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The Relaxation Energy of Vacancies and Impurities In a Molecular Lattice

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ABSTRACT

The energy of relaxation and relaxation of surrounding atoms are computed for vacancies, large and small impurity atoms, vacancy impurity atom di-defects, and di-vacancies in a fcc (argon) lattice, assuming a Lennard-Jones potential and neglecting all kinetic energy effects. It is found that at normal lattice spacing the energy correction is small for all types of defects considered. Under compression, relaxation energy increases rapidly. Relaxations are always small. It is found that formation of a vacancy next to an impurity is preferred to formation of isolated vacancy. Concentration of di-vacancies is found to be very small except at temperatures approaching the melting point.

INTRODUCTION

Although some measurements have been made from which the energy of the formation of a vacancy can be deduced, it has not been possible to deduce the changes that occur in the immediate neighborhood of the vacancy. In order to investigate in detail the lattice distortion in the immediate vicinity of a vacancy, resort must still be made to theoretical models. The classical method has been to assume a potential function for the molecule under consideration, and then with simplifying assumptions, minimize the energy of the system. This technique has not been applied extensively to ionic crystals, it cannot be applied to metals, and probably is of only qualitative significance when applied to molecular solids. Obviously, as long as only the potential energy is considered, the calculation is strictly valid only at 0°K. The usual subject for computations of this nature is argon. The monatomic nature of the molecule and the symmetry of the lattice minimize the work that must be done to obtain an answer. To date, the only problem that has been considered has been the formation of a vacancy in argon at the normal interatomic distance. In this paper, a more refined examination is made of this problem. In addition calculations are made for the substitution of an impurity atom in the lattice, for the formation of a vacancy next to the impurity atom, for the formation of two adjacent vacancies, and also for the effect of a change of interatomic distance on the energy of formation of the vacancy, and for the effect of a change in the potential function.

This paper will examine two of the more elementary lattice defect problems, namely perturbation of an infinite face centered cubic molecular crystal in the neighborhood of a vacancy of an impurity atom and the stability of di-defects in fcc molecular crystals. In the present calculations only the potential energy is considered, and since the vibrational contribution to the energy is not considered, the results are reasonably valid only at 0°K. Argon is used as the solid and consequently the problem is simplified by the symmetry of the lattice and the nonatomic nature of the molecule. Presumably the results obtained here would apply qualitatively to other molecular crystals.

Several calculations of the energy of formation of a vacancy have been carried out in which the authors neglected kinetic effects. Girifalco and Streetman[1] carried out calculations on a bcc lattice, considering all points in a large box around the defect but neglecting distant neighbors. They found the nearest and next-nearest neighbors relaxing inwards and a large (20%) energy correction due to relaxation. Kanzaki[2] calculated relaxations around a vacancy in Ar (fcc) using a Lennard-Jones 6-10 potential. However he assumed the effect of relaxation on the energy was second order in the relaxation and considered only nearest and next-nearest neighbor interactions. He found that the nearest neighbors relaxed towards the vacancy and the next-nearest away- the relaxation of the next-nearest neighbors being greater than that of the nearest. Hall[3] also calculated the effect of a vacancy on a fcc lattice and assumed a second order relation between relaxation and energy. He found the nearest and next-next-nearest neighbors relaxing inwards towards the vacancy and the next-nearest relaxing outwards. His findings showed that the relaxations fall off rapidly with distance from the defect.

Nardelli and Repanai-Chiarotti[4] and Foreman and Lidiard[5] have carried out dynamical calculations based on the Einstein model. Nardelli's relaxations agree with those found here and his relaxation energy is much larger than that found considering only potential effects. Foreman also determined the energy of formation of a vacancy from heat capacity data for solid argon and found that the predicted relaxation energy was not large enough to account for the smallness of the energy of formation of a vacancy, which was 25% lower than expected.

Alder, Vaisnys, and Jura[6] have calculated the relaxation of the surface of a semi-infinite fcc molecular lattice and have found that the spacing between layers is greatest at the surface, falling off steadily to the equilibrium distance as one goes deeper into the lattice.

Stripp and Kirkwood[7] have calculated the interaction of separated vacancies and have found that they attract with a force whose potential varies as $1/r^6$ where r is the separation of the defects.

Johnson[8] has carried out static calculations on the stability of di-vacancies in metals and have found them to be stable in certain configurations.

Our calculations of the relaxations around a vacancy in a fcc lattice show that the nearest and next-next-nearest neighbors move towards the defect, and that the next-nearest move away. This is in accord with the latest calculations.[3,4,5] The correction in the energy of formation of the defect due to relaxation is small at zero pressure. In the present calculations the treatment is more general than in the earlier static results in that the calculations are not restricted by the assumption that only second order terms in the relaxation are

significant and that distant neighbors may be neglected. Since the same, or essentially the same, treatment can be used when foreign atoms are present or for a compressed lattice, results are also presented for these calculations. We have also calculated the energy of formation of a vacancy next to another vacancy and next to a neon or krypton impurity. In all cases the energy required to produce the vacancy is lower than that in the perfect lattice. Relaxations around the di-defects and energy corrections were small as in the case isolated defects.

CALCULATIONS

The model adopted for the infinite crystal is: (1) all quantum effects may be neglected, which limits the results to heavy atoms because of the neglect of the zero point energy; (2) only the potential energy need be considered, thereby limiting the treatment to 0°K; (3) the total potential is pairwise additive; and (4) the atoms interact with Lennard-Jones potential of the form

$$V(r) = \frac{\beta}{r^m} - \frac{\alpha}{r^6}$$

where r is the distance between the atoms. Calculations were carried out both for m = 12 and m = 7, the latter value was used for an isolated vacancy since recent work by Alder and Van Thiel[9] indicates that argon has a 6-7 potential at high pressure. It was also assumed that the concentration of defects is so small that their interactions may be neglected.

Of all of the assumptions made in the calculations, the one most open to question is that concerning pair-wise additivity. For the perfect

lattice, this assumption will not be in error by more than a few percent at the most. However, in the treatment of the problems considered here, the error may be large. Sparney[10] has estimated that an error of as much as 10-30% might be made when the van der Waals forces are considered to be pair-wise additive. Jansen[11] has shown that consideration of three body forces can explain the stability of the face centered structure with respect to the hexagonal close packed system. The latter, does not really show the necessity for the use of three body sums since the energy difference between the two structures is very small, only a few tenths of a percent. Rossi and Danon[12] have indicated that inclusion of three body forces introduce a large error in the predicted energy of vaporization. They attribute this error to either neglected four body forces or a poor potential function.

On the basis of these assumptions the potential energy of the lattice can be written,

for m = 12,

$$E_T = -\frac{N}{2} \sum_{i,j} V(r_{ij})$$

$$= \frac{N}{2} \left(\frac{\beta A_{12}}{r_o^{12}} - \frac{\alpha A_6}{r_o^6} \right)$$

where

$$A_n = \sum_{\substack{x,y,z \\ x+y+z = \text{even}}} \frac{1}{(x^2 + y^2 + z^2)^{n/2}}$$

where E_T is twice the energy of vaporization, α and β are the parameters in the potential function, r_o is the interatomic distance and N is the number of atoms in the lattice. Following the earlier work of Alder et al.,[6] the edge of the unit cell is made 2, which places the restriction that the sum of the coordinates must be even, and the nearest neighbor distance is made unity. Under these circumstances the following values are found for the parameters of the argon lattice:

$$\alpha = 1.0000000$$

$$\beta = 0.59569996$$

$$A_6 = 14.45392103$$

$$A_{12} = 12.13188018$$

The last two were calculated by the method of Lennard-Jones and Ingham,[6] and is in agreement with their earlier calculations.

