

²⁶E. N. Economou and Morrel H. Cohen, Phys. Rev. B **4**, 396 (1971).

²⁷V. S. Pugachev, *Theory of Random Functions* (Pergamon, Oxford, 1965), pp. 136–140 and 273.

²⁸R. VonMises, *Mathematical Theory of Probability and Statistics* (Academic, New York, 1964), pp. 289–305.

²⁹The statement that the distribution of the quantity $X_i^{(N)}$ is a normal one means only that for arbitrary a and b

$$\lim \int_a^b P_i^{(N)}(x) dx = \int_a^b \Phi(x) dx \text{ as } N \rightarrow \infty,$$

where $P_i^{(N)}$ is the distribution function of $X_i^{(N)}$, and Φ is a normalized Gaussian with mean value and standard deviation equal to $\lim \langle X_i^{(N)} \rangle$ as $N \rightarrow \infty$ and $\lim \sigma_{X_i^{(N)}}$ as $N \rightarrow \infty$, respectively (see Refs. 27 and 28). It should be emphasized that the stronger condition $\lim P_i^{(N)}(X) = \Phi(X)$ as $N \rightarrow \infty$ is not in general true and as a consequence one cannot in general calculate the moments of $X_i^{(N)}$ using the normal distribution. This observation is particularly relevant to the present case, where, as Anderson pointed out (Ref. 4), the distributions of $T_i^{(N)}$ (and hence of $X_i^{(N)}$) are long tailed. This long tail in the distribution $P_i^{(N)}$ makes a zero contribution to any integral of the form $\int_a^b P_i^{(N)}(x) dx$ as $N \rightarrow \infty$, but a nonzero contribution to integrals of the form $\lim \int_a^\infty x^n P_i^{(N)}(x) dx$ as $N \rightarrow \infty$ for $n > 0$. Thus the central limit theorem should be used with extreme caution in the present case; e.g., it cannot be used to simplify Anderson's original analysis (Ref. 4), where an integral of the type $\lim K^N \int_{A_N}^\infty P_i^{(N)}(x) dx$ as $N \rightarrow \infty$ must be calculated with $\lim A_N \rightarrow \infty$ as $N \rightarrow \infty$, and $K > 1$.

³⁰This statement is correct only if the shift in the levels (due to the different sites omitted) is not much larger than the average level spacing. One can argue in favor of the latter statement assuming that the eigenstates are localized in a fashion similar to that suggested by classi-

cal percolation theory [i.e., that they tend to become extended as we approach the mobility edge in an essentially one-dimensional way (channels)]. In this case the shift of the levels is of the order $1/l$, where l is the length of the channel; the average spacing of the levels in a one-dimensional potential well of length l is of the order of $1/l$, i.e., of the same order of magnitude as the level shift. However, since the fluctuation of the potential along the channel is not uniform, one expects that the average level spacing in the channel would be larger than the corresponding uniform potential well. Thus the level shift is expected to be of the same order of magnitude or less than the average level spacing.

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Vacancy-Formation Entropy in Cubic Metals

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Vacancy-formation entropies were computed for a number of face-centered-cubic solids from vibrational frequency distributions which were computed from pair potentials. The formation entropy is a monotonic function of the vacancy relaxation, computed from the same pair potential. It is shown that the relaxation of the nearest neighbors to the vacancy in fcc solids can be described by $\delta_1 = -5.8 \times 10^{15} (K/\alpha V)^2$, where δ_1 is in percent, K is the compressibility, α the linear thermal-expansion coefficient, and V is the molar volume. The computed vacancy-formation entropies are described by $\Delta S = 1.83 + 3.4 \times 10^{15} (K/\alpha V)^2$ in units of k /vacancy. Similar relations are obtained for bcc metals. The experimental relations found for model solids are used to predict vacancy relaxations and formation entropies from experimental values of K , α , and V . Vacancy relaxations are predicted to be less than 0.2% of the normal neighbor distance in most fcc metals and 2–5% in bcc metals. Vacancy-formation entropies are predicted to be $1.8k$ – $2.0k$ in most fcc metals and $2.2k$ – $2.6k$ in bcc metals. The predictions for the entropy are in satisfactory agreement with experimental data, where reliable data exist.

I. INTRODUCTION

There are questions as to the self-diffusion mechanism in rare-gas solids¹ and noble metals.²

It is known that vacancies play an important role. This has motivated a number of workers to attempt to calculate the formation entropy,^{3–12} motion entropy,^{7,8} formation energy,^{5,7,10,11,13–16} and motion

energy^{7, 14, 17-19} of vacancies in rare-gas solids^{5-7, 10-12, 14, 15} and simple metals.^{3, 4, 8, 13, 16-19} These works have assumed a potential to describe the atom-atom interactions in the solid and have used this interaction to calculate the defect properties.

There are two serious difficulties in the works cited above: (a) The computed defect properties are quite sensitive to the assumed potential,^{14, 16} which is generally not known well enough to give a definitive result; (b) there are considerable problems involved in calculating defect entropies. In the standard approach,³⁻⁹ one calculates force constants from the potential, and uses the Einstein approximation to calculate the entropy. Unfortunately, the Einstein approximation is sufficiently inaccurate that it is difficult to assess the validity of the numerical results.

