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Self-Diffusion Coefficient in Solid Argon*

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Self-diffusion in argon crystals is discussed on the basis of the mobility of vacancies, and in the scheme of the "absolute rate theory." Detailed calculations are made for the heat of activation Q and for the pre-exponential factor D_0 including quantum corrections. The change of potential energy is evaluated first by minimizing the lattice energy with respect to the displacement of the four atoms around the diffusing particle, next by calculating first-order elastic relaxation of the entire lattice. The change of vibrational properties is evaluated in the Einstein approximation. Including the contributions for the hole formation, the values $D_0=4.20\times10^{-4}$ cm² sec⁻¹, $Q=13.85\times10^{-2}$ ev, are found at $T=80°$K; the zero-point energy contributes 5% to the heat of activation.

1. INTRODUCTION

The problem of determining theoretically the self-diffusion coefficients of crystals is usually viewed in the well-known simplified scheme of the absolute rate theory.

It has been recently suggested by Rice[1] that this approach is not satisfactory in principle, mainly because neglecting the dynamical correlation between atoms "masks much of the physical situation." Rice himself developed a dynamical theory which avoids the above difficulties. At this stage, however, Rice's approach is not suitable for accurate calculations of diffusion coefficients; practical applications can be made only under rather restrictive assumptions[2] whose implications can hardly be guessed.

From another point of view, Vineyard[3] showed that the results of the "absolute rate theory" are quite consistent with the rigorous formulation of transport phenomena in solids, when applied to the total phase space of the system, and provided the configurational integral of the system at the saddle point between the initial and final configurations is evaluated in terms of an harmonic potential.

However, it seems to the writers that the reliability of the harmonic approximation at the saddle point configuration is subject in turn to the existence of a transition state, so that Vineyard's work does not seem to justify completely the scheme of the absolute rate theory. We shall return to this subject in a subsequent paper.[4]

It would be interesting to obtain *a posteriori* quantitative indications on the limits of the absolute rate theory, by comparing the results of reliable calculations to accurate experimental data. While there exist a large number of experimental data on self-diffusion in solids, very few complete calculations have been carried out so far; they concern the self-diffusion coefficient of copper, and the activation energy of alkali metals and of some ionic crystals. Moreover, all the theoretical results are necessarily affected by crude approximations and, although very important indications on the atomic mechanism of diffusion have been obtained, no quantitative comparison with experimental data can be attempted. The numerical values of the activation energy of copper calculated by different authors differ by as much as 100%. In metallic solids, as well as in ionic crystals and valence crystals, it is practically impossible, so far, to carry out accurate calculations. In the case of metals, and probably also of valence crystals, this is mainly due to the difficulty of treating the contribution of valence electrons to the activation energy; in ionic crystals the difficulty arises from the polarization effects.

The situation is more promising in the simplest group of Van der Waals crystals, i.e., "inert gas" crystals. As is known, this type of solid is the most suitable for fundamental studies on crystal lattices because of its simplicity: essentially "two-body" forces of central type, short-range interatomic potential, and no additional polarization effects. Moreover, the validity of the adiabatic theorem for large displacements makes it possible to include the electronic contribution in a well-defined potential function. If we apply the absolute rate theory to the evaluation of the self-diffusion coefficients of the heavier inert gas crystals, such as Ar, Kr, and Xe, where quantum effects are relatively small, the limits of the theoretical scheme should not be masked by the approximation introduced in order

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[1] S. A. Rice, Phys. Rev. **112**, 804 (1958); S. A. Rice and N. A. Nachtrieb, J. Chem. Phys. **31**, 139 (1959).

[2] A. W. Lawson, S. A. Rice, R. D. Corneliussen, and N. H. Nachtrieb, J. Chem. Phys. **32**, 447 (1960); O. P. Manley and S. A. Rice, Phys. Rev. **117**, 632 (1960).

[3] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

[4] G. Nardelli, Nuovo cimento (to be published); preliminary communication at the XLVI Conference of the Italian Physical Society.

actually to solve the problem, as is the case with the other substances.

