\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial P}{\partial T}\right)_V=-V\left(\frac{\partial P}{\partial V}\right)_T\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P=K\alpha\,, \qquad (21)$$

connecting $(\partial S/\partial V)_T$ with the compression modulus K and the volume expansion coefficient α.

The effect of $\vec{s}^{\infty}$ is much more difficult to calculate and represents a major numerical problem. Here we will only show that for large distances R from the vacancy the leading contribution to ΔS_1^{∞} of a volume element $d\vec{R}$ at distance R varies as $1/R^6$. This dependence will be exploited in Sec. III. According to Zener[13] one can calculate S_1 via the temperature dependence of the free energy of formation F_1, $S_1=-(\partial F_1/\partial T)_V$. Since the long-range displacements $\vec{s}^{\infty}$ are small and slowly varying, their contribution to F_1 can be calculated using continuum theory, i.e.,

$$\Delta F_1\sim\frac{1}{2}\int d\vec{R}\sum_{ijkl}C_{ijkl}(T,V)\epsilon_{ij}^{\infty}(\vec{R};T,V)\times\epsilon_{kl}^{\infty}(\vec{R};T,V)\,. \qquad (22)$$

Thus S_1 is determined by the temperature dependence of the elastic constants C_{ijkl} and of the strains ϵ_{ij}^{∞}. Since the latter vary as $1/R^3$, the integrand varies as $1/R^6$. The outer region of a sphere of radius R therefore gives a contribution proportional to $1/R^3$.

E. Frequency factors in diffusion

The diffusion constant for tracer diffusion involving single vacancies is given by

$$D_1=a^2f_1e^{S_1/k}e^{-E_1/kT}\Gamma_1\,, \qquad (23)$$

where a is the lattice constant, f_1 is the correlation factor ($f_1=0.781$ for fcc), and Γ_1 is the jump frequency for the migration. Similarly for divacancies in fcc, one has

$$D_2=4a^2f_2e^{S_2/k}e^{-E_2/kT}\Gamma_2\,, \qquad (24)$$

with f_2 being the divacancy correlation factor ($f_2=0.468$ in fcc). From the classical theory of Vineyard[14] the jump frequency can be obtained in terms of the eigenfrequencies for the equilibrium configuration (ω_α^e, $\alpha=1,\ldots,3N$) and the eigenfrequencies for the saddle-point configuration (ω_α^s, $\alpha=1,\ldots,3N-1$)

$$\Gamma_1=\left(\frac{1}{2\pi}\right)\left(\frac{\prod_{\alpha=1}^{3N}\omega_\alpha^e}{\prod_{\alpha=1}^{3N-1}\omega_\alpha^s}\right)e^{-E_M/kT}=\left(\frac{\omega^*}{2\pi}\right)e^{-E_M/kT}\,. \qquad (25)$$

Here E_M is the activation energy for migration. For the saddle-point configuration the eigenfrequency ω_{3N}^s describing the motion of the jumping atom towards the vacancy has to be left off [since this is an unstable mode, one has $(\omega_{3N}^s)^2<0$]. The diffusion constants without the temperature dependence we will refer to as $\tilde{D}$.

$$D=\tilde{D}e^{-(E_1+E_M)/kT}\,. \qquad (26)$$

Quite analogously to the expression for S_1, one can also give equivalent representations for the jump frequency Γ_1 or the effective frequency ω^* in terms of the determinants of the dynamical matrices or in terms of local frequency spectra. For example

$$\omega^*=[(\det\phi^e/\det\phi^s)(\omega_{3N}^s)^2]^{1/2}\,,$$

since

$$\det\phi^s=\prod_{\alpha=1}^{3N}M(\omega_\alpha^s)^2\,. \qquad (27)$$

Thus in order to calculate ω^*, one has, in addition to the determinants of ϕ^e and ϕ^s, to calculate the frequency $(\omega_{3N}^s)^2$ of the "decay mode" of the saddle-point configuration. Otherwise, however, the problem is quite similar to the one for the formation entropy.