ISOLATED METHOD DEFECTS

With the above assumptions the energy required to evaporate a single atom from the lattice is

$$E_D^\circ = \beta A_{12} - \alpha A_6$$

$$= 7.22696051 \text{ Energy units}$$

$$= 2E_V$$

where E_V is the mean energy of vaporization per atom of the lattice.

If the lattice is allowed to relax around the defect, the energy of formation of the defect, E_D, is obtained by considering all potential

pairs involving relaxing atoms

$$E_D = E_D^\circ + \Delta E$$

where ΔE is the change in the potential from the relaxed to the relaxed state.

The vacancy is assumed to be at (0,0,0). Assuming that only the nearest neighbors to the defect relax and that they relax radially and symmetrically, $(1,1,0) \rightarrow (1-\delta,1-\delta,0)$, the energy of a single nearest neighbor, with relaxation δ, is

$$E(\delta) = \sum_{\substack{x^2+y^2+z^2=2n \\ n>1}} V(1-\delta-x,\ 1-\delta-y,z)$$
$$+ V(2-2\delta,\ 2-2\delta,0) + 2V(2-2\delta,0,0) + 4V(1-\delta,0)$$
$$+ 4V(2-2\delta,\ 1-\delta,\ 1-\delta)$$

To simplify the calculations, the infinite sum is expanded as follows:

$$E_1(\delta) = \sum_{\substack{x^2+y^2+z^2=2n \\ n>1}} V(1-\delta-x,\ 1-\delta-y,z)$$

$$= \sum_{\substack{x^2+y^2+z^2=2n \\ 1<n\leq 16}} V(1-\delta-x,\ 1-\delta-y,z)$$

$$+ \sum_{\substack{x^2\ y^2+z^2=2n \\ n>16}} V(1-\delta-x,\ 1-\delta-y,z)$$

$$= E_{11}(\delta) + E_{12}(\delta)$$

$E_{11}(\delta)$ is evaluated by direct summation while $E_{12}(\delta)$ is obtained from a power series.

$$
\begin{aligned}
E_{12}(\delta) = & - .08233486 \\
& - .03180536\{(\delta x)^2 + (\delta y)^2 + (\delta z)^2\} \\
& - .00568384\{(\delta x)^4 + (\delta y)^4 + (\delta z)^4\} \\
& - .00057929\{(\delta x)^6 + (\delta y)^6 + (\delta z)^6\} \\
& - .00007195\{(\delta x)^8 + (\delta y)^8 + (\delta z)^8\} \\
& - .00712398\{(\delta x)^2(\delta y)^2 + (\delta x)^2(\delta z)^2 + (\delta y)^2(\delta z)^2\} \\
& - .0156962\ \{(\delta x)^4(\delta y)^2 + (\delta y)^4(\delta z)^2 \\
& \qquad + (\delta x)^4(\delta z)^2 + (\delta z)^4(\delta x)^2 \\
& \qquad + (\delta y)^4(\delta z)^2 + (\delta z)^4(\delta y)^2\} \\
& + .002707\{(\delta x)^4(\delta y)^4 + (\delta x)^4(\delta z)^4 \\
& \qquad + (\delta y)^4(\delta z)^4\} \\
& - .0002403\{(\delta x)^6(\delta y)^2 + (\delta y)^6(\delta x)^2 \\
& \qquad + (\delta x)^6(\delta z)^2 + (\delta z)^6(\delta x)^2 \\
& \qquad + (\delta y)^6(\delta z)^2 + (\delta z)^6(\delta y)^2\} \\
& + .00285632\{(\delta x)^2(\delta y)^2(\delta z)^2\} \\
& - .002608\{(\delta x)^4(\delta y)^2(\delta z)^2 + \\
& \qquad (\delta x)^2(\delta y)^4(z)^2 + \\
& \qquad (\delta x)^2(\delta y)^2(\delta z)^4\}
\end{aligned}
$$

The power series expansion is used rather than an integral as integration will not yield as accurate an answer when the lower limit is this small.

The power series expansion given is for a point at (0,0,0) going to $(\delta x, \delta y, \delta z)$. It is not feasible to expand

$$E_1(\delta) = E_{11}(\delta) + E_{12}(\delta)$$

in a power series over all points because of the slowness with which such a series converges.

Summing over the twelve nearest neighbors, the expression for the energy is

$$\begin{aligned} E(\delta) = 6\{&V\,(2-2\delta,\ 2-2\delta, 0) + 2V\,(2-2\delta, 0, 0) \\ &+ 4V\,(1-\delta, 1-\delta, 0) + 4V\,(2-2\delta, 1-\delta, 1-\delta)\} \\ &+ 12E_{11}(\delta) + 12E_{12}(\delta). \end{aligned}$$

Note that to obtain the total energy contribution of the twelve nearest neighbors, the interactions of the nearest neighbors with each other must be multiplied by six, not twelve, so that each pair is counted only once.

With this we may write

$$\Delta E = E(\delta) - E(0)$$

where E is expanded as above.

Similar and obviously more complex expressions are written if more atoms are permitted to relax.

To minimize the energy, only ΔE need be considered since this is the only term in which the relaxations appear.

Minimization of ΔE was performed in a step wise manner. First the solution for the relaxation of the nearest neighbors was obtained.

This was then the basis for the first approximation when the nearest and next-nearest neighbors were considered. The solution of this was then used as a starting point for the most complete calculations performed. Calculations were made on an IBM 7094 and an SDS 910. The minimum for ΔE for each mole of relaxation examined was found by a half interval technique. Because of the machine time and labor required to carry the calculations to neighbors more distant from the defect and the qualitative significance of the results, computations were made only for the first three layers around the vacancy.

Calculations for an impurity atom are essentially the same as for a vacancy; this was done for a large and a small impurity atom. In this the constants used for argon[14]

$$r_o = 1 \text{ unit} = 3.79 \text{ Å}$$

$$2E_V = 7.22696 \text{ units} = 2828\ 10^{-16} \text{ ergs}$$

were modified as follows: Ar-KR and Ar-Ne pair potentials were related to the 6-12 potentials of Ar,[14] Ne,[14] and Kr[15] in the following way. If r_{A-A} represents the gas equilibrium distance and U_{A-A} the depth of the well in the gas

$$r_{A-B} = \frac{r_{A-A} + r_{B-B}}{2}$$

$$u_{A-B} = (u_{A-A}\ u_{B-B})^{\frac{1}{2}}$$

RESULTS

Calculations for the relaxation of the nearest neighbors was initially carried out assuming that the relaxation would preserve the xy, xz, and yz planes as planes of symmetry. This involves six independent variables and it was found, with this condition, that E_D is minimized by a relaxation which preserves the full (rotational) symmetry about the defect. Calculations for completely independent relaxation of the twelve nearest neighbors, a thirty-six variable problem, were not performed.

For the next- and next-next-nearest neighbors it was assumed that the relaxations would also have the high symmetry established for the nearest neighbors.