Both problems mentioned above can be surmounted. In the case of the inaccurate potential, one has available two approaches. One may look for a new "best" potential. This approach has the disadvantage that the new "best" potential may not be good enough or may give results which differ from those obtained with some other "best" potential. The second solution to the inaccurate potential problem is to seek results which do not depend strongly on the potential and then to attempt to relate these model-independent results to experiment. This is the approach of the work presented here. We calculate, with a method described below, the vibrational-vacancy-formation entropy in a number of solids described by several different types of pair potentials. We show that there is a simple relation between the vacancy-formation entropy and vacancy relaxation (distortion around the vacancy). This vacancy relaxation is related to the anharmonicity of the pair potential, which is, in turn, related to the high-temperature thermal-expansion coefficient and the compressibility, which can be determined experimentally. Thus, for any solid, it is possible to use computationally determined correlations to estimate the vacancy-relaxation and -formation entropy from experimental observables. In this work we examine face-centered-cubic (fcc) and body-centered-cubic (bcc) metals and estimate vacancy properties. The same procedures could be applied to noncubic metals and possibly polyatomic solids.

The inaccuracy of the Einstein approximation for the entropy can be avoided by employing a procedure first used by Land and Goodman²⁰ to calculate defect vibrational frequencies and then by the author¹² to calculate the entropy of mono- and divacancies in rare-gas solids. In creating a vacancy, one goes from a lattice with n sites and n atoms to a lattice of $n+1$ sites and n atoms. The only effect of this process on the vibrational frequencies of the lattice (and hence on the entropy) is through the change in

the force constants near the vacant site. (The removed atom becomes just another bulk atom.) The vibrational frequencies and the entropy of vacancy formation can be calculated by considering a perfect cluster of n atoms in an infinite lattice and then a cluster of n sites and $n-1$ atoms in the same lattice. Comparison of these two clusters gives an approximation to the vacancy properties. As n , the cluster size, approaches infinity, the above procedure gives the vacancy properties.

We used the above procedure to calculate the formation entropy of a single vacancy and the binding entropy of the divacancy in argon.¹² In the earlier work, we obtained adequate agreement with experiment for the single vacancy and showed that the Einstein approximation gives seriously incorrect results for the divacancy.

In this paper, we calculate the vacancy-formation entropy for a number of models of cubic metals and then show how our model results can be used to estimate the formation entropy of vacancies in real metals. The paper is organized as follows: In Sec. II we express formally the relations required to calculate the vacancy entropy for a model. In Sec. III we describe and discuss the models employed in this work. In Sec. IV we show that the computational technique does give a well-defined result and compute the vacancy entropies. In Sec. V we discuss the possible relation of our computations and real materials. Finally, in Sec. VI we attempt to predict the vacancy-formation entropy of several solids and examine the relation between our predictions and existing experimental data.

II. THEORY

Consider a cluster of n atoms on n sites within a perfect crystal. The n atoms vibrate as coupled harmonic oscillators and the remainder of the crystal is held fixed. The vibrations of the n atoms can be described by a $3n \times 3n$ force-constant matrix $K_{n,n}$. This force-constant matrix may be diagonalized by suitable matrix operations to give its $3n$ eigenvalues, $k_{n,n}(i)$, $i = 1, \dots, 3n$. The normal vibrational frequencies are

$$\nu_{n,n}(i) = (1/2\pi) (k_{n,n}(i)/m)^{1/2}, \quad (1)$$

where m is the mass of the atom. Finally, the entropy per atom, in this cluster approximation, is

$$S_{n,n}(T) = \frac{k}{n} \sum_{i=1}^{3n} \left(\frac{u(i)}{e^{u(i)} - 1} - \ln(1 - e^{-u(i)}) \right), \quad (2)$$

where

$$u(i) = h\nu_{n,n}(i)/kT. \quad (3)$$

If a central atom is removed from the original n -atom cluster, we have left $n-1$ atoms plus a vacancy. The vibrations of these $n-1$ atoms are

described by a $(3n-3) \times (3n-3)$ matrix, $K_{n-1,n}$, with eigenvalues $k_{n-1,n}(i)$, $i=1, \dots, 3n-3$, and normal mode vibrational frequencies $\nu_{n-1,n}(i)$. The entropy per atom for the cluster with a vacancy, $S_{n-1,n}(T)$, may then be calculated from the frequencies.

At this point, we may calculate an approximation to the entropy of formation of the vacancy. We started with n atoms having entropy $S_{n,n}(T)$ per atom. After forming the defect, we have $n-1$ atoms with entropy $S_{n-1,n}(T)$ and one atom which has been removed to another bulk site. But $S_{n,n}(T)$ is the appropriate approximation to the entropy of a bulk atom. Hence, in the n -atom-cluster approximation, the entropy of forming a vacancy is given by

$$\Delta S_n(T) = (n-1)[S_{n-1,n}(T) - S_{n,n}(T)]. \quad (4)$$

The entropy of forming a vacancy in an infinite lattice is then

$$\Delta S_v(T) = \lim_{n \rightarrow \infty} \Delta S_n(T). \quad (5)$$

We will show in Sec. III that $\Delta S_v(T)$ is well defined and that our limit process converges. In this definition of ΔS_v , we have neglected entirely any effects which come from other than the lattice vibrations, such as the temperature dependence of the energy.⁷ We also neglect surface contributions to the entropy,²¹ which are thought to be small.⁸

III. MODELS

We have employed several standard models of simple solids. All of these models utilize empirical pair potentials. The particular models to be employed were chosen because they have previously been used to calculate relaxations around vacancies. Thermal-expansion effects are omitted in all of these models.