F. Isotope factor for diffusion

For an isotropic tracer one has to know the mass dependence of ω^*. Since the eigenfrequencies ω_α^2 are, in the case of unequal masses, given by the eigenvalues of the dynamical matrix

$$D_{ij}^{mn}=(M^m)^{-1/2}\phi_{ij}^{mn}(M^n)^{-1/2}\,,$$

we obtain for the effective attempt frequency in the generalization of Eq. (27)

$$\omega=\left(\frac{\det[(M^m)^{-1/2}(\phi_{ij}^{mn})^e(M^n)^{-1/2}]}{\det[(M^m)^{-1/2}(\phi_{ij}^{mn})^s(M^n)^{-1/2}]}(\omega_{3N}^s)^2\right)^{1/2}.$$

Since the masses are the same in the equilibrium and in the saddle-point configuration, the mass factors of both determinants cancel each other, so that the only mass dependence comes from the frequency ω_{3N}^s of the localized "decay mode."[15] Its frequency can be calculated by perturbation theory from the Rayleigh quotient

$$(\omega_{3N}^s)^2=\frac{\sum_{mn}(\vec{u}_{3N}^m,\phi^{mn}\vec{u}_{3N}^n)}{\sum_m(\vec{u}_{3N}^m)^2M^m}\,.$$

By inserting a mass change $M^T=M^0+\delta M$ of the isotopic tracer atom, one obtains for the change of ω^* (see Ref. 15):

$$\frac{\delta\omega^*}{\omega^*}=\frac{\delta\omega_{3N}^s}{\omega_{3N}^s}=-\frac{1}{2}\frac{\delta M}{M^0}(\vec{u}_{3N}^T)^2=-\frac{1}{2}\frac{\delta M}{M^0}\Delta K\,.$$

The so-defined isotope factor ΔK is given by the square of the tracer amplitude $\vec{u}_{3N}^T$ in the normalized decay mode $\vec{u}_{3N}$. Its deviation from $\Delta K = 1$ gives a measure of the delocalization of this saddle-point mode and therefore of the coupling of the tracer to its nearest neighbors.

III. DETERMINANT METHOD

The determinant expressions (8) and (27) were used for calculating the entropy of formation of vacancies and the diffusion constant for Cu employing three potentials: a Born-Mayer form, a Morse form, and a nearest-neighbor Morse form. Similar calculations were done for α-Fe employing a spline potential developed by Chang and Graham.[16,17] In the Cu case both single and divacancies were investigated, in the α-Fe case only single vacancies.

The Born-Mayer potential used was of the form

$$V(r) = Ae^{-Br}, \tag{28}$$

with $A = 22\,563$ eV and $B = 5.1020$ Å^{-1}. This potential was used initially by the vineyard group. A pressure must be applied to the crystal from the outside to ensure equilibrium. This potential yields relatively large relaxations in the neighborhood of defects, but does not give an accurate value for the formation energy of a vacancy.

The Morse potential was of the form

$$V(R) = D(e^{-2\alpha(R-R_0)} - 2e^{-\alpha(R-R_0)}), \tag{29}$$

with

$$D = 0.179\,99 \text{ eV}, \quad R_0 = 0.713\,46a, \quad \alpha = 8.355\,26a^{-1},$$

and R in units of $a = 3.603$ Å. The potential was smoothly cut off at $R = 1.2a$. It is fitted to lattice constant, bulk modulus, and vacancy formation energy of Cu. With this potential both single and divacancies were studied.

For the case of the perfect lattice it was not necessary to calculate relaxations and only necessary to calculate $\ln\det\phi$. This was done successively for various shells of equivalent atoms. The shells were oriented about a particular atom in the lattice (which then for the defect case becomes the vacancy). Calculations were performed for crystallites usually containing from 100 to 200 atoms. It was found that fewer atoms would not be sufficient to give the desired accuracy for $[\ln(\det\phi)]/N$, where N is the number of atoms. Several test cases were run to determine the nature of the N dependence and accuracy obtainable, employing up to 430 atoms, and making use of the symmetry of the lattice. Since, in conjunction with the vacancy calculations, it is necessary to use the same total number of atoms, the results for the perfect lattice have been multiplied by $(N-1)/N$ for a single vacancy and $(N-2)/N$ for a double vacancy. The error introduced by this normalization should decrease with increasing N.

To obtain the relaxations of the atoms in the neighborhood of the defect an iterative method was employed which minimizes the energy as a function of a certain number of parameters chosen to describe the relaxations with maximum use of symmetry. For the larger crystallites the DEVIL program, originally developed at Harwell, was used. In its present form the program utilizes a mixture of steepest- and conjugate-gradient[32] methods to calculate the configuration which minimizes the potential energy. In order to calculate saddle points, geometrical constraints can be built in.