Those relaxations minimizing ΔE, and ΔE are given in Tables 1-8. Relaxations are expressed in terms of the coordinates. The lattice point with coordinates (x,y,z) relative to the defect at (0,0,0) was relaxed to the new position ($x-\delta x$, $y-\delta y$, $z-\delta z$) and δx, xy, and δz are tabulated beneath x, y, and z. ΔE is given for each relaxation in the units defined above.

In each case the energy of formation of the defect in the unrelaxed lattice, E_D^0, is given. E_D^0 is the difference in energy between the perfect argon lattice and the defective (unrelaxed) lattice. For a Kr impurity energy is released on substitution of the impurity atom for the Ar atom, and the effect of the relaxation is to increase the amount of energy released. Creation of a vacancy or substitution of a Ne for an Ar atom requires energy and the relaxation decreases the amount required.

At first, the relaxations appear to be intuitively incorrect. However, an examination of the geometry of the lattice shows that for each relaxation, the motion of the atoms always increases the overlap with some atoms and decreases the overlap with others. The inward relaxation of the nearest neighbors is obvious, and the small magnitude of the relaxation can be accounted for on the basis of the fact that some of the nearest neighbors of the vacancy are also nearest neighbors of the relaxing atom. For example, the atom at (1,1,0) has as its nearest neighbors atoms at (1,0,1), (1,0,-1), (0,1,1), and (0,1,-1). The inward motion of these atoms increases the overlap between the atom (1,1,0) and the four mentioned atoms relaxing inwards that are its nearest neighbors as well as the nearest neighbors of the vacancy. At the same time the overlap with the vacancy disappears, and the overlap with the remaining seven nearest neighbors is decreased. Thus the total relaxation and its direction are the result of both increasing and decreasing overlaps.

Again for second nearest neighbors any movement in the lattice increases overlap, serving to keep the relaxation small. However, here the interaction between two of the relaxing (next-nearest neighbor) atoms is small and the most important term is the absence of the attraction of the center atom, thus leading to a relaxation outward. The behavior of the third nearest neighbors cannot be accounted for in this way. The largest term seen by a third nearest neighbor is not the absence of the attraction of the central atom, which is already a very small term. Rather the important terms are due to the motion of its own

nearest neighbors (two of which are nearest neighbors to the defect and one a next-nearest neighbor). It is into the potential hole created by the movement of these nearest neighbors that the third nearest atom moves. As pressure on the lattice is increased (interatomic distance is decreased), nearest neighbors of the vacancy are farther up on the repulsive side of the central atom and so can relax further into the hole. Next nearest neighbors are less strongly attracted to the central atom and so move less away from the central atom. At sufficiently high pressure they would actually move toward the defect. The increased movement of the first two layers toward the vacancy leaves the third nearest neighbors a larger hole in which to relax, and so their motion toward the center increases with pressure. That the relaxation of the third nearest neighbors contributes more to ΔE than the second nearest is understandable as there are twenty-four next-next-nearest neighbors and only six next-nearest neighbors.

Expectedly, the relaxations of the atoms around a krypton (large) impurity are of the opposite sign from those around a vacancy, and a neon (small) impurity affects the lattice qualitatively like a vacancy, except that the attraction of the neon increases the relaxations.

For relaxations around an internal defect ΔE is found to coverge less rapidly than for surface relaxations.[6] Also the numerical values of the relaxations for internal effects are of less significance than those for surfaces, as these calculations are highly dependent on the repulsive potential, which is not accurate, while the latter depend mostly on the $1/r^6$ attractive potential, whose form is well established.

Correcting the energy of formation of a defect by the amounts determined for three layers of relaxation, we find the following:

Vacancy:

$r/ro = 1.00$

6 - 12 Potential

$E_D^\circ = 7.226961 = 2E_V$

$E_D = 7.180463 = 1987E_V$

$\frac{\Delta E}{E_D} = -6.4 \times 10^{-3}$

6 - 7 Potential

$E_D^\circ = 7.226961 = 2E_V$

$E_D = 7.072137 = 1.958E_V$

$\frac{\Delta E}{E_D} = -2.18 \times 10^{-2}$

$r/ro = .90$

6 - 12 Potential

$E_D^\circ = 1.609058$

$E_D = .233165$

$\frac{\Delta E}{E_D} = -5.90$

6 - 7 Potential

$E_D^\circ = 4.532935$

$E_D = 3.444041$

$\frac{\Delta E}{E_D} = -3.16 \times 10^{-1}$

Krypton Impurity

$$E_D^\circ = -1.431417$$

$$E_D = -1.541059$$

$$\frac{\Delta E}{E_D} = 7.1 \times 10^{-2}$$

Neon Impurity

$$E_D^\circ = 3.943454$$

$$E_D = 3.838793$$

$$\frac{\Delta E}{E_D} = 2.7 \times 10^{-2}$$

By varying the interatomic distance used in the calculations it is possible to consider formation of vacancies under high pressure or at a hypothetical distended lattice. This was done for interatomic distances ranging from 1.06 to .84 times the normal distance; the results of these calculations are shown in Tables III and IV.

As expected the relaxations inward increased with decreasing separation. For a 6-12 potential the sign of the first relaxation changes at about 1.03 the normal distance so that nearest neighbors relax away from the vacancy. The volume at this distance corresponds roughly to the volume in liquid argon. Whether this correspondence is coincidental or of some significance has not been studied as the behavior of the lattice under high pressure was of greater interest to us.

At sufficiently small separations, even before the energy of vaporization becomes positive, the potential energy of formation of a vacancy becomes negative. There are two processes which may be examined in the formation of a vacancy: a constant volume process, in which case ΔA is the important thermodynamic function, and a constant pressure process for which ΔF is of interest.

For constant pressure creation of a vacancy we consider an interior atom removed to the surface of the crystal (and neglect surface relaxations). Then

$$\Delta F = \Delta E + P\Delta V - T\Delta S$$

where ΔE now refers to the energy of formation of a vacancy with relaxations, $T = 0$, and P is obtained from the potential from

$$P = -\frac{1}{2}\left(\frac{\partial E_D^\circ}{\partial r}\right)_T = -\left(\frac{\partial E_D^\circ}{\partial r}\right)_T \frac{1}{\left(\frac{\partial V}{\partial r}\right)_T}$$

noting that E_D° is twice the average energy of vaporization. For $r = .9$ we obtained

6 - 12 Pot

$\Delta F = 23.408$

6 - 7 Pot

$\Delta F = 11.73$

The constant volume process, for the formation of one vacancy per n atoms, may be regarded in the following way: Starting with n atoms with separation r, we go to n atoms and a vacancy in a lattice with

interatomic distance $r' = \left(\frac{n}{n+1}\right)^{1/3} r$. For this process we may readily compute ΔA and obtain the following values for the formation of one vacancy per n atoms, with r = .9:

6 - 12 Pot

n	ΔA
100	23.798
1,000	23.447
10,000	23.415

6 - 7 Pot

n	ΔA
100	11.856
1,000	11.747
10,000	11.742

Comparing the values of ΔF and ΔA found with the average energy of vaporization at zero pressure (3.66), we would expect that at some not too high temperature the lattice would disorder, whatever the actual form of the potential is. This is in agreement with the shock work of Alder et al.[9] who found a first order transition in solid Argon lying on the extension of the normal melting curve.

