PHYSICAL REVIEW B VOLUME 14, NUMBER 4 15 AUGUST 1976

Equilibrium vacancy concentration measurements in solid argon*

L. A. Schwalbe†

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 20 October 1975)

The direct technique of simultaneously measuring bulk and lattice expansion, to determine equilibrium vacancy concentrations, has been applied to solid argon. The results indicate that thermal vacancy concentrations do not exceed 0.025% even at the highest temperatures. Although the data obtained were not sufficiently precise to allow unique values to be determined for the formation parameters, it would appear from semiempirical considerations that both these results and previous ones, from a similar investigation of solid krypton, cannot be explained consistently within the context of presently existing theory.

I. INTRODUCTION

Interest in noble-gas solids arose originally when it was realized that their properties could be effectively described by models employing only two-body interatomic potentials.[1] In time, however, there was gradually accumulating evidence for the existence of nonpairwise contributions to the crystal potential in addition to these two-body forces. Many-body effects were seen in third virial coefficient,[2] elastic constant,[3] stacking-fault density,[4] as well as other liquid and solid-state data,[5] for instance. Although it is now generally agreed that many-body interactions of a long-range nature can be fairly well described by terms in the perturbation expansion of atomic multipole moment interactions[6] (such as, for example, the Axilrod-Teller-Muto triple-dipole term), the extent of short-range overlap (Jansen) type contributions has been a subject of considerable controversy.[7] With regard to this problem, there has been some interest in vacancy concentration data since they yield formation energy values which are known to be sensitive to such many-body interactions.

In recent years, an abundance of experimental data has been collected and compared with theoretical predictions.[8] The results of a number of these investigations have been sufficiently accurate and precise that vacancy contributions are within the limits of experimental resolution. It is well known, for instance, that the thermal expansivity, heat capacity, and isothermal compressibility are affected in rather well-defined ways by generation of lattice vacancies in sufficiently dilute concentrations.[9] These correction terms generally involve values for the formation energy and entropy, ϵ_f and s_f, respectively, both of which are in principle readily deduced from vacancy concentration data, along with the formation volume v_f which it may be possible to determine independently of these measurements.[10] There are, of course, other interesting phenomena which can influence the behaviors of these thermodynamic quantities in similar ways. As an example, the effects due to the explicit anharmonicities of the lattice vibrations are not entirely understood at the present time.[11] It is, therefore, desirable to have independently determined the effects of vacancies so that the extent of other influences can be deduced.

In addition, vacancy data could provide rather fundamental information about such processes as self-diffusion or possibly even the melting phase transition. In the noble-gas solids, as well as in other close-packed substances, bulk self-diffusion is generally thought to proceed predominantly via a monovacancy mechanism; however, with the experimental results of Losee and Simmons[12] at his disposal, Burton[13] has presented rather plausible arguments for a significant if not dominant divacancy diffusion mechanism in solid krypton. Also there have been quite a number of attempts to explain the melting phenomenon of these materials. Some of the proposed theories have involved vacancy production or interaction mechanisms[14] of various sorts so that it is at least conceivable that the present experimental results could eventually be useful to test the accuracy of some of these melting theories.

The desire for this sort of information has already motivated several attempts to measure vacancies in the noble-gas solids. The results of these investigations are presented in Table I. The earliest were semiempirical determinations from accurate specific-heat data by Flubacher and coworkers[15] for argon and by Beaumont and co-workers[16] for krypton. At high temperatures, they observed what they thought to be an anomalous increase in their measured C_p values and attributed this rise to the formation of thermal vacancies. By extrapolating their specific-heat data from low temperatures where vacancy effects are known to be negligible and by assuming that this extrapolated function adequately represented the lattice specific heat, they attempted to deduce values for vacancy

TABLE I. Previous determinations of vacancy concentrations n/N and estimates of their activation parameters, ϵ_f and s_f, the formation energy and entropy, respectively. In the cases labeled semiempirical, triple-point vacancy concentrations were calculated from the quoted formation parameters to allow for convenient comparison with the empirical results.

Authors	$10^4(n/N)$	ϵ_f (meV)	s_f/k
Semiempirical			
Beaumont and co-workers (Ref. 16)	137	55.5 ± 5.6	3.4 (+0.5, −1.1)
Morrison (Ref. 18)	44	78.9	5.5
Foreman and Lidiard (Ref. 17)			
for $v_f=\frac{1}{2}v_a$	112	68.5	5
for $v_f=v_a$	270	75.9	6.9
Kuebler and Tosi (Ref. 19)	110	69.4	5.1
Hillier and Walkley (Ref. 20)	...	51.6	...
Empirical			
Peterson and co-workers (Ref. 22)	<20	...	...
Smith and Chapman (Ref. 24)	<13	...	...
Bronsfeld and co-workers (Ref. 26)	<20	...	...
Van Witzenberg (Ref. 25)	37	...	...
Pritchard and Gugan (Ref. 27)	<10	...	...

concentrations and the respective activation parameters. Vacancy results derived in this manner are, however, known to be rather uncertain because of the arbitrary nature of the extrapolation procedure.

Evidently the specific heat is quite sensitive to anharmonic effects and it was thought by some that more reliable vacancy estimates could be derived by comparing these experimental data in various forms with thermodynamic quantities predicted by theoretical models of the idealized perfect crystal.[17-20] Unfortunately, all of these semiempirical approaches ultimately appear to be rather futile since a realistic crystal potential function has yet to be determined with sufficient accuracy. McGlashan,[21] for instance, was able to fit the Flubacher specific-heat curve at the highest temperatures by assuming a comparatively simple specific form for the potential and including no vacancy effects whatsoever.

In addition to these techniques, there have also been experiments performed in which attempts were made to determine vacancy concentrations by more direct means.[22-27] In the earliest of these, Peterson and co-workers[22] compared the densities which they derived from their x-ray lattice-parameter measurements with the comparatively crude macroscopic bulk density data existing at that time[23]; however, these results were found to be only sufficiently accurate to allow an upper limit to be established. Subsequently, more careful measurements of macroscopic density[24-26] were used in similar estimates, but even these later data failed to be much more conclusive.

In principle, at least, density comparisons of this sort constitute a very direct method for determining vacancy concentrations; however, there are a number of difficulties involved with their application. Among these are problems with temperature scale mismatching if the measurements are performed on different specimens. Also the presence of macroscopic cracks or vapor voids, which in general cannot be annealed out of the specimen, introduce error in the bulk density data. Even uncertainties in Avogadro's number can limit the accuracy with which x-ray lattice parameters are converted to x-ray density values.