In order to simulate the vibrational behavior in a nearly infinite crystal, the atomic region (about 5.000 atoms) where relaxations are allowed, was always much larger than the inner region, where dynamical displacements were allowed (about 100–500 atoms). This procedure turned out to be very important, especially since the coupling matrix of the inner region involves interactions with outer atoms, the displacements of which have to be known accurately.

The calculated numbers for the formation entropy still depend appreciably on the number N of atoms in the inner region. It was therefore necessary to extrapolate these values for an infinite crystal ($N \to \infty$). According to continuum theory (Eq. 22) the region outside an inner sphere of radius R gives a contribution varying as $1/R^3$ to the formation entropy. Since N is proportional to R^3, this translates into a $1/N$ dependence

$$S(N)/k = S(\infty)/k + \text{const}/N. \tag{30}$$

The values obtained for different crystallites containing up to N atoms, $S(N)$, is plotted in Fig. 1 versus $1/N$. The numbers at the points refer to the number of shells taken into account (3–19). Considerable fluctuations of the points appear and a general $1/N$ dependence is not seen. Apparently this behavior is connected with the anisotropy of the elastic displacements: Each shell added contains only equivalent atoms having very specific orientations with respect to the cubic axes. In fact the fluctuations can be corrected with the size and sign of the atomic relaxations in the last shell. Nevertheless the procedure converges and the limiting value $S(\infty)$ is estimated by the enveloping straight lines in Fig. 1.

The entropy values obtained by this limiting procedure were then corrected to the real value for a finite crystal by calculating the image correction of Eq. (20). Rather than using experimental values for K and α, we have for consistency estimated these corrections for each potential em-

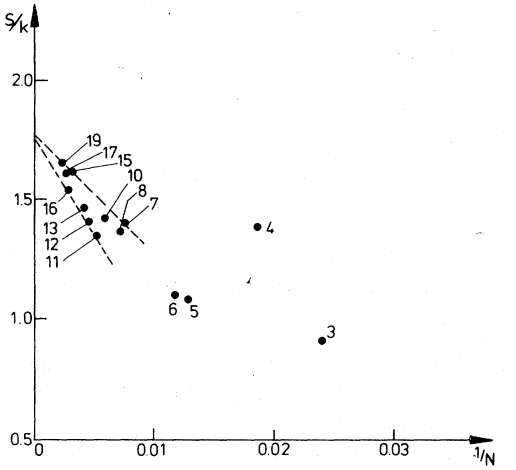

Fig. 1. Formation entropy of a vacancy for the Born-Mayer potential as a function of the number of atoms N (numbers of diagram represent shells) which are allowed to vibrate. The results are not corrected for the image expansion.

ployed by calculating

$$\frac{\partial S}{\partial V}=\frac{k}{2}\partial_V \ln\det\phi \qquad (31)$$

numerically. The effect of the finite size of the outer region with $N_a \approx 5.000$ atoms can be estimated as follows: Using isotropic continuum theory the boundary condition of "vanishing displacements" at an outer sphere of radius R_a (as assumed in the previous calculations) gives for the inner sphere of radius R_i a volume change due to image forces of $-\Delta V^\infty(R_i/R_a)^3$ so that the total volume change of the inner sphere is $\Delta V^\infty[1-(R_i/R_a)^3]$ or $\Delta V^\infty(1-N/N_a)$ instead of ΔV^∞. To correct for this we have to add for the above correction to the usual image term ΔV^I the smaller contribution $\Delta V^\infty N/N_a$.

Since the elements of the coupling matrix depend on a sum of terms of a pair potential which usually include terms only up to the near neighbors, many of the elements will be zero. Because of this, the methods of sparse matrix analysis[18] were used to shorten the calculation. In addition the coupling matrix possesses considerable symmetry which can be employed to simplify the calculation. For example, using inversion symmetry about the vacancy enables the matrix to be split up into four subparts. It would then have the form

$$\phi=\begin{pmatrix} B & C \\ C & B \end{pmatrix}. \qquad (32)$$

The determinant of ϕ can thus be obtained from two subdeterminants of rank $\frac{1}{2}N$:

$$\det\begin{pmatrix} B & C \\ C & B \end{pmatrix}=\det(B+C)\det(B-C). \qquad (33)$$