DI-DEFECTS

Method

In this section we assume (1) that there are two neighboring vacancies located at (0,0,0) and (1,1,0), (2) that only nearest neighbors to the di-defect relax and (3) that the relaxations retain the symmetry of the lattice. On this basis it becomes possible to write an expression for the relaxation energy similar to that of an isolated vacancy. This expression can be readily modified to calculate relaxation energies for a vacancy next to an impurity atom or, as with the isolated vacancy, for vacancy formation in a compressed lattice.

Next to such a di-defect there are eighteen nearest neighbors plus the impurity atom in that case. The problem becomes one of minimizing an energy function in sixteen variables. This was done on an IBM 7094 using the same technique employed with the isolated defect. Fortunately, it was found that the modified half interval technique used did lead to a convergent solution.

Results

The di-defect results are given in Table 9. The energy required to produce a given defect in a perfect lattice without relaxation is E_D°, the relaxation energy is ΔE, and the energy required to produce the defect is E_D. Obviously

$$E_D = E_D^\circ + \Delta E$$

The energy required to introduce a vacancy next to the other part of the defect (vacancy or impurity) in a relaxed lattice, E_V, is the quantity of real interest in these calculations. This value is also given in Table 9. The energy scale used in this table is that defined in the isolated defect calculations and used throughout this paper.

The relaxations themselves are presented in Table 10. A discussion of the relaxation calculations is contained in Appendix I. In all cases the relaxations themselves are small, being of the same order of magnitude as for isolated defects. It was found that a krypton atom relaxed 1.5% into the vacancy and a neon atom relaxes 3.6%. These relaxations are small as for the pure material, the impurity atom rapidly increases its overlap with its other nearest neighbors. Relaxations into the di-vacancy behaved like those into the isolated vacancy. All nearest neighbors relaxed inwards towards the vacancy-vacancy and the neon-vacancy defects. In the case of a krypton-vacancy defect, the neighboring atoms moved towards the vacancy and away from the krypton impurity as expected from the isolated defect calculations.

Comparison of E_V in Table 9 with the energy required to produce an isolated vacancy indicates that the energy of formation of a vacancy next to another defect is lower than that for an isolated vacancy. Free energies for formation of vacancies are correspondingly lower. This is in agreement with the attraction of vacancies predicted by Stripp et al.[7]

It is possible from these results to estimate the relative concentrations of various defects. Following Kröger and Vink,[16] we write the concentration of a given defect [D] as

$$[D] = e^{S_D/k} e^{-E_D/kT}$$

where S_D is the entropy of formation of the defect and E_D is the total energy required to produce the defect. S_D may be calculated from elementary statistics. E_D may be separated into a kinetic energy term, K_D, and a potential energy term, E_D. This latter term has been obtained in this paper for various modes of vacancy formation. If we assume that, in the formation of a vacancy, K_D is independent of the location of the vacancy, we obtain

$$\frac{[D_1]}{[D_2]} = \frac{e^{S_{D_1}/k} e^{-E_{D_1}/kT}}{e^{S_{D_2}/k} e^{-E_{D_2}/kT}}$$

for the relative concentrations of two types of (vacancy) defects. $\frac{[D_1]}{[D_2]}$ is plotted in Fig. 1 and 2 for various types of vacancies, where $[D_2]$ is always the concentration of isolated vacancies as in a pure argon lattice. $[D_2]$ has been estimated by Foreman and Lidiard[5] to be .1% near the melting point of argon. From a knowledge of the concentration of isolated vacancies in pure argon, we can obtain the concentration of various types of di-defects.

From Fig. 1 we see that the formation of a vacancy next to a krypton atom is strongly preferred at low temperatures and less so at higher temperatures. Concentration of vacancies next to neon impurities behaves similarly. Concentration of di-vacancies is insignificant in

comparison with the concentration of vacancies except at high temperatures (> 80°K) where we approach the melting point of argon; this is shown in Fig. 2.

The preference for formation of a vacancy next to an impurity causes a decrease in the average energy of formation of a vacancy in impure argon, particularly at low temperatures; average energy of vacancy formation is plotted in Fig. 3 as a function of krypton concentration at various temperatures. The values shown here for high impurity concentration are almost certainly not valid since the impurities will interact, and this interaction has not been included in the calculations. Similar curves are obtained for neon.

Throughout these calculations we have considered the process in which an argon atom is moved from the interior of the lattice to infinity. The process of physical significance involves the removal of the interior atom to the surface of the crystal. This process requires roughly E_V less energy than the removal of the atom to infinity, where E_V is the average energy of vaporization of the pure lattice. This term does not affect any of the results presented thus far. Considering this term, the energy required to produce a vacancy in an impure lattice may be obtained from Fig. 3 for the process of physical significance. This we have used to estimate the concentration of vacancies in an impure argon lattice at 80°K, which is shown in Fig. 4. Impurities are seen to increase the concentration of vacancies. Again values for large impurity concentrations are not significant. Even in impure samples the concentration of vacancies predicted by this model is much smaller than that determined experimentally.[5]

CONCLUSIONS

The qualitative behavior of the relaxations around a vacancy are fairly independent of the exact form of the repulsive potential. As one would intuitively expect, the effect of high pressure is to drive surrounding atoms further into the hole left by a vacancy. For atoms more distant from a defect than second nearest neighbors, the most important contribution to their motion is the behavior of their own nearest neighbors.

Relaxations around small atoms are qualitatively like those around vacancies, while relaxations around large atoms are opposite to sign to those around vacancies.

At high pressure it was found that an order-disorder transition could occur at not too high temperature.

It was found that formation of a vacancy next to another defect is energetically preferred to formation of an isolated vacancy. We have shown that the concentration of vacancies next to impurity atoms is higher than that which would be expected from a random distribution of vacancies, particularly at low temperatures. From this we conclude that the concentration of vacancies at a given temperature increases with impurity concentration.

We have also shown that the concentration of di-vacancies is insignificant in pure argon except at high temperatures (> 80°K) where we approach the melting point of pure argon.

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APPENDIX I

For di-defects, as with isolated defects, we have assumed that the relaxations retain as much of the symmetry of the lattice as possible. Accordingly, we have separated the relaxing atoms into equivalent points.

$$(1, 0, 1) \equiv (1, 0, -1) \equiv (0, 1, 1) \equiv (0, 1, -1) = \{A\}$$
$$(-1, 0, 1) \equiv (-1, 0, -1) \equiv (0, -1, 1) \equiv (0, -1, -1) = \{B\}$$
$$(1, -1, 0) \equiv (-1, 1, 0) = \{C\}$$
$$(1, 2, 1) \equiv (1, 2, -1) \equiv (2, 1, 1) \equiv (2, 1, -1) = \{D\}$$
$$(2, 0, 0) \equiv (0, 2, 0) = \{E\}$$
$$(1, 1, 0) = \{F\}$$
$$(-1, -1, 0) = \{G\}$$
$$(2, 2, 0) = \{H\}$$

The relaxation of the atoms in set {A} in then described by three variables; {B} by three variables; {C} by two; {D} by three; {E} by two; and {F}, {G} and {H} by one variable, for a total of sixteen variables.

The energy was minimized with respect to these sixteen variables in the same manner as for the isolated defect.

When the di-defect is two vacancies additional symmetry appears:

$$\{C\} \equiv \{D\} \equiv \{E\}$$
$$\{G\} \equiv \{H\}$$

and the total number of variables to be considered is reduced to ten. The energy was minimized as before.