(i) *Nearest-neighbor harmonic interactions only.* The only parameter in this potential is a scale factor, the force constant. All nearest-neighbor harmonic potentials are identical except for the scale factor. We have used this potential for both fcc and bcc solids. It is well known that infinite bcc lattices are unstable for this potential. The surrounding rigid matrix in our calculations stabilizes the

TABLE I. Morse-potential parameters for cubic metals.

Metal	α (\AA^{-1})	r_0 (\AA)	D (eV)
Pb	1.1836	3.733	0.2348
Ni	1.4199	2.780	0.4205
Cu	1.3588	2.866	0.3429
Ca	0.80535	4.569	0.1623
Fe	1.3885	2.845	0.4174
Ba	0.65698	5.373	0.1416
Na	0.58993	5.336	0.06334

TABLE II. Relaxations of near neighbors about a vacancy in fcc metals in percent of normal distances. Negative values refer to motion into the vacancy. Data are from Girifalco and Weizer (Ref. 25).

Metal	1st	2nd
Pb	-1.42	0.43
Ni	-2.14	0.39
Cu	-2.24	0.40
Ca	-2.73	0.41

cluster in bcc. Though the potential is not strictly applicable to bcc, its use is instructive. One feature of the nearest-neighbor harmonic interaction is significant: there are no relaxations around the vacancy.

(ii) *Morse potential.* The interactions between two atoms separated by r is given by

$$V(r) = D(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}), \quad (6)$$

where D , α , and r_0 are coefficients which must be fit to the properties of the material. We used the coefficients which were determined by Girifalco and Weizer²² for the fcc metals Pb, Ni, Cu, and Ca and the bcc metals Fe, Ba, and Na. The potential parameters were obtained by fitting experimental values for the energy of vaporization, the lattice constant, and the compressibility and are in Table I. These potential parameters do not necessarily exactly describe the materials. Lincoln *et al.*²³ used the same experimental quantities and obtained Morse-potential parameters differing from Girifalco's by as much as 10%; they also showed that the Morse potential does not adequately describe the third-order elastic coefficients. In addition to these objections, it is well known²⁴ that pseudopotentials describe metals more accurately than Morse potentials.

Several authors^{25, 26} have used Girifalco and Weizer's Morse-potential parameters²² to calculate the relaxations around a vacancy (Tables II and III). As can be seen with the bcc metals (Table III), the calculation of the relaxations from the potential is subject to some uncertainties. We are not able to ascertain which set of relaxations is best and employ Grimes and Rice's data.²⁶ We do this as these are the most recent and hopefully eliminate earlier mistakes, and because Grimes and Rice suggest that their discrepancies with Wynblatt and Gostein²⁷ may result from different crystal sizes and shapes. Grimes and Rice point out, however, that even more neighbor relaxations may be important.

(iii) *Lennard-Jones 6-12 potential.* The interaction between two atoms separated by r is given by

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (7)$$

TABLE III. Relaxations of near neighbors about a vacancy in bcc metals in percent of normal distances. Negative values refer to motion into the vacancy. Data are from Girifalco and Weizer (GW) (Ref. 25), Wynblatt and Gjostein (WG) (Ref. 26) and Grimes and Rice (GR) (Ref. 27).

Metal	1st	2nd	3rd	4th	Ref.
Fe	-6.07	2.12	-0.25		GW
	-6.8	2.3	-0.7		WG
	-6.96	2.71	-0.66	0.27	GR
Ba	-7.85	2.70	-0.70	0.33	GW
	-8.4	3.3	-1.0		WG
	-8.21	2.66	-0.80	0.21	GR
Na	-10.80	3.14	-3.43	0.20	GW
	-10.0	3.2	-1.2		WG
	-9.74	2.26	-1.01	0.05	GR

In this work we have used potential constants appropriate to argon.²⁸ The Lennard-Jones 6-12 potential is often applied to the study of defects in rare-gas solids,^{5-7,10-12,14,15} though it is not the best possible pair potential^{29,30} and many-body effects may be quite important.^{1,14,31,32} Burton and Jura³³ calculated the relaxations of argon around a vacancy for the normal zero-pressure interatomic distance and for a number of compressions and dilations of the solid. In this work we use some of their data—namely the normal nearest-neighbor distance and distances which give relaxations comparable to the Morse-potential relaxations, Table II, or give zero relaxation as given by nearest-neighbor interactions; one distance was examined because of the outward relaxation of the neighbors to the vacancy. The values of r/r_0 and the neighbor relaxations employed here are in Table IV.

(iv) *Lennard-Jones 6-7 potential.* The interaction between two atoms separated by r is given by

$$V(r) = D[(\sigma/r)^7 - (\sigma/r)^6]. \quad (8)$$

Burton and Jura³³ also used this potential, with constants appropriate to argon, to calculate relaxa-

TABLE IV. Relaxations of near neighbors around a vacancy in fcc argon with a Lennard-Jones 6-12 potential. Distances are in percent of normal distance. Negative values refer to motion into the vacancy. r_0 is the zero-pressure nearest-neighbor distance; r is the nearest-neighbor distance assumed in the calculations. Data are from Burton and Jura (Ref. 33).

r/r_0	1st	2nd
0.92	-1.377	0
1.00	-0.606	0
1.00	-0.606	0.171
1.03	0.010	0
1.05	0.660	0

tions around a vacancy for a number of values of the nearest-neighbor distance. In this work, we use some of their data; the values of r/r_0 and the relaxations employed are in Table V.