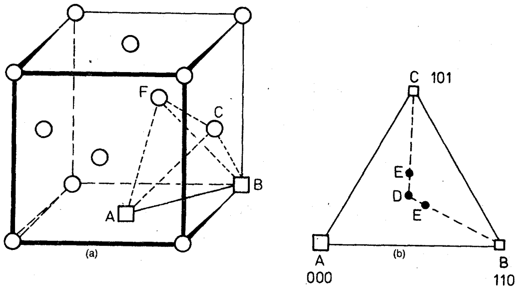

FIG. 2. (a) Configuration of a divacancy in fcc crystals. The positions A and B are empty. (b) Elementary jump of the divacancy. Atom C jumps to the site B. The saddle-point position E does not coincide with the center of the triangle nor does it lie in the plane of the triangle. The potential energy along the jump path therefore shows a "double-hump" structure with maxima at E.

This method was used to check some of the calculations for accuracy.

The position of the saddle point for a single vacancy in Cu is halfway between nearest-neighbor atoms. In this position the symmetry has decreased so that it requires more parameters to solve for the relaxations. To find the negative eigenvalue of the ϕ matrix it is necessary to solve for all the eigenvalues and pick out the negative one. It was found in the case of the single vacancy that the negative eigenvalue does not change appreciably with the number of atoms chosen in the dynamic calculation. About 50 are sufficient to obtain an accurate value. By examining the eigenvector of the negative eigenvalue it was found that the amplitude of four equidistant first neighbors is only 2% of the amplitude of the jumping atom. Thus the "vibration" is strongly localized.

The situation for the saddle point of the divacancy was more difficult to deal with. Figure 2(a) shows the initial positions of the two vacancies A and B, and the atom C that is jumping into position B. It is not obvious what path C will take in getting to B and thus the exact position of the saddle point. Figure 2(b) shows the triangle formed by atoms A, B, and C, and the center of the triangle D. Since atom F is closer to this plane than the corresponding atom in the opposite direction it is reasonable to expect that the position of atom C at the saddle point will lie "below" the triangle shown. To find the exact position many calculations were made for the energy of the crystal with C in different positions. For the case of the Morse potential it was found that the position of C for the saddle point in the coordinate system where A is 000, B is 110, and the original position of C is 101, is given by 0.7403, 0.2597, 0.3658. Point E is quite close to point D which has the coordinates 0.6667, 0.3333, 0.3333 and the energy

TABLE I. Results of the calculations for single vacancies and divacancies in Cu using Born-Mayer and Morse potentials.

	Potential	S_1/k	$(\omega^*/2\pi)$ sec^{-1}	$\omega^*/\omega_{\max}$	$(\lvert\omega^s_{3N}\rvert/2\pi)$ sec^{-1}	$\tilde{D}$ cm^2 sec^{-1}	ΔK
$1V$	Born-Mayer	1.6	9.5×10^{12}	1.5	1.8×10^{12}	0.045	0.96
	Morse	2.3 (2.35)	$17\ \times10^{12}$	2.0	2.7×10^{12}	0.12	0.96
	nearest-neighbor Morse	2.0 (2.08)					
$2V$	Morse	4.0	$27\ \times10^{12}$	3.2	3.1×10^{12}	3.7	0.90

difference between the two points is only 0.0021 eV, giving rise to a "double-hump" potential curve for the motion of the diffusing atom. Because of this behavior the negative eigenvalue of ϕ turned out to be very small. In addition another rather small positive eigenvalue appeared which in turn helped to give rise to a rather large value for the diffusion constant since this small positive eigenvalue appears in the denominator of the effective frequency factor.

A slight modification of the Morse potential was also used for some single vacancy calculations with nearest-neighbor interactions only. This was accomplished by using a nearest neighbor Morse potential with R_0 equal to $(\frac{1}{2}\sqrt{2})a$, which means that the nearest neighbors are positioned at the minimum of the curve. In this case no relaxations are produced with a vacancy present.