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Table I. Vacancy

6 - 12 Potential r/ro = 1.00

E_D° = 7.22696051

(1,	1,	0)	(2,	0,	0)	(2,	1,	1)	ΔE
6.055×10^{-3}	6.055×10^{-3}	0	-	-	-	-	-	-	-.041823
6.055×10^{-3}	6.055×10^{-3}	0	-3.412×10^{-3}	0	0	-	-	-	-.045159
6.420×10^{-3}	6.420×10^{-3}	0	-3.433×10^{-3}	0	0	8.80×10^{-4}	5.39×10^{-4}	5.39×10^{-4}	-.046498

Table II. Vacancy

6 - 7 Potential r/ro = 1.00

E_D° = 7.22696051

(1,	1,	0)	(2,	0,	0)	(2,	1,	1)	ΔE
1.3751×10^{-2}	1.3751×10^{-2}	0	-	-	-	-	-	-	-.143454
1.3770×10^{-2}	1.3770×10^{-2}	0	-5.484×10^{-3}	0	0	-	-	-	-.148911
1.4766×10^{-2}	1.4766×10^{-2}	0	-5.579×10^{-3}	0	0	2.287×10^{-3}	1.410×10^{-3}	1.410×10^{-3}	-.154824

Table III Vacancy

6 - 12 Potential r/ro Variable

r/ro	(1,	1,	0)	E_D°	ΔE
1.05	-6.603×10^{-3}	-6.603×10^{-3}	0	6.761496	-.019650
1.03	-1.02×10^{-4}	-1.02×10^{-4}	0	7.036087	-.000007
1.02	2.328×10^{-3}	2.328×10^{-3}	0	7.136259	-.004286
1.01	4.330×10^{-3}	4.330×10^{-3}	0	7.202887	-.018025
1.00	6.055×10^{-3}	6.055×10^{-3}	0	7.226961	-.041823
.99	7.514×10^{-3}	7.514×10^{-3}	0	7.199039	-.076673
.98	8.789×10^{-3}	8.789×10^{-3}	0	7.106940	-.123933
.96	1.0844×10^{-2}	1.0844×10^{-2}	0	6.670301	-.263063
.94	1.2470×10^{-2}	1.2470×10^{-2}	0	5.766433	-.478522
.92	1.3773×10^{-2}	1.3773×10^{-2}	0	4.181091	-.798415
.90	1.4836×10^{-2}	1.4836×10^{-2}	0	1.609058	-1.262866
.88	1.5732×10^{-2}	1.5733×10^{-2}	0	-2.385581	-1.928867

Table IV. Vacancy

6 - 7 Potential r/ro Variable

r/ro	(1,	1,	0)	E_D°	ΔE
1.06	5.059×10^{-3}	5.059×10^{-3}	0	6.825005	-.009336
1.04	8.562×10^{-3}	8.562×10^{-3}	0	7.029627	-.034751
1.02	1.1416×10^{-2}	1.1416×10^{-2}	0	7.172315	-.078346
1.00	1.3751×10^{-2}	1.3751×10^{-2}	0	7.226961	-.143454
.98	1.5720×10^{-2}	1.5720×10^{-2}	0	7.159317	-.234808
.96	1.7344×10^{-2}	1.7344×10^{-2}	0	6.924518	-.358770
.94	1.8719×10^{-2}	1.8719×10^{-2}	0	6.463812	-.523677
.92	2.0000×10^{-2}	2.0000×10^{-2}	0	5.700246	-.740313
.90	2.1032×10^{-2}	2.1032×10^{-2}	0	4.532935	-1.022693
.88	2.1989×10^{-2}	2.1989×10^{-2}	0	2.829418	-1.388885
.86	2.2821×10^{-2}	2.2821×10^{-2}	0	.415428	-1.862389
.84	2.3547×10^{-2}	2.3547×10^{-2}	0	-2.938880	-2.473718

Table V. Vacancy

6 - 12 Potential r/ro = .9

E_D° = 1.609058

(1,	1,	0)	(2,	0,	0)	(2,	1,	1)	ΔE
1.4836×10^{-2}	1.4836×10^{-2}	0	-	-	-	-	-	-	-1.262866
1.4853×10^{-2}	1.4853×10^{-2}	0	-1.919×10^{-3}	0	0	-	-	-	-1.267608
1.6140×10^{-2}	1.6140×10^{-2}	0	-2.129×10^{-3}	0	0	3.582×10^{-3}	2.157×10^{-3}	2.157×10^{-3}	-1.375893

Table VI. Vacancy

6 - 7 Potential r/ro = .9

E_D° = 4.532935

(1,	1,	0)	(2,	0,	0)	(2,	1,	1)	ΔE
2.1032×10^{-2}	2.1032×10^{-2}	0	-	-	-	-	-	-	-1.022693
2.1070×10^{-2}	2.1070×10^{-2}	0	-3.594×10^{-3}	0	0	-	-	-	-1.029296
2.2875×10^{-2}	2.2875×10^{-2}	0	-4.008×10^{-3}	0	0	4.899×10^{-3}	2.953×10^{-3}	2.953×10^{-3}	-1.088894

Table VII. Krypton Impurity

6 - 12 Potential

$E_D^\circ = -1.431417$

(1,	1,	0)	(2,	0,	0)	(2,	1,	1)	ΔE
-7.985×10^{-3}	-7.985×10^{-3}	0	-	-	-	-	-	-	-.102724
-7.985×10^{-3}	-7.985×10^{-3}	0	1.414×10^{-3}	0	0	-	-	-	-.103268
-8.555×10^{-3}	-8.555×10^{-3}	0	1.414×10^{-3}	0	0	-1.826×10^{-3}	-1.114×10^{-3}	-1.114×10^{-3}	-.109642

Table VIII. Neon Impurity

6 - 12 Potential

$E_D^\circ = 3.943454$

(1,	1,	0)	(2,	0,	0)	(2,	1,	1)	ΔE
9.051×10^{-3}	9.051×10^{-3}	0	-	-	-	-	-	-	-.096738
9.051×10^{-3}	9.051×10^{-3}	0	-2.312×10^{-3}	0	0	-	-	-	-.098311
9.781×10^{-3}	9.781×10^{-3}	0	-2.375×10^{-3}	0	0	1.899×10^{-3}	1.180×10^{-3}	1.180×10^{-3}	-.104661

Table IX.

Defect	E_D°	ΔE	E_D	E_V
Vac-Vac				
$R/R_0 = 1$				
6 - 12 Potential	14.0496209	- .1022076	13.9474133	6.8639068
Vac-Vac				
$R/R_0 = .90$				
6 - 12 Potential	3.44563803	-3.39767718	.04796085	- .298232
Vac-Kr	5.3710344	- .14000805	5.2310264	6.5528014
Vac-Ne	10.96794706	- .18145669	10.78649037	6.94769737

Table X

The vacancy is at (0,0,0) and the second defect at (1,1,0). The point (x,y,z) (given as $\begin{pmatrix} x \\ y \\ z \end{pmatrix}$ in the Table) goes to (x-δx, y-δy, z-δz). $\begin{pmatrix} \delta x \\ \delta y \\ \delta z \end{pmatrix}$ is given for each second defect and point investigated. For comparison, relaxations around a single vacancy in a perfect lattice are given under Ar for those points considered in di-defect studies.