II. APPARATUS AND PROCEDURE

The present experimental procedure is similar to that used several years ago in experiments first with aluminum and the noble metals[28] and then later with solid krypton[12] and neon.[29] The thermal expansion of these substances is due partly to anharmonic effects in which the distances between the lattice planes increase and partly to the addition of substitutional atomic sites upon creation of vacancies within the crystal. Along with the bulk volume change and quite independently of these measurements, the lattice parameter a and its changes with temperature can be measured directly by x-ray diffraction. If some linear di-

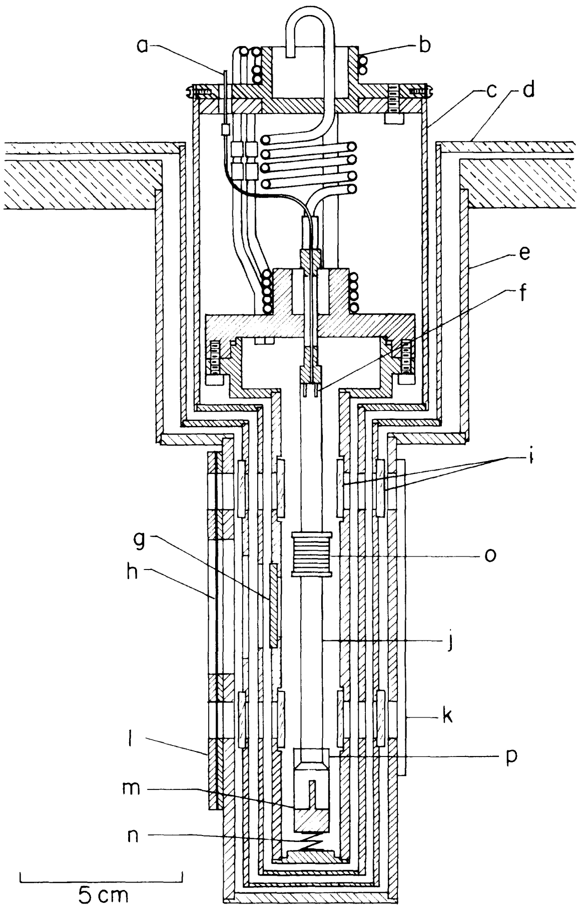

FIG. 1. Cross-sectional view of cryostat tail section. (a) Capillary for specimen gas. (b) Lower end of liquid-helium reservoir. (c) Liquid-helium-temperature radiation shield (gold-plated copper). (d) Liquid-nitrogen-temperature radiation shield (gold-plated copper). (e) Vacuum jacket (nickel-plated copper). (f) Electromagnets for holding marker beads. (g) Beryllium x-ray window. (h) Myler x-ray window. (i) Heat-absorbing glass window. (j) Mylar specimen tube. (k) Single piece of heat-absorbing glass for two rear windows on vacuum jacket. (l) Brass frame for Mylar x-ray window. (m) Copper specimen tube base. (n) Copper spring. (o) Movable heater. (p) Lucite reducer. Thin beryllium x-ray windows are also fastened to shields (c) and (d).

mension of the specimen is denoted by l, then it can be shown quite simply that the net added concentration of substitutional atomic sites $\Delta N/N$ is given by the approximate expression

$$\frac{\Delta N}{N} \cong 3\left(\frac{l-l_0}{l_0} - \frac{a-a_0}{a_0}\right) = 3\left(\frac{\Delta l}{l_0} - \frac{\Delta a}{a_0}\right), \qquad (1)$$

where the quantities l_0 and a_0 are reference lengths measured at some temperature for which the concentrations of thermal defects are negligible. In the present experiment, these reference parameters were chosen to be those measured at or extrapolated to 70 K; the error in the above expression is then on the order of only a few percent and is therefore negligible.

The experimental apparatus and procedure were described in detail by Losee and Simmons[12]; their original helium cryostat, orientable x-ray camera, and microscope assembly were used with some modifications. The specimens were grown and measured in the "rigid-tail" section shown in greater detail in the cross-sectional view of Fig. 1. This portion of the apparatus was modified slightly in design and completely rebuilt.[29] The new tail section is about 2.5 cm longer than the original one; this additional length allowed sufficient room for the wide-based sample tube which was intended to provide greater mechanical stability for the free-standing crystals.

All specimens were prepared from "research-grade" 99.9995% pure argon in which the principal impurity was $N_2 \leqq 3$ ppm. Gas for samples No. 1 and No. 2 was obtained from the Matheson Company and that for sample No. 3 from Scientific Gas Products Co. Although no impurity analyses were made after completion of the runs, a number of precautions were observed in order to maintain high-purity samples. Each time before gas was transferred from the high-pressure bottle to the sample tube, the connecting gas handling system was evacuated for several days and then purged a few times with pure argon. An estimate of the contamination introduced from small leaks and adsorbed gases was made by closing off the vacuum from this system and monitoring the pressure for several days with a thermocouple gauge. The pressure was seen to increase at an approximately uniform rate of about 2 mTorr h^{-1} which indicated that the gas system (of total volume about 1 liter) probably introduced only a negligible amount of impurities to the sample during the approximate 2-h period in which the liquid was condensed. Also in the present experiment, new argon was used for each sample and then discarded after completion of the run. This procedure is desirable in that gradual contamination of recollected gas is avoided and is economically feasible since pure argon is relatively inexpensive.

The length data were then taken for as long as the crystal remained in a free-standing position which was usually only a few days. In practice and under ideal conditions, length changes could be measured to the nearest 1 or 2 μm; however, it often happened that unstable surface features of the crystal either distorted, diffused or displaced the images of the beads and thereby rendered a sizable portion of the length data either very uncertain or altogether useless. It should be mentioned that these problems were even more serious for krypton, with its higher refractive in-

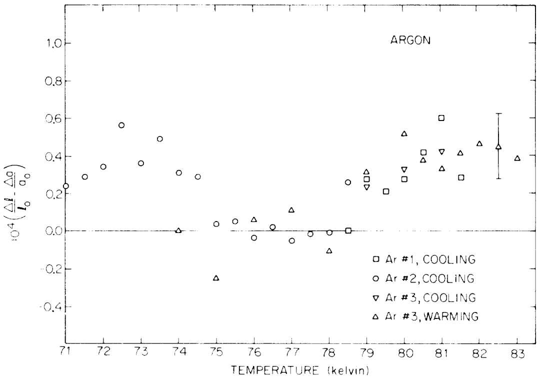

FIG. 2. Comparison of the argon length and lattice parameter measurements $(\Delta l/l_0 - \Delta a/a_0)$ as a function of temperature; l_0 and a_0 refer to those measured or extrapolated values at 70 K. The observed effect is actually quite small. For instance to $T = 83$ K, it was seen that $\Delta l/l_0 \approx \Delta a/a_0 \cong 83\times10^{-4}$ whereas their difference, indicated on the graph, is only about 1% of this value.

dex, than they were for argon. This becomes apparent when the real scatter in the data from the two experiments is compared.