Table I gives the results obtained for the case of Cu for the various potentials used. The entropy values in the brackets were calculated using the Green's-function approach (Sec. IV). It is to be noted that the formation entropy and the diffusion constant are considerably lower with the Born-Mayer potential than with the Morse potential. This seems to be a consistent feature for the Born-Mayer. The divacancy formation entropy with the Morse is less than twice the value for the single vacancy yielding a binding entropy of about $0.6k$. The effective jump frequencies ω^* are always considerably higher than the maximum frequency of the ideal lattice as calculated with the Born-Mayer or Morse potential. The frequencies ω^s_{3N} of the unstable saddle-point mode are about one-third of the corresponding maximum frequency. The relatively large value of $\tilde{D}_{2V}$ has already been explained in part as due to the double-hump potential for the saddle point. The isotope factor $\Delta K = 0.96$ for the single vacancy reflects the strong localization of the decay mode: Practically, only the jumping atom moves. This is, to a lesser extent, also true for the divacancy with $\Delta K = 0.90$.

Calculations have also been carried out for a typical bcc metal, α-Fe, to see if any new difficulties arise in treating bcc structures. Two potentials were tried. First, the Johnson potential,[19,20] which is a spline fit at two different points. It was found in working with this potential that at the fitting points the second derivative of the potential is not continuous, and since second derivatives of the energy with respect to coordinate positions enter into the coupling matrix it gives results that jump irregularly. Especially in connection with the saddle-point configuration for the single vacancy the results are quite sensitive to this feature.

These difficulties can be overcome by using the potential of Chang and Graham,[16,17] slightly modified for a smooth fit.[21] $r \leq 2.40$ Å:

$$V(r) = 14.2674r^4 - 137.650r^3 + 499.723r^2 - 809.804r + 494.557; \tag{34}$$

2.40 Å $< r <$ 3.3894 Å:

$$V(r) = -0.15614r^4 + 0.815729r^3 + 1.24594r^2 - 12.2405r + 16.0187\,.$$

At the fitting point derivatives up to and including the third are continuous so that it should give rise to no irregularities. The V has the units of eV and r of Å.

Calculations were performed for single vacancies in α-Fe for the entropy of formation and vacancy diffusion. Similar methods to these described previously were employed. The only difficult calculation was for the saddle point for vacancy diffusion, which shows a double-hump behavior similar to that found by Johnson. The saddle point was found at a relative position of 0.39 of the distance between nearest-neighbor atoms instead of the central 0.5 position. The energy difference is again small here (0.03 eV) and the corresponding negative eigenvalue has a small magnitude.

Calculations for α-Fe gave a value of 2.1 for S_1/k, 34×10^{12} sec^{-1} for $\omega^*/2\pi$, 0.89 for ΔK and 0.16 cm^2/sec for the diffusion constant. Because of the double-jump behavior of the saddle-point position it would be interesting to investigate a possible connection with the phase transition that occurs from α-Fe to γ-Fe. Burton[11] gives two values for the entropy of formation of vacancies of the solid (3.14 for S_1/k) and the other obtained from a functional form in $K/\alpha V$ where K is the compressibility, α the linear-thermal-expansion coefficient and V the molar volume, (2.17). Our value appears to agree well with the second of these calculations.

IV. GREEN'S-FUNCTION METHOD

In this approach we make use of the advantages of the standard Green's-function description for the vibrational behavior of defect crystals. It is convenient to use this method for infinite crystals since the changes $\varphi = \phi - \phi^0$ between the coupling matrices of the defect and ideal lattices can normally be restricted to the vicinity of the defect. Then the Green's function $G(\omega) = (\phi - M\omega^2)^{-1}$ that describes the vibrational behavior of the defect lattice is easily obtained from the ideal lattice Green's function $G^0(\omega) = (\phi^0 - M\omega^2)^{-1}$. Once having calculated $G^0(\omega)$ one has to perform only simple inversions of matrices with dimensions given by the range of φ. Here we will give an extension of this method in order to calculate the formation entropies of vacancies.

From the equation for S_1 in terms of the frequency spectra $Z(\omega)$, and the expression for $Z(\omega)$ in Sec. II, we obtain

$$S_1 = k\int_0^{\omega_{\max}} d\omega\, 2M\omega \ln\omega \sum_{m,\,i\,(m\neq 0)} \langle mi\,|\,\delta(M\omega^2 - \phi) - \delta(M\omega^2 - \phi^0)\,|\,mi\rangle\,, \tag{35}$$

and by integration

$$S_1 = \frac{k}{2}\sum_{m,\,i\,(m\neq 0)} \langle mi\,|(\ln\phi^0 - \ln\phi)|\,mi\rangle\,, \tag{36}$$

where the difficulty lies in calculating the logarithms of the infinite-dimensional matrices ϕ and ϕ^0. By using the ideal lattice static Green's function $G^0 = (\phi^0)^{-1}$ we will show how to transform this equation into an equation where only finite-dimensional matrices occur.