	Di-defect		Relaxations	
$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$	Vac.	Ne	Ar	Kr
$\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$	0 0 0	-3.5937×10^{-2} -3.5937×10^{-2} 0	6.420×10^{-3} 6.420×10^{-3} 0	1.7026×10^{-2} 1.7026×10^{-2} 0
$\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$	7.880×10^{-3} -7.851×10^{-3} 2.113×10^{-2}	8.242×10^{-3} -1.1821×10^{-2} 2.6435×10^{-2}	6.420×10^{-3} 0 6.420×10^{-3}	4.194×10^{-3} 1.0234×10^{-2} -7.685×10^{-3}
$\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$	7.880×10^{-3} -7.851×10^{-3} -2.1113×10^{-2}	8.242×10^{-3} -1.1821×10^{-2} -2.6435×10^{-2}	6.420×10^{-3} 0 -6.420×10^{-3}	4.194×10^{-3} 1.0234×10^{-2} 7.685×10^{-3}
$\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$	-7.851×10^{-3} 7.880×10^{-3} 2.1113×10^{-2}	-1.1821×10^{-2} 8.242×10^{-3} 2.6435×10^{-2}	0 6.420×10^{-3} 6.420×10^{-3}	1.0234×10^{-2} 4.194×10^{-3} -7.685×10^{-3}
$\begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}$	-7.851×10^{-3} 7.880×10^{-3} -2.1113×10^{-3}	-1.1821×10^{-2} 8.242×10^{-3} -2.6435×10^{-2}	0 6.420×10^{-3} -6.420×10^{-3}	1.0234×10^{-2} 4.194×10^{-3} 7.685×10^{-3}

(Table X continued)

$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$	Vac.	Ne	Ar	Kr
$\begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix}$	-6.333×10^{-3} -8.00×10^{-4} 5.922×10^{-3}	-7.216×10^{-3} -1.552×10^{-3} 6.240×10^{-3}	-6.420×10^{-3} 0 6.420×10^{-3}	-4.980×10^{-3} 1.230×10^{-3} 6.240×10^{-3}
$\begin{pmatrix} -1 \\ 0 \\ -1 \end{pmatrix}$	-6.333×10^{-3} -8.00×10^{-4} -5.922×10^{-3}	-7.216×10^{-3} -1.552×10^{-3} -6.240×10^{-3}	-6.420×10^{-3} 0 -6.420×10^{-3}	-4.980×10^{-3} 1.230×10^{-3} -6.240×10^{-3}
$\begin{pmatrix} 0 \\ -1 \\ 1 \end{pmatrix}$	-8.00×10^{-4} -6.333×10^{-3} 5.922×10^{-3}	-1.552×10^{-3} -7.216×10^{-3} 6.240×10^{-3}	0 -6.420×10^{-3} 6.420×10^{-3}	1.230×10^{-3} -4.980×10^{-3} 6.240×10^{-3}
$\begin{pmatrix} 0 \\ -1 \\ -1 \end{pmatrix}$	-8.00×10^{-4} -6.333×10^{-3} -5.922×10^{-3}	-1.552×10^{-3} -7.216×10^{-3} -6.240×10^{-3}	0 -6.420×10^{-3} -6.420×10^{-3}	1.230×10^{-3} -4.980×10^{-3} -6.240×10^{-3}
$\begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}$	4.121×10^{-3} 1.31×10^{-4} 0	3.603×10^{-3} -5.95×10^{-4} 0	6.420×10^{-3} -6.420×10^{-3} 0	6.513×10^{-3} -9.750×10^{-3} 0
$\begin{pmatrix} -1 \\ 1 \\ 0 \end{pmatrix}$	1.31×10^{-4} 4.121×10^{-3} 0	-5.95×10^{-4} 3.603×10^{-3} 0	-6.420×10^{-3} 6.420×10^{-3} 0	-9.750×10^{-3} 6.513×10^{-3} 0
$\begin{pmatrix} -1 \\ -1 \\ 0 \end{pmatrix}$	-6.079×10^{-3} -6.079×10^{-3} 0	-6.328×10^{-3} -6.328×10^{-3} 0	-6.420×10^{-3} -6.420×10^{-3} 0	-5.566×10^{-3} -5.566×10^{-3} 0
$\begin{pmatrix} 2 \\ 2 \\ 0 \end{pmatrix}$	6.079×10^{-3} 6.079×10^{-3} 0	7.343×10^{-3} 7.343×10^{-3} 0	* * *	-2.900×10^{-3} -2.900×10^{-3} 0

(Table X continued)

$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$	Vac.	Ne	Ar	Kr
$\begin{pmatrix} 1 \\ 2 \\ 1 \end{pmatrix}$	8.00×10^{-4} 6.333×10^{-3} 5.922×10^{-3}	3.22×10^{-4} 8.710×10^{-3} 8.554×10^{-3}	5.39×10^{-4} 8.80×10^{-4} 5.39×10^{-4}	9.47×10^{-4} -5.356×10^{-3} -6.069×10^{-3}
$\begin{pmatrix} 1 \\ 2 \\ -1 \end{pmatrix}$	8.00×10^{-4} 6.333×10^{-3} -5.922×10^{-3}	3.22×10^{-4} 8.710×10^{-3} -8.554×10^{-3}	5.39×10^{-4} 8.80×10^{-4} -5.39×10^{-4}	9.47×10^{-4} -5.356×10^{-3} 6.069×10^{-3}
$\begin{pmatrix} 2 \\ 1 \\ 1 \end{pmatrix}$	6.333×10^{-3} 8.00×10^{-4} 5.922×10^{-3}	8.710×10^{-3} 3.22×10^{-4} 8.554×10^{-3}	8.80×10^{-4} 5.39×10^{-4} 5.39×10^{-4}	-5.356×10^{-3} 9.47×10^{-4} -6.069×10^{-3}
$\begin{pmatrix} 2 \\ 1 \\ -1 \end{pmatrix}$	6.333×10^{-3} 8.00×10^{-4} -5.922×10^{-3}	8.710×10^{-3} 3.22×10^{-4} -8.554×10^{-3}	8.80×10^{-4} 5.39×10^{-4} -5.39×10^{-4}	-5.356×10^{-3} 9.47×10^{-3} 6.069×10^{-3}
$\begin{pmatrix} 2 \\ 0 \\ 0 \end{pmatrix}$	-1.31×10^{-4} -4.121×10^{-3} 0	1.884×10^{-3} -7.592×10^{-3} 0	-3.433×10^{-3} 0 0	-1.0688×10^{-2} 7.714×10^{-3} 0
$\begin{pmatrix} 0 \\ 2 \\ 0 \end{pmatrix}$	-4.121×10^{-3} -1.31×10^{-4} 0	-7.592×10^{-3} 1.884×10^{-3} 0	0 -3.433×10^{-3} 0	7.714×10^{-3} -1.0688×10^{-2} 0

* Not calculated.