After the length measurements were made, the crystal was cooled to helium temperature so that its orientation could be determined from a Laue x-ray photograph. Finally, lattice-parameter measurements were taken with the large, orientable, rotating, Bragg-back-reflection x-ray camera described by Batchelder and Simmons.[30] The results of three data runs are described in Sec. III.

III. RESULTS AND DISCUSSION

The data from three separate argon vacancy runs are plotted together in Fig. 2. It is immediately apparent that a large effect, similar to the one observed by Losee and Simmons in krypton, is certainly not present in argon. In the temperature range between 70 and 79 K most of the data are from crystal No. 2. Their strange behavior in the neighborhood of 74 K and below was not considered to be real but rather the result of some feature on the surface of the crystal which shifted the apparent position of one of the marker beads. For temperatures below 70 K, precise length measurements were generally not possible because of such surface irregularities.

The small high-temperature rise, on the other hand, was thought to be due to the formation of vacancies although in the following analysis this interpretation is viewed with some caution. One reason for this is that even though the surface of the crystal was observed to remain comparatively regular for temperatures above about 76 K, if the anomalous offset of the data from crystal No. 2 below 74 K is the result of some systematic error in the length measurement as described above, then one should probably not entirely rule out the possibility of some similar difficulty at high temperatures. Another is that the data from crystal No. 1 did not extend below 78.5 K so that their reference parameter l_0 had to be chosen somewhat arbitrarily. This means that within their temperature range, they can only indicate changes of vacancy concentrations rather than their absolute values. With this in mind, it is interesting to note that the slight rise indicated by these data is consistent with that shown by the measurements from crystal No. 3.

Because of the scatter in the present data, a few words should be said concerning the statistical uncertainties. The largest of these were introduced from the length measurements. It was thought that the change in the macroscopic length of the crystal with temperature could be determined to the nearest micron; that is, that the position of each bead could be measured to the nearest 0.5 μm. This uncertainty corresponds approximately to a wavelength of visible light and therefore, represents a limit to the precision attainable by the present optical microscope technique. Since typical distances between the upper and lower sets of marker beads were ~ 75 mm, this leads to an uncertainty of $\delta(\Delta l/l_0) \approx 1.3\times10^{-5}$.

Temperature measurements for both length and lattice-parameter data were precise, within a common scale, to about 5 mK; the uncertainty involved in each case is $\delta(\Delta l/l_0) = \delta(\Delta a/a_0) = \alpha\Delta T \approx 0.3\times10^{-5}$, where α is the coefficient of linear thermal expansion. Finally, from the Bragg equation and considerations of camera geometry, the error in the lattice parameter resulting from the uncertainty δx in the measured x-ray spot position on the film is given by

$$\delta a/a = [\cos^2(\pi - 2\theta)/2\tan\theta]\,\delta x/D\ , \qquad (2)$$

where θ is the Bragg angle and D is the specimen to film distance. The spot position was measured typically to the nearest $\delta x = 0.05$ mm; this introduced an error no greater than $\delta a/a = 0.9\times10^{-5}$. It was found that the average absolute deviation of the measured-lattice parameter values from the smooth curve is about 0.5×10^{-5}. On the basis of this discussion, scatter of this magnitude is not unreasonable. The error bar $\Delta = \pm 1.7\times10^{-5}$ shown in Fig. 2 graphically represents the square root of the sum of the squares of these uncertainties.

Errors of a systematic nature are more difficult to anticipate and analyze. It has already been pointed out[12] that some of these, such as the temperature scale mismatch problem or possible errors introduced by varying concentrations of sample impurities, for instance, were automatically avoided by the technique of measuring lengths and lattice parameters simultaneously, that is, on the same specimen and in the same apparatus. Significant systematic deviations resulting from a peculiar crystal orientation or grain boundary structure can probably be ruled out since measurements were carried out on several different samples. Also errors arising from creep or possibly a nonisotropic distribution of vacancy sources and sinks are seen to be negligible owing to the reproducibility of the effect in both cooling and warming runs with the same specimen.

Recall that the quantity actually measured in this experiment, $\Delta N/N$, is defined to be the extra relative number of thermally generated atomic sites. It will be assumed in the following analysis that $\Delta N = n$, where n is the concentration of monovacancies although, in general, divacancies, interstitials, and higher-order clusters of these point defects also contribute to ΔN. Some theoretical justification of this assumption can be given, however. A very crude estimate of the divacancy binding energy ϵ_2^b can be made if only nearest-neighbor interactions are considered in the absence of lattice and electronic relaxations. The binding energy in this case is just that due to the "missing bond" and it follows that ϵ_2^b is approximately $\frac{1}{12}$ of the monovacancy formation energy (~6.5 meV).

A more reliable estimate of this quantity has been made by Burton[13] whose model included effects of lattice relaxations, zero-point atomic vibrational energy, and three-body interactions. His results have shown the divacancy binding energy in argon to be about 8.7 meV which is roughly the same as the crude estimate above. In a later publication, Burton[31] calculated the binding entropy and found it to be probably small and negative. If for the purpose of establishing an upper limit for divacancy effects it is assumed that $s_2^b = 0$, then it may be shown that the divacancy contribution to ΔN at the highest temperatures is only about 2% of that due to monovacancies.

At the present time, no theoretical numbers exist for trivacancy formation parameters; however, crude estimates similar to the "broken-bond" approximation described above indicate that contributions due to these and other higher-order clusters are also negligible. Cotterill and Doyama[32] have calculated formation energies for both vacancy and interstitial type defects in krypton and xenon using a Morse pair potential and a static lattice model. These results indicate that the relative concentrations of interstitials in argon can probably be neglected also.