By defining two subspaces C and R, where C contains the vacancy and R all other atoms, we have

$$\phi^0 = \begin{pmatrix} \phi^0_{CC} & \phi^0_{CR} \\ \phi^0_{RC} & \phi^0_{RR} \end{pmatrix} \text{ and } \phi = \begin{pmatrix} 0 & 0 \\ 0 & \phi_{RR} \end{pmatrix}. \tag{37}$$

In order to extend the summation over all atoms we introduce an auxiliary matrix

$$\hat{\phi} = \begin{pmatrix} \phi^0_{CC} & 0 \\ 0 & \phi_{RR} \end{pmatrix} \text{ with } \ln\hat{\phi} = \begin{pmatrix} \ln\phi^0_{CC} & 0 \\ 0 & \ln\phi_{RR} \end{pmatrix}, \tag{38}$$

and obtain

$$S_1 = \frac{k}{2}\sum_{m,\,i} \langle mi\,|\ln\phi^0 - \ln\hat{\phi}\,|\,mi\rangle - \frac{k}{2}\sum_{i} \langle 0i\,|\ln\phi^0 - \ln\hat{\phi}\,|\,0i\rangle\,. \tag{39}$$

The last term can be rewritten in terms of the Einstein frequency ω_E and the local spectrum $z^0(\omega)$ of the ideal lattice whereas the first term can be expressed as the trace. For cubic crystals we obtain

$$S_1 = \tfrac{1}{2}k(\mathrm{Tr}\,\ln\phi^0 - \mathrm{Tr}\,\ln\hat{\phi}) - 3k\int_0^{\omega_{\max}} d\omega\,\ln\left(\frac{\omega}{\omega_E}\right) z^0_x(\omega)\,. \tag{40}$$

Since the matrices ϕ^0 and $\hat{\phi}$ are symmetric, we can change the first term as follows

$$\mathrm{Tr}\,\ln\phi^0 - \mathrm{Tr}\,\ln\hat{\phi} = \ln(\det\phi^0) - \ln(\det\hat{\phi}) = -\ln\det[(\phi^0)^{-1}\hat{\phi}] = -\ln\det(1 + G^0\varphi)\,, \tag{41}$$

where we have introduced the static Green's function $G^0 = (\phi^0)^{-1}$ and the difference between the coupling constants $\varphi = \hat{\phi} - \phi^0$.

If we now consider two subspaces D and R, where D contains all atoms with changed coupling constants and R all other atoms, the matrix φ has only nonzero elements in subspace D:

$$\varphi = \begin{pmatrix} \varphi_{DD} & 0 \\ 0 & 0 \end{pmatrix}. \tag{42}$$

Then we obtain

$$\det(1 + G^0\varphi) = \det\begin{pmatrix} 1 + G^0_{DD}\varphi_{DD} & 0 \\ G^0_{RD}\varphi_{DD} & 1 \end{pmatrix} = \det(1 + G^0_{DD}\varphi_{DD})\,, \tag{43}$$

and for the entropy

$$S_1 = -\tfrac{1}{2}k\ln\det(1 + G^0_{DD}\varphi_{DD}) - 3k\int_0^{\omega_{\max}} d\omega\,\ln\left(\frac{\omega}{\omega_E}\right) z^0_x(\omega)\,. \tag{44}$$

The importance of this equation is in the fact that only matrices and determinants in subspace D have to be calculated which is especially convenient when the coupling parameters are restricted to a small number of atoms contained in a few shells. A similar expression was obtained by Govindarajan[22] for the case of a substitutional defect.

Numerical calculations were carried out using three potentials appropriate for Cu, the Morse potential and the Born-Mayer potential of Sec. II, and a pure nearest-neighbor potential, for which the results are independent of parameters used.

In the case of nearest-neighbor interaction there are no relaxations in the presence of the vacancy and the changes of coupling constants are restricted to nearest neighbors. As an exact result for an infinite crystal we obtain the value

$$S_1 = 2.08k\,, \tag{45}$$

with the integral term yielding the contribution 0.25. This is about 20% higher than the value 1.73 obtained in the Einstein approximation.