IV. COMPUTATIONS

The first computations¹² were made for nearest-neighbor atomic interactions, model 1. The force-constant matrices were diagonalized on an IBM 360/91 computer using a matrix-diagonalization routine³⁴ developed by Kortzeborn of IBM. In previous studies involving matrix diagonalization,³⁵ we have found that the standard IBM-Scientific-Subroutine-Package matrix-diagonalization procedure does not give sufficiently reliable eigenvalues. Calculations were made for clusters of up to 88 sites. All of the clusters were formed by adding closed shells of near neighbors to a central site. The central site was the vacancy in the cluster. The values of ΔS_n , Eq. (4), were calculated in the high-temperature limit, where they no longer are temperature dependent. Table VI contains the computed values of ΔS_n for the nearest-neighbor interactions for an fcc lattice.

As can be seen from Table VI, the vacancy-formation entropy converges nicely as n increases. Based on Table VI, it appears that clusters including fourth-nearest neighbors are adequate to estimate defect properties. All further computations in this paper are for clusters of six shells (87 sites) in fcc solids and seven shells (88 sites) in bcc solids. We could not examine larger clusters without using very elaborate matrix-manipulation procedures³⁶ as our computer does not have sufficient storage. Diagonalization of the 261×261 matrix for a 87 atom cluster requires 850 000 bits of storage on our IBM 360/91 computer and costs approximately 25 dollars.

The high-temperature vacancy-formation entropy ΔS_v [Eq. (5)] was computed for all the models described in Sec. III using 87 site clusters for fcc solids and 88 sites for bcc solids. The results of these computations are in Tables VII (fcc) and VIII (bcc).

TABLE V. Relaxations of near neighbors around a vacancy in fcc argon with a Lennard-Jones 6-7 potential. Distances are in percent of normal distance. Negative values refer to motion into the vacancy. r_0 is the zero-pressure nearest-neighbor distance; r is the nearest-neighbor distance assumed in the calculations. Data are from Burton and Jura (Ref. 33).

r/r_0	1st
0.88	-2.199
1.00	-1.375
1.06	-0.506

TABLE VI. ΔS_n , the high-temperature entropy of formation of a vacancy in the n site approximation. N is the number of closed shells of near neighbors added to the central atom/vacancy. The data are for nearest-neighbor interactions and an fcc lattice.

n (No. of sites)	N (No. of shells)	ΔS_n (k /vacancy)
13	1	1.50
19	2	1.53
43	3	1.68
55	4	1.81
79	5	1.84
87	6	1.83

V. RELATION BETWEEN COMPUTATION AND EXPERIMENT

Three conclusions are immediately apparent from Tables VII and VIII: (a) Compression of the solid increases the vacancy-formation entropy; (b) vacancy entropies can vary widely within one lattice structure; (c) vacancy entropies are somewhat higher in bcc solids than in fcc solids.

The third of these observations has an obvious explanation: In bcc solids there are only eight nearest neighbors as compared with 12 in fcc solids; therefore, the lattice is looser around a bcc-solid vacancy than around an fcc-solid vacancy.

This section is devoted to an explanation of observations (a) and (b). We will show that there are systematic variations in the entropy and will attempt to relate these variations to the properties of the materials. We will ultimately obtain empirical

TABLE VII. Computed high-temperature vacancy-formation entropies for a number of fcc models. The models are described in Sec. III.

Material	Model	ΔS_v (k /vacancy)
General	Nearest-neighbor interactions, No. 1	1.83
Pb	Morse potential, No. 2	2.76
Ni	Morse potential, No. 2	3.10
Cu	Morse potential, No. 2	3.17
Ca	Morse potential, No. 2	3.47
Ar	L-J 6-12 potential, No. 3 $r/r_0 = 1.00$, two shells relaxing	2.24
	L-J 6-12 potential, No. 3 one shell relaxing	
	$r/r_0 = 0.92$	2.61
	$r/r_0 = 1.00$	2.30
	$r/r_0 = 1.03$	1.94
	$r/r_0 = 1.05$	1.47
	L-J 6-7 potential, No. 4	
	$r/r_0 = 0.88$	2.98
	$r/r_0 = 1.00$	2.69
	$r/r_0 = 1.06$	2.30

relations which can be used to predict the vacancy-formation entropy in fcc and bcc solids. Most of the discussion here will be devoted to fcc solids, as we have examined a number of such, Table VII.

In Fig. 1, we have plotted the calculated vacancy formation entropy in fcc solids, Table VII, against the calculated relaxation of the first-nearest neighbor to the vacancy for the various models employed here, Sec. III, Tables II, IV, and V. It is apparent from the plot that the vacancy entropy varies monotonically with the vacancy relaxation. The actual variation in the figure is linear and the deviations of the entropies from the straight line are less than 2%. We do not attach any special significance to the linear relation. It is interesting to note that the relaxation uniquely determines the entropy. It is, however, important to stress that we have examined only four types of potentials; other potentials might give vacancy entropies which do not lie close to the curve shown.