In view of all of this, therefore, the data appear to indicate that the equilibrium concentration of thermal vacancies in argon does not exceed 2.5×10^{-4} even at the highest temperatures. If the hypothesis is made that vacancy concentrations of this order of magnitude are sufficiently small that their mutual interactions may be neglected, then from elementary statistical mechanical considerations, their atomic fraction at any given temperature and pressure is

$$n/N = \exp(-g_f/kT), \quad g_f = \epsilon_f - Ts_f + Pv_f ,$$

where g_f, ϵ_f, s_f, and v_f are, respectively, the molar Gibbs free energy, energy, entropy, and volume of formation. A more instructive form for this expression at low pressures[33] is

$$\ln n/N = -\epsilon_f/kT + s_f/k , \tag{3}$$

since then it can be seen that the formation energy and entropy values are easily determined directly from an Arrhenius plot of the data.

It is apparent that narrow limits cannot be determined for both ϵ_f and s_f simultaneously from this equation as Losee and Simmons were able to do. Nevertheless, one can determine ranges of these values which are compatible with the upper limit $(n/N)_{\text{max}}$ established above from the relationship

$$\ln(n/N)_{\text{max}} \geqq -\epsilon_f/kT + s_f/k , \tag{4}$$

which follows directly from Eq. (3). These ranges are displayed graphically in Fig. 3; according to Eq. (4), (ϵ_f, s_f) coordinates located in the half-plane indicated by the arrows are those which are consistent with the present vacancy results. Although this plot probably represents all of the information which may be rigorously derived from the present data, further conclusions of a semi-empirical nature will be discussed in Sec. V.

IV. THEORETICAL RELATIONSHIPS

A. Energy of formation

It may be shown by using arguments similar to those presented originally by Burton[13] that the vacancy formation energy ϵ_f can be written

$$\epsilon_f = |E_p| + \sum_{n=3}^{\infty} -(n-2)\, E_n + \Delta E_{\text{relax}} + \Delta E_{\text{vib}} , \tag{5}$$

where E_p is the static lattice energy of the crystal, E_n is the contribution to E_p due to purely n-body interactions, ΔE_{relax} represents the energy contributions resulting from lattice and possible electronic relaxations about the vacant site, and, finally, ΔE_{vib} is the change in the vibrational energy of the crystal associated with the creation of a single monovacancy.

An approximate value for the static lattice energy may be inferred from the measured sublimation energy[16] which is just the enthalpy differ-

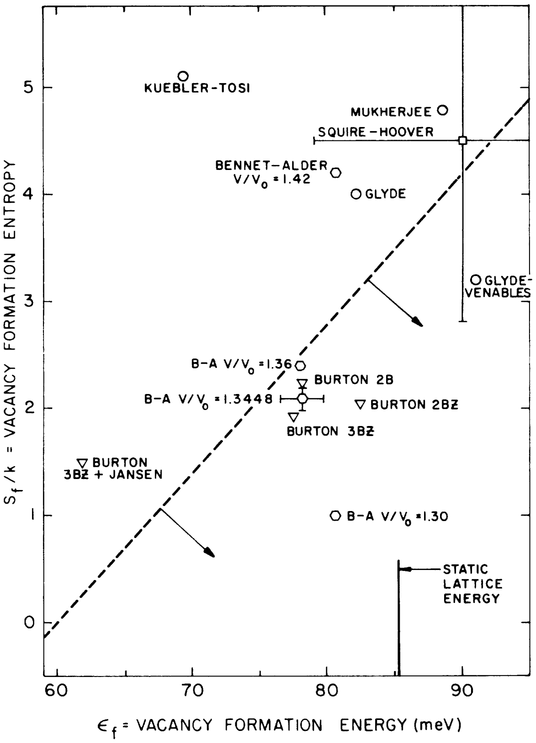

FIG. 3. Activation parameter plane—(ϵ_f, s_f) coordinates located within the region indicated by the arrows represent vacancy formation energy and entropy values which are consistent with the present data. Plot also includes various theoretical estimates for comparison. The abbreviation B-A represents a Bennett and Alder calculation for the indicated hard sphere density. Calculations by Burton made for the two-body-interaction model both with and without zero-point effects are labeled 2BZ and 2B, respectively. Those incorporating three-body potentials and zero-point energies are denoted by 3BZ; "+ JANSEN" indicates the inclusion of superexchange.

ence between the solid and vapor phases

$$L = H_v - H_s \,. \tag{6}$$

If third- and higher-order virial coefficients can be ignored, the enthalpy of the vapor is simply

$$H_v = \tfrac{5}{2} RT - RT^2 P \frac{dB_P}{dT} \,, \tag{7}$$

where B_P is the second pressure virial coefficient. The enthalpy of the solid is

$$H_s = E_p + E_{\text{vib}} + P v_s \,, \tag{8}$$

where E_{vib} is the vibrational energy and v_s is the molar volume. Then by combining these equations, one finds that

$$E_p = \tfrac{5}{2} RT - RT^2 P \frac{dB_P}{dT} - L - E_{\text{vib}} - P v_s \,. \tag{9}$$

With the exception of the vibrational energy term, all of the quantities in this expression for the static lattice energy can be measured directly. An estimate for E_{vib} can be made from the quasiharmonic model in the high-temperature limit

$$E_{\text{vib}} \cong 3RT[1 + \tfrac{1}{20}(\Theta_D/T)^2] \,, \tag{10}$$

where for argon the Debye temperature $\Theta_D = 83.5$ K is used.[16] With this relationship, the static lattice energy value for argon at its triple point is found to be $E_p = -85.7 \pm 0.3$ meV.

Equation (10) yields only approximate values for E_{vib}, however, since the quasiharmonic model does not properly account for the dependence of the vibrational energy on the explicit anharmonicity of the crystal potential. These effects are often described by the leading anharmonic coefficient A in an expansion of the vibrational free energy[34]:

$$F = F^{\text{h}} + F^{\text{anh}} = F^{\text{h}} + 3R[-\tfrac{1}{2} A T^2 + B + O(T^{-2})] \,. \tag{11}$$

Although a precise value for this parameter has not been determined experimentally for argon,[19,35] order-of-magnitude estimates[36] typically range from -10^{-4} to -10^{-3} K^{-1} so that the resulting effect upon E_{vib} could be as large as 4% at the highest temperatures. With these considerations, the above E_p value could, therefore, be 0.9 meV too large.