In the case of the Morse potential the relaxations are rather small. If φ is restricted to the fourth shell (55 atoms), we obtain

$$S_1 = 2.35k\,. \tag{46}$$

In the case of the Born-Mayer potential it was impossible to obtain sufficient accuracy due to the large relaxations involved. Calculations were performed up to the sixth shell (87 atoms) yielding a much lower value (1.32) than in the case of the Morse potential. However, an estimate of the error due to the restriction to six shells gave a correction of the same magnitude as the value itself. This indicates that calculations for a much larger number of atoms would have to be performed which were not possible on the computer used.

To show the effects of the relaxations, calculations for the two last potentials were carried out with and without relaxations. In the case of the Morse potential the change from no relaxations to full relaxations was small (2.28 to 2.35). However, in the case of the Born-Mayer potential, the change was large (2.52 to 1.32) again verifying the importance of large relaxations.

It is instructive to examine the local vibrational spectra of the atoms in the vicinity of the vacancy which can be calculated from the imaginary part of the defect-lattice Green's function:

$$z_i^m(\omega) = (2M\omega/\pi)\,\mathrm{Im}G_{ii}^{mm}(\omega)\,. \tag{47}$$

Contrary to the ideal lattice where for cubic symmetry the local spectrum agrees for all directions, the spectra of atoms in the presence of the vacancy depend on the direction. In Figs. 3(a)–3(c) we show the spectrum for the nearest-neighbor atom at position 110 in the three principal directions [110], [1$\bar{1}$0], and [001] for the case of the Born-Mayer potential and for the [110] direction for the case of the Morse potential (Fig. 4). In either case no localized modes were found. The main difference from the ideal spectrum occurs in the [110] direction where the frequency distribution is considerably shifted to lower frequencies. This can be explained by the absence of the

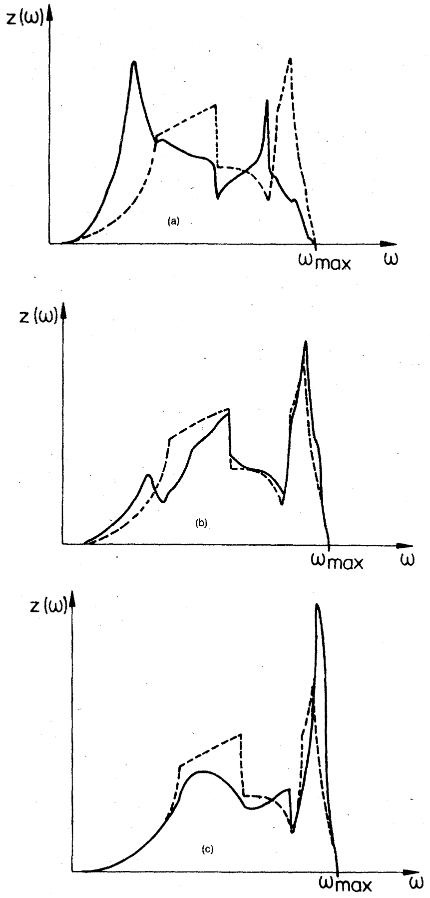

FIG. 3. Local vibrational spectra for a nearest neighbor of the vacancy by using the Born-Mayer potential. For comparison the spectrum for the ideal lattice is shown for the same potential (dashed line). The vacancy is located at 000, the nearest neighbor at 110. (a) Vibrations of the nearest neighbor in the direction [110], i.e., towards the vacancy. (b) Vibrations in the direction [1$\bar{1}$0]. (c) Vibrations in the direction [001].

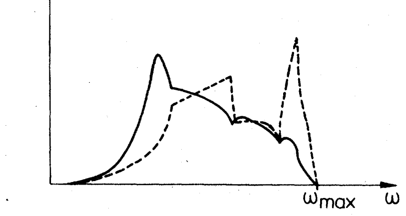

FIG. 4. Local frequency spectrum of a nearest neighbor for vibrations in [110] direction by using the Morse potential, compared with the spectrum for the ideal lattice (dashed line) with Morse-potential interaction.

coupling to the vacancy in this direction and is also reflected in the particular lowering of the Einstein frequency for this direction. The local spectrum for the other two directions of the nearest neighbor and for all directions of more distant neighbors are much more like the ideal spectrum. In the case of the [001] direction there appears to be a shift to higher frequencies, probably due to the strengthening of the nearest-neighbor bonds.