At this point we will explain why the vacancy entropy increases with increasing inward relaxation. Consider an atom in a one-dimensional line of atoms with an anharmonic potential, Fig. 2. If the interaction is not confined to just the nearest neighbors, the zero-pressure nearest-neighbor separation r_0 will not be the minimum-energy separation for the potential, σ . Rather the long-range attraction will cause the atoms to be slightly closer to each other than σ . If we expand the potential energy of the atom about the minimum-energy separation, we find

$$V(\Delta) = B\Delta^2 - C\Delta^3, \quad (9)$$

where

$$\Delta = X - \sigma \quad (10)$$

and X is the distance between two atoms. At equilibrium, r_0 is less than σ and Δ is negative. The nearest-neighbor vibrational force constant is

$$k = \frac{1}{2} \frac{\partial^2 V}{\partial \Delta^2} = B - 3C\Delta = B - 3C(r_0 - \sigma). \quad (11)$$

Now suppose we create a vacancy at 0 as shown in Fig. 2. The atom adjacent to the vacancy relaxes

TABLE VIII. Computed high-temperature vacancy-formation entropies for a number of bcc models. The models are described in Sec. III.

Material	Model	ΔS_v (k /vacancy)
General	Nearest-neighbor interactions, No. 1	2.03
Fe	Morse, No. 2	3.14
Ba	Morse, No. 2	3.64
Na	Morse, No. 2	4.59

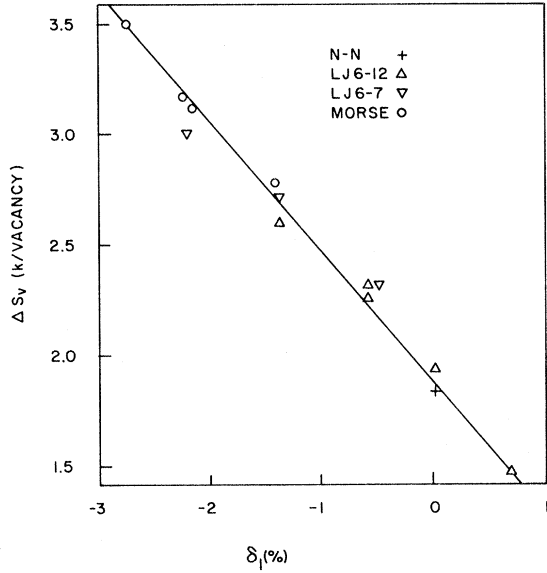


FIG. 1. Computed vacancy-formation entropies for a number of fcc solids using nearest-neighbor (N-N), Lennard-Jones 6-12 (LJ 6-12), Lennard-Jones 6-7 (LJ 6-7), and Morse potentials plotted against the computed percentage relaxation of the first-nearest neighbors to the vacancy, δ_1 .

towards the vacancy by δ . Hence it relaxes *away* from its nearest neighbor by δ to a separation $r_0 + \delta$. But from (11) the nearest-neighbor force constant is *decreased* to

$$k = \frac{1}{2} \frac{\partial^2 V}{\partial \Delta^2} = B - 3C(r_0 + \delta - \sigma) \quad (12)$$

and the change in the nearest-neighbor force constant is

$$\Delta k = -6C\delta. \quad (13)$$

Therefore, the larger the inward relaxation, the greater is the decrease in the nearest-neighbor force constant. But the entropy is determined by the force constants. The smaller the force constant, the larger is the entropy. Hence, a large inward relaxation of the atoms adjacent to the vacancy causes a large increase in the entropy.

We have shown simply that the relation between relaxation and entropy in Fig. 1 is reasonable. Similar reasoning explains why compression of a solid causes an increased relaxation of the vacancy (see Table VII, argon data): The more the solid is compressed, the more repulsive the nearest-neighbor interaction becomes.

We have shown, so far, that it is physically reasonable that the vacancy-formation entropy increases as the inward relaxation of the nearest neighbors increases. This occurs because of the anharmonicity of the potential. We will now attempt to find an

empirical relation between the vacancy relaxation and experimentally accessible parameters which describe the harmonic and anharmonic aspects of the solid, the compressibility, and the thermal-expansion coefficient.

Suppose we write the change in energy of a solid when its nearest-neighbor distance r is changed as

$$\Delta U(r) = c(r - r_0)^2 - g(r - r_0)^3. \quad (14)$$

(This is the simplest anharmonic expansion.) Then the isothermal bulk compressibility is given by

$$K = (9/2\sqrt{2})(r/c) \quad (15)$$

for fcc solids, and the high-temperature linear thermal-expansion coefficient is given by³⁷

$$\alpha = (1/r)(3g/4c^2)k, \quad (16)$$

where k is Boltzmann's constant. Note that c/g has units of cm. Hence c/gr is a dimensionless quantity which describes the relative harmonic and anharmonic contributions to the solid.

Combining (15) and (16) we find that

$$c/gr = (k/3\sqrt{2})(K/\alpha r^3). \quad (17)$$

Hence, $K/\alpha V$, where V is the molar volume, is a measure of the anharmonicity.

We have calculated c , g , α , K , and $K/\alpha V$ for our four fcc metals described by Morse potential and for argon at its normal atomic distance described by the Lennard-Jones 6-7 and 6-12 potentials. The parameters were not computed for dilated and compressed argon, as the expansion in (14) is not applicable to them—their energy also contains a linear term in the nearest-neighbor distance. The computed quantities are in Table IX.