The second term in Eq. (5)

$$\sum_{n=3}^{\infty} -(n-2)E_n \tag{12}$$

defines the explicit dependence of the vacancy formation energy on many body interactions. Evidently the static lattice energy contribution arising from all strictly n-body potentials E_n contributes $n-2$ times to ϵ_f, and it is because of this comparatively sensitive dependence that formation energies have been thought to be rather effective probes of higher-order interactions.

The extended nature of the charge distribution of these neutral atoms gives rise to their long-range multipole moment interactions. For these type potentials, the first term in Eq. (12), E_3, is often represented by the Axilrod-Teller-Muto[37] triple-dipole interaction alone. Although other higher-order, long-range, three-body potentials have been calculated,[6] these have generally been found to be negligible. An exception is the dipole-dipole-quadrupole interaction which yields a small but significant contribution to E_3; however, it is known that the three-body, fourth-order dipole energy is nearly equal to it in magnitude and opposite in sign so that these terms effectively cancel each other. Chell and Zucker,[38] among others, have performed the appropriate lattice sums for fcc crystals; their resulting expression yields the following high-temperature triple-dipole energies: E_3 (83 K) = 4.55 meV and E_3 (115 K) = 7.62 meV for argon and krypton, respectively.

If the dominant three-body or triplet potential is then given by the dipole-dipole interaction in the third-order perturbation term, it should not be unreasonable to assume that the dominant four-body or quadruplet potential is given by the same interaction in fourth order. Bade[39] used a Drude model to show that only a small fraction (~ 2.5%) of this fourth-order energy actually arises from quadruplet interactions, however. If the equation which he derived is used to calculate the second term in the sum (12), it is found that $2E_4 \approx 0.05$ meV for argon and $2E_4 \approx 0.11$ meV for krypton. Contributions from n-body interactions where $n > 4$ become increasingly more difficult to evaluate; however, the relative magnitudes of the triplet and quadruplet energies indicate that the sum converges very rapidly in spite of the $(n-2)$ factor in each term so that long-range many-body contributions to ϵ_f other than the triple-dipole potential are thought to be relatively insignificant.

Druger[40] calculated formation energies for a model in which dipole-dipole interactions were assumed for a collection of Lorentz oscillators. Although relaxation and vibrational effects were neglected explicitly, his method did allow for the summation of all orders of nonpairwise contributions to the interaction energy of a substitutional impurity in the monatomic crystal. From this interaction energy relationship, he derived an equation for the energy required to remove an atom from the lattice by letting the oscillator frequency of the impurity approach infinity. However, he demonstrated that this expression could be obtained alternatively by using Burton's[13] general arguments if the nth order perturbation term of the total energy were identified with the n-body contribution. Since, as Bade has pointed out, this identification is not strictly valid, Druger's approach may, therefore, not be entirely correct.

Jansen has suggested that higher-order, short-range interactions can occur from multiple electron overlap exchange among the outer shells of neighboring atoms. His original investigations[41] of such effects were in connection with cohesive energy calculations and the relative stability of the fcc phase for these substances, but they also demonstrated that the short-range three-body energies might significantly affect predicted vacancy formation energies as well.[42] Jansen's atomic model consisted of single effective electron Gaussian wave functions characterized by width parameters which were determined from long-range behavior. For argon and xenon[43] he calculated three-body energies of $E_3 = -0.24\ E_p$ and $E_3 = -0.58\ E_p$, respectively.

There has been considerable disagreement about the assumptions and details of Jansen's work.[2,44] Swenberg[45] has pointed out that Jansen's wave functions yield nearest-neighbor overlaps more nearly descriptive of metals than insulators and that negligible three-body effects result if realistic Gaussian width parameters are used. Recently Tremblay and Glyde[46] estimated short-ranged many-body potential contributions to ϵ_f by applying the extended Hückel theory to 12- and 13-argon-atom cluster models. They found that these contributions increased the vacancy formation energy by only about 1.2% (i.e., ~ 0.9 meV) and, furthermore, that these many-body forces induced little additional lattice relaxation about the vacant site. In addition, they felt that such effects were unlikely to explain the 25% discrepancy between observed and predicted ϵ_f values in krypton.

Accurate quantitative information about these interesting many-body effects can be deduced, however, only if sufficiently reliable estimates are available for the remaining terms in Eq. (5). So far, it has not been possible to determine values for relaxation or vibrational energy change contributions by experimental techniques; it is, therefore, necessary to rely upon estimates derived from theoretical considerations.

There have been a number of lattice relaxation energy calculations made,[12] that is, estimates of the energies associated with the changes in the equilibrium positions of the atoms neighboring the vacant site. These calculated values are all found to be rather small, typically on the order of 2% of the crystal static lattice energy (~ 1.7 and ~ 2.3 meV for argon and krypton, respectively).

Along with these effects, one may also be concerned with electron cloud relaxations or energy contributions associated with possible induced polarizations of the neighboring atoms. It is clear that some net polarization effects due to electron cloud distortions will result from overlap repulsions between a given atom and its neighbors and that these energies are already accounted for to some extent in the estimated lattice relaxation contribution to the $\Delta E_{\mathrm{relax}}$ term. The only existing calculation of such effects is that by Doniach and Huggins[47] who considered a shell model for solid argon with parameters determined from refractive index and exciton absorption data. Their results indicated an electronic relaxation energy of about 10% of the binding energy per atom or $\Delta E_{\mathrm{elec\ relax}} \approx 17.1$ meV for argon. Although their calculation did not include a similar estimate for krypton, the same prescription would yield a value of $\Delta E_{\mathrm{elec\ relax}} \approx 23.4$ meV for this substance. In view of these apparently rather large contributions, it would seem that both relaxation energies should properly be solved for in some self-consistent fashion though such a calculation has not yet been made. One may hesitate to accept the

Doniach-Huggins result because of the approximate nature of the model which they used; however, there is presently no existing evidence to indicate that such effects can be safely ignored.