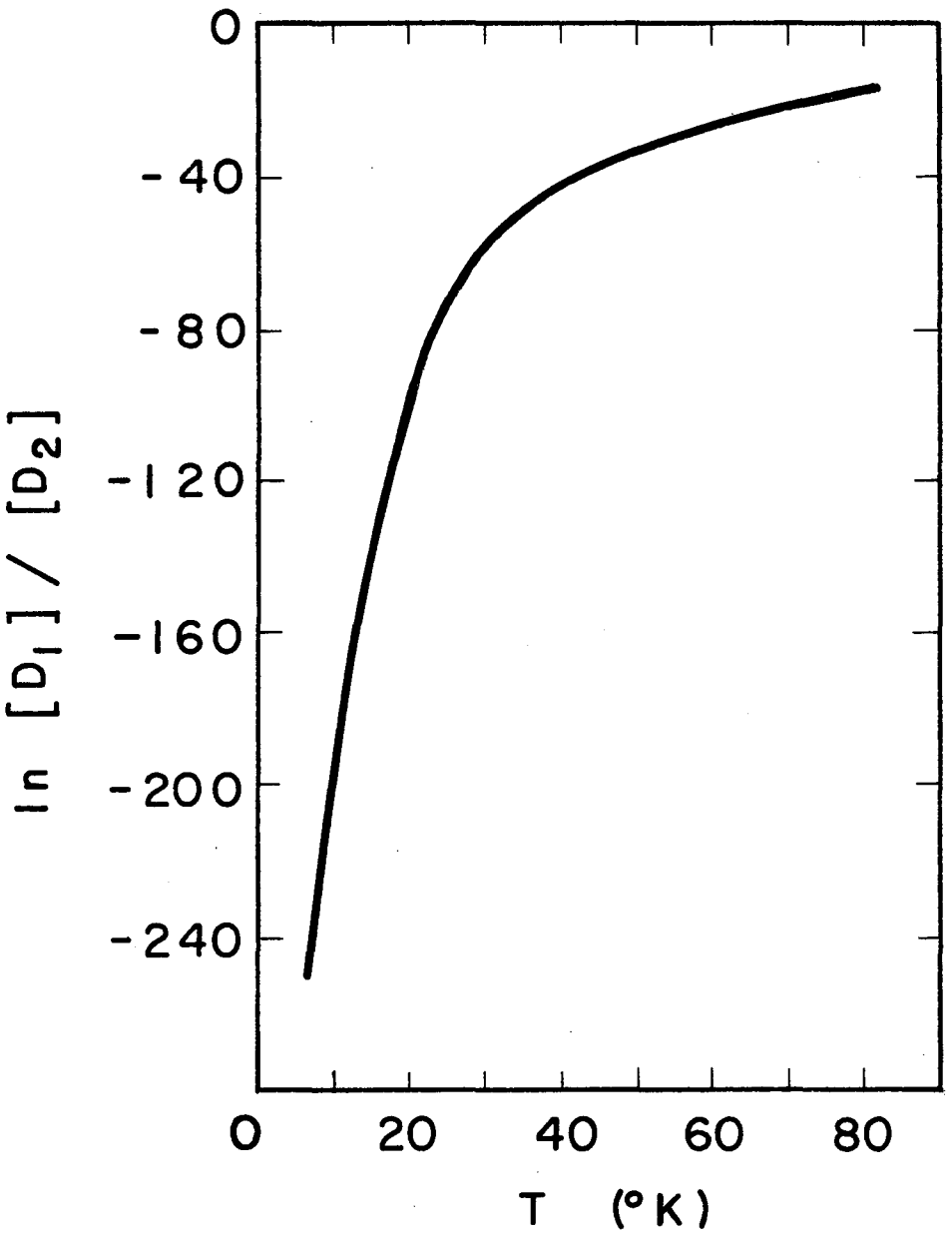
FIGURE CAPTIONS

Figure 1. $\ln \frac{[D_1]}{[D_2]}$ where $[D_2]$ is concentration of isolated vacancies in pure Ar and $[D_1]$ of di-vacancies in pure Ar.

Figure 2. $\ln \frac{[D_1]}{[D_2]}$ where $[D_2]$ is concentration of isolated vacancies in pure Ar and $[D_1]$ is the concentration of vacancies adjacent to Kr atoms in argon with .1% Kr.

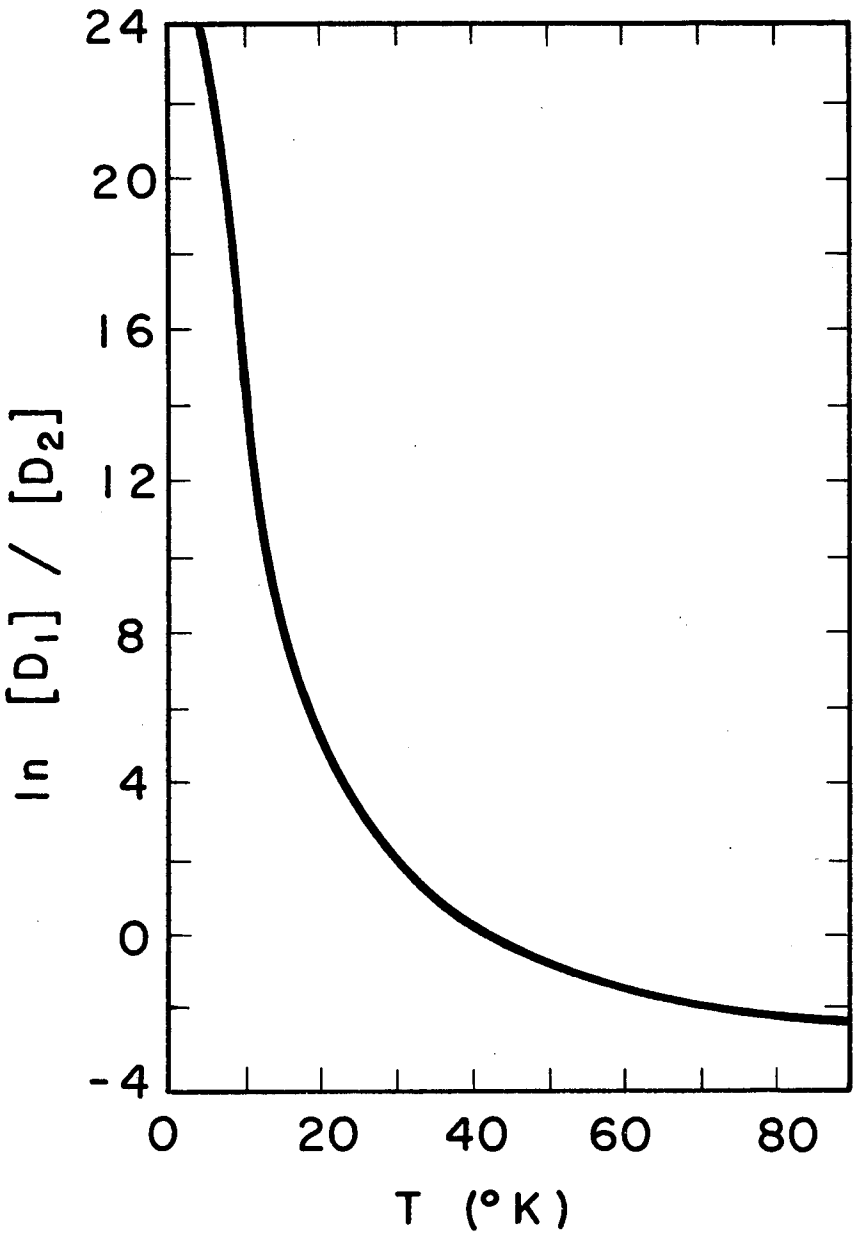
Figure 3. Average energy of creation of a vacancy in an impure lattice vs. -log (krypton concentration). Energy of vaporization from pure lattice is taken as 1.