In Fig. 3, we have plotted $K/\alpha V$ against the relaxation of the first-nearest neighbors to the vacancy in the fcc solids. We have not included the nearest-neighbor potential, model 1, as it is not a long-range interaction and $\alpha = 0$ for it. $K/\alpha V$ was taken from Table IX and the relaxations are from Tables II,

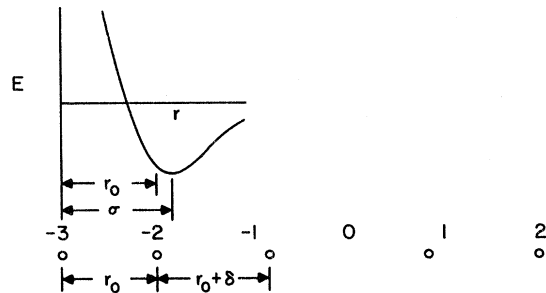


FIG. 2. Schematic representation of a vacancy at 0 in a one-dimensional line of atoms. r_0 is the normal interatomic spacing. δ is the relaxation. The energy is also represented schematically as a function of distance. σ is the pair minimum-energy separation.

TABLE IX. Computed value of c and g [see Eq. (14)], K , the isothermal compressibility, α , the high-temperature thermal-expansion coefficient, and $K/\alpha V$, where V is the molar volume for six fcc solids.

Material	c (erg cm ⁻²)	g (erg cm ⁻³)	K (cm ² dyn ⁻¹)	α (°K ⁻¹)	$K/\alpha V$ (× 10 ⁹)
Ar					
6-7 potential	0.78×10^3	0.97×10^{11}	154×10^{12}	44×10^{-5}	14.6
6-12 potential	4.1	7.1	29	11.5	10.5
Pb	50	61	2.2	0.72	16.6
Ni	166	250	0.47	0.37	19.2
Cu	128	180	0.63	0.45	19.6
Ca	26	220	4.8	0.86	21.7

IV, and V. The relaxations for these six fcc solids can be described to within $\pm 7\%$ by

$$\delta_1 = -5.8 \times 10^{15} (K/\alpha V)^2, \quad (18)$$

with δ_1 in percent and K , α , and V in cgs units. Finally, in Fig. 4, we plot the vacancy-formation entropy ΔS_v for these six fcc solids against $(K/\alpha V)^2$. Here the data can be fit within $\pm 2\%$ by

$$\Delta S_v = 1.83 + 3.7 \times 10^{15} (K/\alpha V)^2, \quad (19)$$

with S in $k/\text{vacancy}$ and $K/\alpha V$ in cgs units.

It is very important to realize that Eqs. 18 and 19 are essentially experimental results. We have done a numerical experiment—computed the vacancy-formation entropy ΔS_v and the vacancy relaxation δ_1 for six model fcc solids. We have shown that our results can be described by simple empirical relations. We have argued physically that the relaxa-

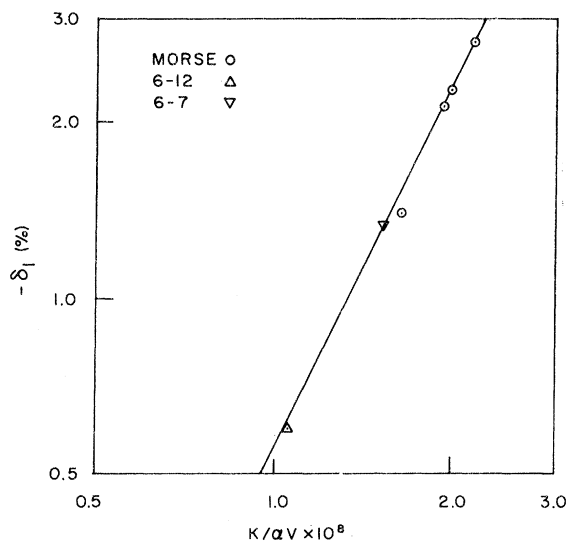


FIG. 3. Plot of $-\delta_1$, the inward relaxation of the nearest neighbors to the vacancy in percent, against $K/\alpha V$ in cgs units on a log-log scale for fcc solids.

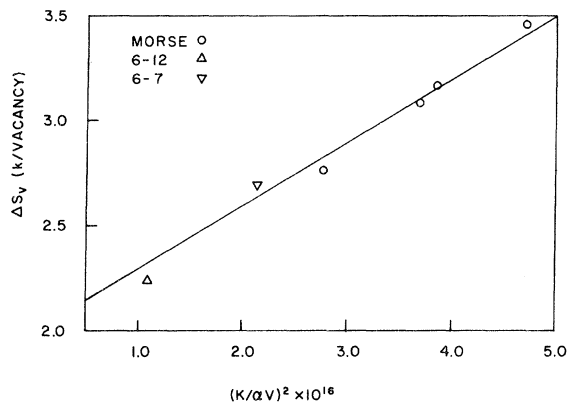


FIG. 4. Plot of computed vacancy-formation entropy, ΔS_v , against $(K/\alpha V)^2$ in cgs units for six fcc solids.

tions and the entropy depends on the relaxations and the anharmonicity. However, we will make no effort to attempt to justify the coefficients which enter into Eqs. 18 and 19.