Another possibly significant contribution to ϵ_f arises from the energy changes of the lattice vibrations which result when the equilibrium positions and force constants of the neighboring atoms are perturbed. Here again there are, unfortunately, few and only inadequate theoretical treatments of such effects so that it is only possible to present rather crude arguments concerning them. As an example, for the simple harmonic model in the high-temperature limit, the equipartition theorem could be applied to show that $\Delta E_{\rm vib} = 0$. However, it was shown earlier that the strict high-temperature limit approximation is not a valid one for argon; that is, the vibrational energy is more nearly represented by an expression similar to Eq. (10). In a crude but clever calculation, Glyde[48] used the analogous expression for an Einstein model solid. He was able to relate the Einstein frequency shifts of the relaxed neighboring atoms to the vibrational energy change, and for temperatures near the triple point he estimated that $\Delta E_{\rm vib} \approx 0.7$ meV. This is, however, still essentially an harmonic approximation, and it was observed earlier that vibrational energies could be quite sensitive to anharmonicities. It is, therefore, reasonable to assume that the anharmonicities associated with the crystal potential function for atoms in the relaxed configuration could significantly affect $\Delta E_{\rm vib}$, but without detailed knowledge of these potentials, reliable estimates are difficult to establish.[49]

B. Entropy of formation

The monovacancy formation entropy s_f is a parameter which describes the local disorder introduced to the lattice (without including mixing entropy contributions). A few theoretical calculations of this quantity have been made[50]—most have involved an approximation whereby this term arises as a result of the vacancy interacting with the lattice vibrations causing a frequency shift of the normal modes. It is found that nearly all calculations of s_f seem to give approximately the same values regardless of the model considered and that these numbers all tend to lie in the range $1.5k$–$4.5k$. Previous vacancy measurements have not produced sufficiently precise formation entropy values to allow definite conclusions to be drawn concerning these specific models, however.

Fortunately, many of the available theoretical estimates of vacancy formation parameters have made for argon. Some of these calculated predictions[51–55] are included in Table II and are plotted along with the present experimental results in Fig. 3 for convenient comparison.

V. COMPARISON

To conclude the discussion, it is of interest to compare the available argon and krypton vacancy results. In order to do this, it is illustrative to reconsider Eq. (5) in its following slightly transposed form:

$$\epsilon_f - |E_p| = -\sum_{n=3}^{\infty} (n-2)E_n + \Delta E_{\rm vib} + \Delta E_{\rm relax} , \qquad (13)$$

so that the empirically determined quantities placed on the left-hand side can be compared directly with the theoretically inferred values on the right-hand side.

The krypton static lattice energy may be estimated according to the procedure described in Sec. IV, that is, from Eq. (9) and the measured calorimetric quantities of Beaumont and co-workers.[16] If a Debye temperature $\Theta_D = 65$ K is assumed[16] and the explicit anharmonic contribution to the vibrational energy is included with $A = -5 \times 10^{-4}$ K^{-1},[12] then it is found that $E_p\,(115\ \mathrm{K}) = -116.9 \pm 1.1$ meV for this substance. The indicated 1% error arises predominantly from the uncertainty in the value chosen for A. With Losee's formation energy value 77.1 ± 8.6 meV, it is found that $\epsilon_f - |E_p| = -39.8 \pm 9.7$ meV.

Unfortunately, the corresponding quantity for argon cannot be inferred as directly because of the uncertainty in the vacancy results; however, a semiempirical estimate can be made in the following way. It was observed earlier that theoretical estimates of formation entropy values typically range from $1.5k$ to $4.5k$. If it is now assumed that such entropy values are reasonable for solid argon, then from Eq. (4), a lower bound for the vacancy formation energy can be inferred:

$$\epsilon_f \geqq -kT_{\rm tp}[\ln(n/N)_{\rm max} - s_{f\ \rm min}] = 70.8\ \mathrm{meV}$$

for argon, where $T_{\rm tp}$ denotes the triple-point temperature, so that

$$\epsilon_f - |E_p| \geqq -15.4\ \mathrm{meV} .$$

According to Eq. (13) these differences are to be compared to the sums of the various contributions on the right-hand side of the expression; these numbers are presented, together with those discussed in Sec. III, in Table III.

The conclusions to be drawn are fairly straightforward. The present argon results appear to be entirely consistent with estimated lattice relaxation, long-range (multipole) and short-range (Hückel) many-body contributions. However, unless there is some large, positive vibrational energy shift, they are not compatible with substantial electronic relaxation effects or short-range (Jan-

TABLE II. Some theoretical estimates of monovacancy formation energies ϵ_f and entropies s_f for solid argon. Older work is cited in these references.

Authors	ϵ_f (meV)	s_f/k	Remarks
Glyde (Ref. 48)	82.2	4.0	Two-body model; see Ref. 12 for comments
Glyde and Venables[a] (Ref. 51)	91.1	3.21	Two-body, 12-6 potential model
Burton[b] (Ref. 13)	78.3	2.24	Zero-temperature, two-body model with lattice relaxation
	82.6	2.05	Including zero-point vibration
	77.6	1.93	Also including triple-dipole three-body effects
	62.0	≥ 1.5	Also includes Jansen forces; s_f represents probable lower limit
Bennett and Alder (Ref. 55)	78.0	2.4	Molecular dynamics of hard-sphere system; these numbers correspond to melting density $V/V_0=1.36$
Squire and Hoover (Ref. 54)	90 ± 11	4.6 ± 1.8	Two-body potential Monte Carlo
Mukherjee (Ref. 52)	88.6	4.78	Quasithermodynamic approximation for triple-point values
Burton and Jura (Ref. 53)	87.2	...	Static lattice relaxation
Druger (Ref. 40)	75.5	...	Includes all orders of long-range nonpairwise interactions, no relaxation or vibrational effects

[a] These authors apparently used inconsistent assumptions concerning temperature dependences of ϵ_f and s_f to calculate "effective values" whereas, in fact, actual ϵ_f values are obtained from local slopes of the experimentally determined Arrhenius plot.

[b] The author is grateful to Dr. J. J. Burton for privately communicating the corresponding entropy values.

sen) three-body overlap energies, at least of the magnitudes presently estimated in the literature. The krypton data, on the other hand, would seem to require sizable contributions from either or both of these effects. The argon and krypton vacancy results, therefore, cannot be explained consistently within the context of the presently existing theory.

It is of course, possible that they may ultimately be reconciled by some additional theoretical studies. Rather than to speculate on these, however, it is of greater interest to briefly discuss the credibility of the existing experimental work. With regard to argon it was already apparent from the earlier density comparison work that large vacancy concentrations, comparable to those in krypton, were not present. The much more accurate results of the present work confirm this conclusion within narrow limits. Moreover the conclusions reached here, concerning the limited extent of short-range interactions in these crystals, have been recently suggested by others.[3]

Although so far there have been no attempts to reproduce the direct vacancy measurements on krypton, presently available experimental evidence does not contradict these results. The problem involved with semiempirical approaches have already been discussed; the agreement between the quoted formation energy value of Beaumont and co-workers[16] for krypton and the later one reported by Losee and Simmons is probably fortuitous. Gavrilko and co-workers[56] measured bulk

TABLE III. Tabulated values for many-body, relaxation, and vibrational energy contributions to the vacancy formation energy ϵ_f. The sum of these quantities should equal $\epsilon_f - |E_p|$, where E_p is the static lattice energy. Energies are written in units of meV.