Figure 4. log [vacancy] vs. -log [impurity] at 80°K.



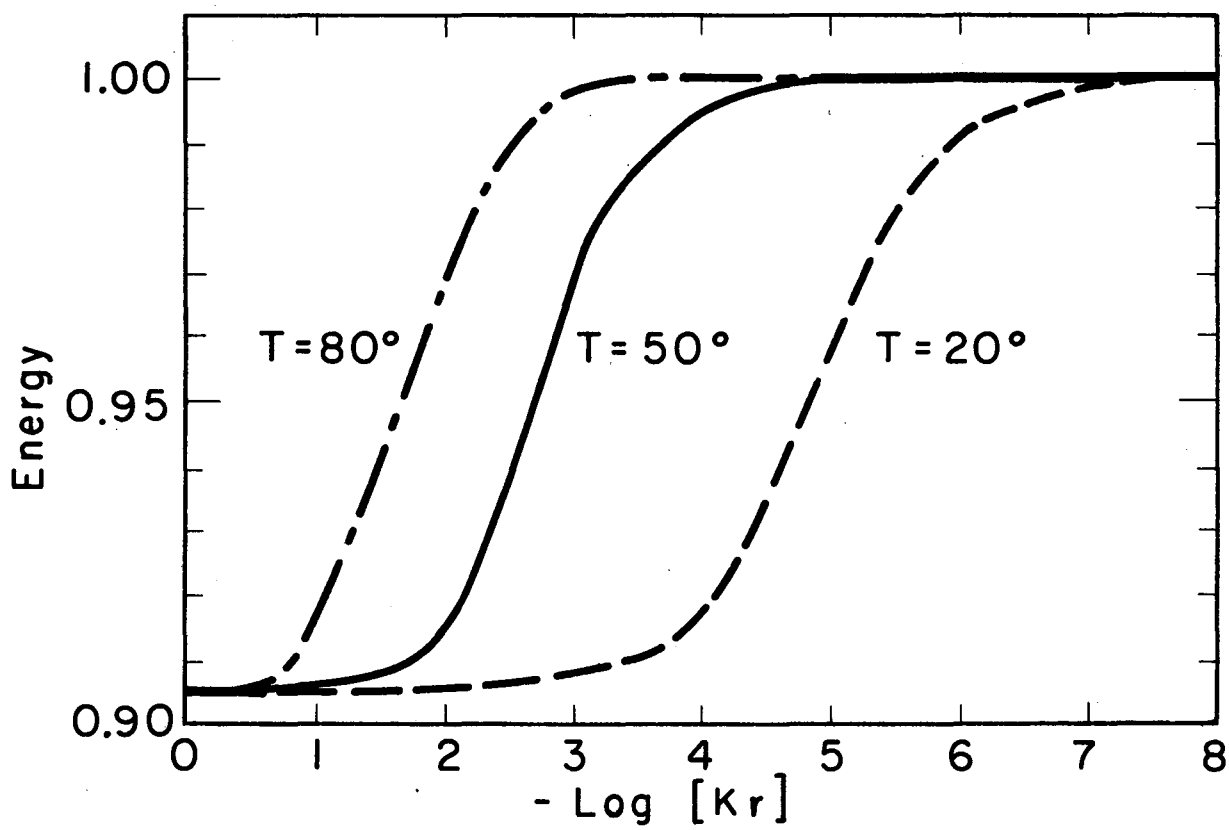
MUB-8154

Fig. 1



MUB-8155

Fig. 2



MUB-8153

Fig. 3

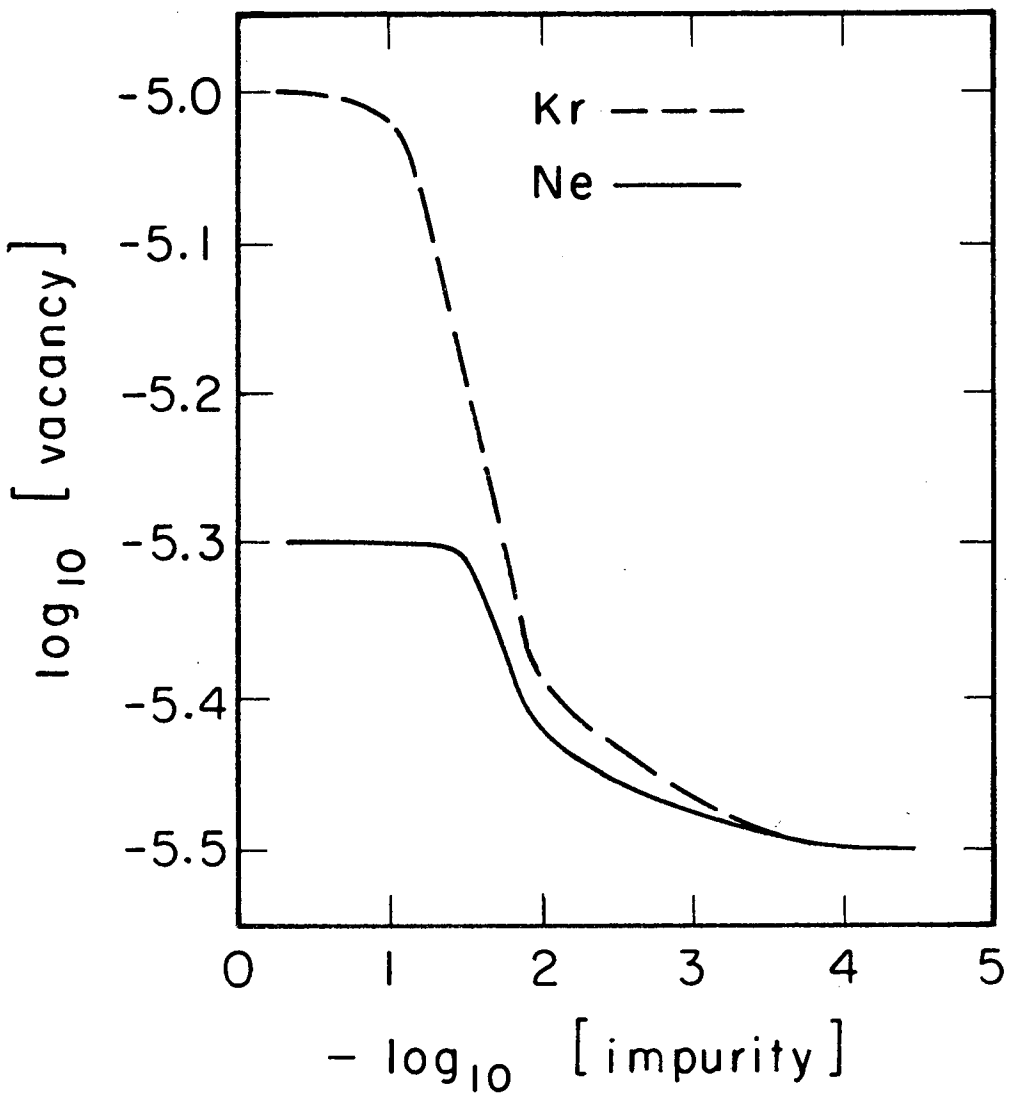


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Fig. 4