In addition to fcc solids, we examined three anharmonic bcc solids, all of which are described by Morse potentials. In Figs. 5 and 6 we plot the relaxations of the first-nearest neighbors and the vacancy-formation entropy against $K/\alpha V$. Our rather limited data for bcc solids can be fit by

$$\delta_1 = -3.54 \times 10^8 K/\alpha V \quad (20)$$

to within $\pm 3\%$ with δ_1 in percent and $K/\alpha V$ in cgs units and by

$$\Delta S_v = 2.03 + 2.98 \times 10^{15} (K/\alpha V)^2 \quad (21)$$

to within $\pm 1\%$ with ΔS_v in units of $k/\text{vacancy}$.

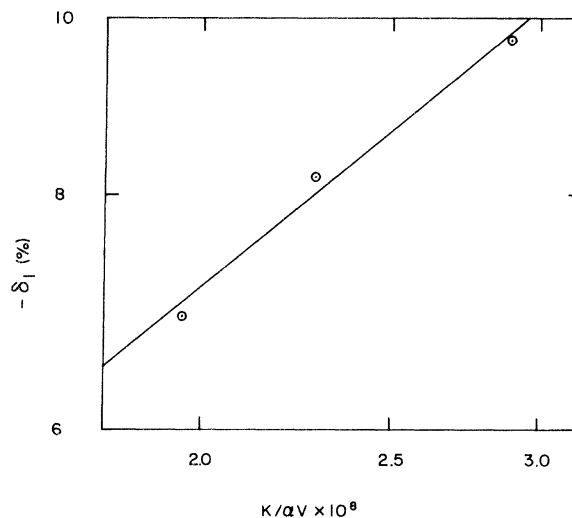


FIG. 5. Plot of $-\delta_1$, the inward relaxation of the nearest neighbors to the vacancy in percent, against $K/\alpha V$ in cgs units on a log-log scale for bcc solids.

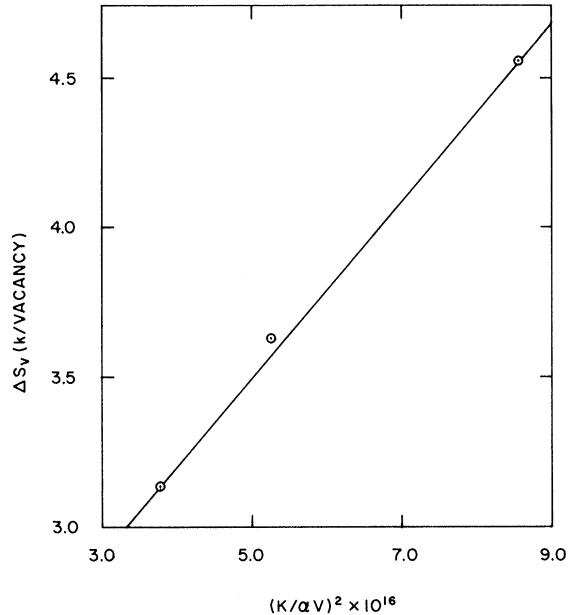


FIG. 6. Plot of the computed vacancy-formation entropy $(K/\alpha V)^2$ in cgs units for three bcc solids.

VI. PREDICTION OF VACANCY-FORMATION ENTROPIES

In Sec. V we have discussed the results of some numerical experiments. We have found that there exist empirical relations between the vacancy-formation entropy ΔS_v and $K/\alpha V$, where K is the isothermal compressibility, α is the linear thermal-expansion coefficient, and V is the molar volume. In this section, we use these relations, Eqs. (18)–(21), to predict vacancy-relaxations and -formation entropies of real materials.

In Table X, we give $K/\alpha V$ for a number of fcc and bcc elements. K is in $\text{cm}^2 \text{dyn}^{-1}$, α in $^\circ\text{K}^{-1}$, and V in cm^3 . The values of α for Li,³⁸ Na,³⁹ K,⁴⁰ Ar,⁴¹ Kr,⁴² Xe,⁴¹ Cu,⁴³ Ag,⁴⁴ Au,⁴⁵ Al,⁴⁶ and Pb⁴⁷ were determined near the melting temperature, as were the values of K for Na,⁴⁸ K,⁴⁰ Ar,⁴¹ Kr,⁴¹ and Xe.⁴¹ K at the melting temperature was estimated by extrapolation from lower temperatures for Cu,⁴⁹ Ag,⁵⁰ Au,⁵⁰ Al,⁵¹ and Pb.⁵² The remaining data was taken from Gschneider's tables at room temperature.⁵³ In general, the calculated values of $K/\alpha V$ in Table IX are somewhat larger than the experimental values in Table X. This occurs because the pair potentials do not adequately describe the anharmonicity of the solid. This is not surprising as it has been shown that the Morse potential gives poor values of the Grüneisen parameter^{22,37} and the third-order elastic coefficients,²³ both of which depend on the anharmonicity.

We have used Eqs. 18–21 to calculate the first-neighbor relaxations and the vacancy-formation

entropies from the values of $K/\alpha V$ in Table X. These are also in the table. As $K/\alpha V$ is small for all of these materials, the predicted inward vacancy relaxations are reasonably small, $< 0.3\%$ for all fcc elements except Ca (0.71%) and Sr (0.90%) and (2–5)% for bcc. The entropies are all in the range 1.8 k –2.0 k for fcc elements except Ca (2.25 k) and Sr (2.37 k) and 2.2 k –2.6 k for bcc solids. It is interesting to note that ΔS_v does not vary widely for a given structure. This occurs because $K/\alpha V$ is not strongly material dependent. Sirdeshmukh⁵⁴ has suggested that $K/\alpha V$ is about 5×10^{-9} for all fcc metals and 10^{-8} for bcc metals. These values imply vacancy-formation entropies of 1.9 k /atom in fcc metals and 2.3 k /atom in bcc metals.