In terms of computational use the Green's-function method takes longer and requires more storage than the determinant method and is unable to perform calculations with a large number of atoms. It is not as flexible with respect to changes of the problems (e.g., for the saddle-point problems). It does however give additional interesting information for the local spectra and yields exact results for infinite lattices, if the force-constant changes are restricted to the vicinity of the defect. To have two independent methods is also very useful for a check on the results.

V. COMPARISON WITH EXPERIMENTAL RESULTS AND DISCUSSIONS

Simmons and Balluffi[23] measured the concentration of vacancies in other metals and on the basis of these suggested a value of $(1.5 \pm 0.5)k$ for the formation entropy of Cu. As pointed out recently by Hehenkamp and Lüdecke[3] these authors used some experimental data, which can no longer be considered as significant. A reevaluation of the same data by Hehenkamp and Lüdecke gave $S_1 = (2.4 \pm 0.5)k$. Resistivity measurements of Hehenkamp and Sander[4] with lower accuracy give $S_1 = (3.5 \pm 1.5)k$. Bourassa and Lengeler[1] have measured the resistivity quenched into Cu single crystals. By assuming the vacancy concentration at the melting point to lie between 150 and 200 ppm, they obtain a value of $(2.20 \pm 0.15)k$ for S_1. Recently Mantl and Triftshäuser[2] obtained by a combination of positron annihilation measurements and of resistivity measurements a value of $S_1 = (2.6 \pm 0.5)k$ for Cu. All these measurements agree very well and compare favorably with the theoretical value of $2.3k$ for the Morse potential. Note however that the value for the Born-Mayer potential is significantly smaller ($S_1 = 1.6k$).

Other experimental work on resistivity has been performed by Lucasson *et al.*[24] and others.[25] On the basis of their results Brudnoy[26] quotes the range of values for the entropy of formation as between $2.9k$ and $3.5k$. From work on specific heat Kraftmekler and Strelkov[27] give a value of $3.7k$.

In connection with diffusion measurements, Weithase and Noack[5] have recently carried out a review of all diffusion measurements for vacancies in Cu (for which one should look for references) in addition to doing some tracer and NMR work of their own. For single vacancies the result for $\tilde{D}$ is 0.114 cm^2/sec for their own tracer measurements and 0.160 cm^2/sec for a combined analysis of all measurements to date. Our results for the Morse potential (0.12 cm^2/sec) thus appears to be reasonably close whereas the Born-Mayer value (0.045) seems to be too small here.

For divacancies the errors involved are usually larger. Weithase and Noack report a value here of $\tilde{D} = 3.4$ cm^2/sec for their own tracer work and 6.4 cm^2/sec for a combined analysis. Our results (3.7 cm^2/sec for a Morse potential) compares very well with their tracer result. Since the results for the divacancy involve the nature of the potential in the region of the double hump for the divacancy in the saddle-point position and the sensitivity to the potential generally, it is not surprising that the calculated value should be different from the combined experimental one.

In the case of α-Fe, Hettich, Mehrer, and Maier[28] report a value of 1.0 cm^2/sec for $\tilde{D}$. Our result (0.16 cm^2/sec) is less than this, indicating possibly that we have not chosen a good potential for α-Fe or that again the double-hump nature of the saddle-point position for a single vacancy is involved.

Concluding from the close agreement with the experimental results, one can say that the short-range Morse potential gives a good description of the vibrational behavior of vacancies in Cu, which we consider as representative of fcc metals. This is in agreement with the general findings of Johnson[19] and Dederichs *et al.*[30] that short-range potentials like the used Morse give a reasonable description of the formation and migration energies of single and divacancies in fcc which is not the case for the Born-Mayer potential nor for the longer-ranged Morse potential of Cotterill and Doyama.[31] Note that the Born-Mayer potential gives also worse values for the formation entropy and especially for the effective diffusion frequency.

Such short-range potentials also lead to relatively small atomic relaxations around the vacancy. Clearly a value of $-0.5V_c$ for the relaxation volume cannot be obtained from these potentials. Further, as, e.g., discussed in,[19,30] these potentials predict that small-vacancy aggregates have a compact three-dimensional form like small voids rather than two-dimensional dislocation loops. It remains to be seen if these predictions based on short-ranged central potentials can be verified experimentally.

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