Energy contribution	Argon	Krypton
$\lvert E_p\rvert$	85.3 ± 0.9	116.9 ± 1.1[a]
$\epsilon_f - \lvert E_p\rvert$	$\geqq -15.4$	-39.8 ± 9.7
ΔE_{vib}	~ 0	~ 0[b]
$\Delta E_{\text{lattice relax}}$	-1.7	-2.3
$\Delta E_{\text{elec. relax}}$	-17.1	-23.4
$-E_3$ (triple dipole)	-4.55	-7.62
$-E_3$ (Jansen superexchange)	-20.5	(-47.9)[c]

[a] Static lattice energy values were calculated with an assumed value $A = -5 \times 10^4$ K^{-1} for the leading anharmonic coefficient of the vibrational free energy.

[b] According to the discussion, the vibrational effects are rather uncertain—the assumption that they are small is, therefore, somewhat arbitrary.

[c] This value was derived by interpolating Jansen's results (Refs. 43 and 41) for argon and xenon.

thermal expansion on solid krypton at high temperatures by using a capacitative transducer technique to determine macroscopic volume changes of their sample with temperature. These numbers, as they later appeared in their corrected form,[57] agreed within the quoted experimental error of ± 5% with the bulk expansion coefficient values determined by Losee. Schoknecht[29] has combined the smoothed expansivity measurements of Gavrilko and co-workers with Losee's x-ray data and has obtained a monovacancy formation energy of $\epsilon_f = 78.7 \pm 8.7$ meV.

Also, Coufal and co-workers[10] employed an optical interferometric technique to measure krypton bulk expansivities and similarly compared their results with Losee's to find that $\epsilon_f = 86.1 \pm 8.7$ meV and $s_f = 2.8(+0.8, -0.9)k$. These estimates both appear to be in rather impressive agreement with Losee-Simmons results; however, it should be mentioned that they are not entirely distinct since they both involve the latter's x-ray lattice parameter values which have not as yet been reproduced independently. Moreover, they are also subject to whatever systematic uncertainties there are introduced by comparing nonsimultaneous measurements in this way.

Coufal and co-workers[10] also measured macroscopic isothermal compressibilities in krypton by their technique. These results were later used by Kupperman[58] who compared them with the lattice compressibility values which he deduced from his pulse-echo polycrystalline sound velocity measurements. Then with the assumption that the formation volume is one atomic volume, he concluded that the vacancy formation energy in krypton was at least as low as the value reported by Losee. Further ultrasonic measurements by Bezuglyi and co-workers[59] were in agreement with those of Kupperman, that is, within their quoted experimental error of about 6%. In a similar way, they estimated from their results that $\epsilon_f = 63.2 \pm 8.6$ meV. At about the same time, Korpiun and co-workers[60] made similar measurements on polycrystalline krypton samples and found a lattice isothermal compressibility which was in substantial agreement with the macroscopic value. However, the limits of error stated in this paper (± 12%) were comparatively large and the significance of this result is, therefore difficult to judge.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Professor R. O. Simmons for his initial suggestion of the problem, for the guidance and support which he provided during the course of this work, and for his thorough criticism of the final manuscript. Thanks are also extended to Professor R. Kent Crawford and Dr. R. W. Wilkins who often shared their insight through many helpful discussions and especially to Dr. W. E. Schoknecht whose careful work and instruction were particularly valuable.

---

*Work supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1198.

†Present address: Q26 Los Alamos Scientific Laboratories, P. O. Box 1663 Los Alamos, N. M. 87545.

[1] E. R. Dobbs and G. O. Jones, Rep. Prog. Phys. 20, 516 (1957).

[2] H. W. Graben, R. D. Present, and R. D. McCulloch, Phys. Rev. 144, 140 (1966).

[3] T. G. Gibbons, M. L. Klein, and R. D. Murphy, Chem. Phys. Lett. 18, 325 (1973).

[4] R. Bullough, H. R. Glyde, and J. A. Venables, Phys. Rev. Lett. 17, 249 (1966).

[5] J. A. Barker, R. A. Fisher, and R. O. Watts, Mol. Phys. 21, 657 (1971).

[6] M. B. Doran and I. J. Zucker, J. Phys. C 4, 307 (1971).

[7] J. J. Burton, Comments Solid State Phys. 3, 82 (1970).

[8] H. R. Glyde and M. L. Klein, Crit. Rev. Solid State Sci. 2, 181 (1971).

[9] W. E. Schoknecht and R. O. Simmons, AIP Conf. Proc. 3, 169 (1971).

[10] H. J. Coufal, R. Veith, P. Korpiun, and E. Lüscher, J. Appl. Phys. 41, 5082 (1970); H. J. Coufal, R. Veith, P. Korpiun, and E. Lüscher, Phys. Status Solidi 38, K127 (1970); P. Korpium and H. J. Coufal, *ibid.* 6, 187 (1971).

[11] M. L. Klein, G. K. Horton, and J. L. Feldman, Phys. Rev. 184, 968 (1969).

[12] D. L. Losee and R. O. Simmons, Phys. Rev. 172, 934 (1968); D. L. Losee and R. O. Simmons, *ibid.* 172, 944 (1968).

[13] J. J. Burton, Phys. Rev. 182, 885 (1969).

[14] V. I. Vladimirov, Fiz. Tverd. Tela 10, 2639 (1968) [Sov. Phys.-Solid State 10, 2077 (1969)].

[15] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Proc. Phys. Soc. Lond. 78, 1449 (1961).

[16] R. H. Beaumont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. Lond. 78, 1462 (1961).

[17] A. J. E. Foreman and A. B. Lidiard, Philos. Mag. 8, 97 (1963).

[18] J. A. Morrison, see p. 101, Ref. 17.

[19] J. Kuebler and M. P. Tosi, Phys. Rev. 137, A1617 (1965).

[20] I. H. Hillier and J. Walkley, J. Chem. Phys. 43, 3713 (1965).

[21] M. L. McGlashan, Discuss. Faraday Soc. 40, 59 (1965).

[22] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Philos. Mag. 12, 1193 (1965); O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. 150, 703 (1966).