Several experimenters have measured vacancy concentrations in metals and krypton. From their measurements, they have attempted to deduce the vacancy-formation entropy. Some of the available

TABLE X. Experimental values of $K/\alpha V$ and predicted values of the nearest-neighbor relaxations to the vacancy δ_1 , and the vacancy-formation entropy for a number of bcc and fcc elements. Negative values of δ_1 correspond to inward relaxations.

bcc elements	$K/\alpha V$ ($\times 10^9$)	δ_1 (%)	ΔS_v ($k/\text{vacancy}$)
Li	10.9	-3.9	2.39
Na	9.2	-3.2	2.27
K	12.8	-4.5	2.53
Rb	6.3	-2.2	2.24
Cs	7.2	-2.5	2.28
Ba	13.1	-4.6	2.55
V	8.7	-3.1	2.26
Cr	8.5	-3.0	2.25
Fe	6.8	-2.4	2.17
Nb	7.6	-2.7	2.20
Mo	7.6	-2.7	2.20
Ta	6.9	-2.4	2.17
W	6.8	-2.4	2.17
fcc elements			
Ar	6.0	-0.21	1.95
Kr	5.1	-0.15	1.92
Xe	6.3	-0.23	1.97
Ca	11.1	-0.71	2.25
Sr	12.5	-0.90	2.37
Ni	6.1	-0.22	1.96
Cu	4.1	-0.10	1.89
Rh	5.2	-0.15	1.92
Pd	5.3	-0.15	1.92
Ag	3.6	-0.07	1.88
Ir	4.8	-0.13	1.91
Pt	4.3	-0.11	1.90
Au	3.0	-0.05	1.86
Al	4.9	-0.14	1.92
Pb	4.0	-0.09	1.89

TABLE XI. Experimental values of the vacancy-formation entropy. The methods used are thermal expansion (TE), heat capacity (HC), quenching (Q), computer analysis of thermal expansion and diffusion data (C).

Material	ΔS (k /vacancy)	Method	Ref.
Al	2.0–2.4	TE	46
	0.8	C	55
Ag	1.5 ± 0.5	TE	44
	0.5	C	56
Au	1.0	TE	45
	0.5	C	57
	3.15	HC	58
Cu	0.5	C	59
	3.7	HC	58
Ni	1.5	C	55
Pb	2.6	TE+Q	60
	0.7 ± 2.0	TE	61
Kr	1.5–3.0	TE	31
	1.9–3.6	TE	32
	2.3–3.9	HC	62
Li	0.9 ± 0.8	TE	38
K	2.55	HC	58
Na	5.8 ± 1.1	TE	39
	2–4	C	55
	3.1–6.5	HC	58
	-3.2 ± 1.6	TE	63

data is summarized in Table XI. We also include Mehrer and Seeger's estimates of the vacancy entropies based on their analyses of diffusion and thermal-expansion data. We have not attempted to list all available experimental data. Kraftmakher⁵⁸ gives a number of additional heat-capacity results. Hoch⁶⁴ has pointed out that the interpretation of heat-capacity experiments is ambiguous and that Kraftmakher's formation entropies may be too high.

The data in Table XI show that vacancy-formation entropies are not well known at this time. This reflects several problems. The thermal-expansion technique is the most reliable technique. However, the experiments on most materials have been carried out by only one group, with the exceptions of

the studies of Kr and Na. In Na, we have a wide range to choose from for ΔS_v . In Kr, the best experiments, Table XI, agree that ΔS_v is in the range 1.5 k –4.0 k ; however, other experiments do not agree with these data for the total vacancy concentration.¹ The experiments themselves are quite difficult⁴⁵ and their interpretation is uncertain.⁵⁷ It appears that the best experimental work on fcc solids is at least compatible with our predicted results, $\Delta S_v \sim 1.8k$ –2.0 k , for fcc elements other than Ca (2.25 k) and Sr (2.37 k). The situation in bcc metals is too uncertain to draw any conclusions.

VII. CONCLUSIONS

In this paper, we have examined vacancy-relaxations and -formation entropies in a number of model solids. We have shown by numerical experiments that the relaxations and formation entropy can be determined empirically from experimental knowledge of the compressibility, thermal-expansion coefficient, and molar volumes. Experimental values of these coefficients suggest that relaxations are <0.3% in fcc solids except Ca (0.71) and Sr (0.90) and (2–5)% in bcc solids; the predicted vacancy entropies are about 1.8 k –2.0 k for fcc solids other than Ca (2.25 k) and Sr (2.37 k) and 2.2 k –2.6 k for bcc solids. These empirically estimated values are compatible with existing experimental data. Unfortunately, the data are not good enough to draw any definite conclusions. The results of these numerical experiments are more accurate than those of most laboratory experiments, which give widely scattered results. Until further laboratory experimental work is done, our predicted entropies must be regarded as the best "experimental" data and may be useful in estimating vacancy entropies for systems for which no better data are available.

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