[23] B. L. Smith, Philos. Mag. 6, 939 (1961); D. C. Piercey, M.Sc. thesis (University of London, 1957) (unpublished); E. R. Dobbs, B. F. Figgins, G. O. Jones, D. C. Piercey, and D. P. Riley, Nature (Lond.) 178, 483 (1965).

[24] B. L. Smith and J. A. Chapman, Philos. Mag. 15, 739 (1967).

[25] W. Van Witzenberg, Phys. Lett. A 25, 293 (1967); W. Van Witzenberg and J. C. Stryland, Can. J. Phys. 46, 811 (1968).

[26] P. M. Bronsfeld, S. K. Kumra, and J. C. Stryland, Bull. Am. Phys. Soc. 16, 63 (1971).

[27] R. G. Pritchard and D. Gugan, Phys. Lett. A 32, 124 (1970).

[28] R. O. Simmons, in *Radiation Damage in Solids, Proceedings of the International School of Physics "Enrico Fermi," Course* XVIII, edited by D. S. Billington (Academic, New York, 1962), p. 568.

[29] W. E. Schoknecht, Ph.D. thesis (University of Illinois at Urbana-Champaign, 1971) (unpublished).

[30] D. N. Batchelder, Ph.D. thesis (University of Illinois at Urbana-Champaign, 1965) (unpublished); D. N. Batchelder and R. O. Simmons, J. Appl. Phys. 36, 2864 (1965); D. N. Batchelder and R. O. Simmons, Phys. Rev. 162, 767 (1967).

[31] J. J. Burton, J. Phys. Chem. Solids 33, 589 (1972).

[32] R. M. J. Cotterill and M. Doyama, Phys. Lett. A 25, 35 (1967); M. Doyama and R. M. J. Cotterill, Phys. Rev. B 1, 832 (1970).

[33] Since v_f is on the order of one or two atomic volumes, even at the highest temperatures $\epsilon_f \gg Pv_f \approx 0.03$ meV. The Gibbs energy is, therefore, usually written simply as $g_f \cong \epsilon_f - Ts_f$.

[34] M. P. Tosi and F. G. Fumi, Phys. Rev. 131, 1458 (1963).

[35] F. Haenssler, K. Gamper, and B. Serin, J. Low Temp. Phys. 3, 23 (1970).

[36] J. A. Reissland, Discuss. Faraday Soc. 40, 123 (1965); J. W. Leech and J. A. Reissland, J. Phys. C 3, 987 (1970).

[37] B. M. Axilrod, J. Chem. Phys. 19, 719 (1951); 19, 724 (1951).

[38] G. C. Chell and I. J. Zucker, J. Phys. C 1, 35 (1968).

[39] W. L. Bade, J. Chem. Phys. 27, 1280 (1957); 28, 282 (1958).

[40] S. D. Druger, Phys. Rev. B 3, 1391 (1971).

[41] L. Jansen, Phys. Lett. 4, 91 (1963); L. Jansen and S. Zimering, *ibid.* 4, 95 (1963); L. Jansen, Phys. Rev. 135, A1292 (1964).

[42] L. Jansen, Philos. Mag. 8, 1305 (1963).

[43] E. Lombardi and L. Jansen, Phys. Rev. 167, 822 (1968).

[44] H. Margenau and J. Stamper, Adv. Quantum Chem. 3, 129 (1967).

[45] C. Swenberg, Phys. Lett. A 24, 163 (1967).

[46] A. Tremblay and H. R. Glyde, Phys. Rev. B 11, 1728 (1975).

[47] S. Doniach and R. Huggins, Philos. Mag. 12, 393 (1965).

[48] H. R. Glyde, J. Phys. Chem. Solids 27, 1659 (1966).

[49] A standard problem in classical statistical mechanics is to calculate the mean thermal energy of a particle oscillating in anharmonic potential with small anharmonic terms: $V(x)=\frac{1}{2}ax^2+bx^3+cx^4$ [see R. E. Peierls, *Quantum Theory of Solids* (Oxford, London, 1955), p. 34]. This energy to second order is given by $E=kT-(3c/a^2)(kT)^2+(15b^2/2a^3)(kT)^2$. The asymmetry of the crystal potential at a lattice site near the vacancy could conceivably be estimated and represented by an appropriately chosen value for b. However, the quartic term is found to contribute in first order whereas the cubic term does so only in second. The relative sensitivity of the mean energy to these anharmonic perturbations is therefore uncertain, and since neither the sign nor the magnitude of c can be determined in any simple or straightforward manner, this model apparently fails to provide even qualitative information about ΔE_{vib}.

[50] K. F. Stripp and J. G. Kirkwood, J. Chem. Phys. 22, 1579 (1954); H. B. Huntington, G. A. Shirn, and E. S. Wajda, Phys. Rev. 99, 1085 (1955); V. Gallina and M. Omini, Phys. Status Solidi 7, 405 (1964); P. Wynblatt, J. Phys. Chem. Solids 30, 2201 (1969); P. L. Land and B. Goodman, *ibid.* 28, 113 (1967).

[51] H. R. Glyde and J. A. Venables, J. Phys. Chem. Solids 29, 1093 (1968).

[52] K. Mukherjee, Phys. Lett. A 25, 439 (1967).

[53] J. J. Burton and G. Jura, J. Phys. Chem. Solids 27, 961 (1965).

[54] D. R. Squire and W. G. Hoover, J. Chem. Phys. 50, 701 (1969).

[55] C. H. Bennett and B. J. Alder, J. Chem. Phys. 54, 4796 (1971).

[56] V. G. Gavriko, V. G. Manzhelli, V. I. Kuchev, and A. M. Tolkachev, Fiz. Tverd. Tela 10, 3182 (1968) [Sov. Phys. Solid State 10, 2524 (1969)].

[57] V. G. Manzhelii, V. G. Gavrilko, and V. I. Kuchev, Phys. Status Solidi 34, K55 (1969).

[58] D. S. Kupperman and R. O. Simmons, J. Phys. C 4, L5 (1971); D. S. Kupperman, Ph.D. thesis (University of Illinois at Urbana-Champaign, 1970) (unpublished).

[59] P. A. Bezuglyi, L. M. Tarasenko, and O. I. Baryshevskii, Sov. Phys.-Solid State 13, 2003 (1972).

[60] P. Korpiun, A. Burmeister, and E. Lüscher, J. Phys. Chem. Solids 33, 1411 (1972).