We choose argon crystals, because the interatomic potential is known with a greater accuracy than for krypton and xenon, and because self-diffusion measurements are in progress at the University of Genova (G. Boato and co-workers). In a previous paper[5] two of us have calculated the vacancy concentration in inert-gas crystals; in this paper we evaluate the self-diffusion coefficient of argon, under the hypothesis that atoms diffuse through a vacancy mechanism. Preliminary results have already been published.[6] Vacancy interchange seems to be the dominant mechanism; a preliminary estimate of the formation energy of interstitials yields values considerably higher (about four times) than for the creation of vacancies. This agrees with the results found in copper (for a review of the theoretical results, see Lazarus.[7] Similarly, the activation energy for direct-exchange diffusion is thought to be much too high; no attempt has been made to consider mechanisms based on the motion of crowdions and of the split interstitial.

Calculations have been performed at 80°K, because experiments will be carried out in a temperature range around this point.

2. PRELIMINARY CONSIDERATIONS

Let us assume for the self-diffusion coefficient for vacancy diffusion the usual expression[8]:

$$D=\bar{\nu}a^2\exp(-\beta\Delta F),\quad \Delta F\equiv\Delta F_h+\Delta F_j, \tag{1}$$

where $\beta\equiv(kT)^{-1}$, a is the lattice constant, $\bar{\nu}$ is a vibrational frequency, and ΔF is the Helmholtz free energy per atom for the activation of the "transition state," including the free energy ΔF_h of formation of a hole. As is known, the above expression implies that there exists a "transition state" which is sufficiently well defined and whose lifetime is sufficiently long that it makes sense to define the thermodynamic properties of the activated atom.

The aim of the present paper is the numerical calculation of the two quantities, $\bar{\nu}$ and ΔF, which appear in (1), in the spirit of the absolute rate theory. Some corrections will be introduced in order to take into account quantum effects, which play a rather important role in argon crystals.

For these purposes we extend the Vineyard formulation[3] to a quantum system. Assuming that the system coordinate involved in the diffusive motion could be treated from a semiclassical point of view,[9] we can write

$$\bar{\nu}=(\beta h)^{-1}[Z_h{}^0(\beta)/Z_h(\beta)]_{\mathrm{ph}}, \tag{2}$$

and

$$\Delta F=\Delta F_h+\Delta F_j=\Delta\Phi+[F_h(\beta)-F(\beta)]_{\mathrm{ph}} \\ +[F_s(\beta)-F_h{}^0(\beta)]_{\mathrm{ph}}. \tag{3}$$

Here $(Z_h)_{\mathrm{ph}}$ and $(Z_h{}^0)_{\mathrm{ph}}$ denote the phonon partition functions for the hole configuration, and for the same configuration when the coordinate of the diffusing particle in the hole direction is constrained at the proper lattice site. $\Delta\Phi$ is the change of lattice energy for the formation of the activated complex, including the formation energy of the hole, and $(F)_{\mathrm{ph}}$, $(F_s)_{\mathrm{ph}'}$, $(F_h)_{\mathrm{ph}}$, $(F_h{}^0)_{\mathrm{ph}}$ are the phonon free energies, respectively, for the perfect lattice, the saddle point, the hole, and the constrained hole configuration.

It is easily verified that the above expressions for $\bar{\nu}$ and ΔF correspond to Vineyard's results, in the classical limit for $\beta\rightarrow 0$. The Helmholtz free energy per atom for the activation of self-diffusion can also be split into three terms:

$$\Delta F=\Delta\Phi+\Delta E_{\mathrm{zpe}}+\Delta F_{\mathrm{th}}; \tag{4}$$

ΔE_{zpe}, and ΔF_{th} are, respectively, the changes of zero-point energy and thermal free energy, including the contribution from the hole formation.

3. METHOD OF CALCULATION

(a) Lattice Energy

The saddle-point configuration is characterized by a large displacement field in the region near the diffusing particle. This situation does not allow the *direct* use of the harmonic theory in order to obtain the displacements, as has been done in the case of a vacancy.[5,10]

We try to solve the elastic problem for the discrete displacement field assuming that only a small part of the crystal, which we call region (I), suffers large displacements, whereas every other atom [region (II)] suffers a displacement small enough to be treated by the elastic theory of discrete media.

In general, starting from an initial deformed configuration, hereafter referred to as the (*) configuration, the potential energy of the crystal can be expanded in a Taylor series:

$$\Phi_s=N\epsilon_L+\Delta\Phi^*+[f]^\dagger\cdot[\xi]+\tfrac{1}{2}[\xi]^\dagger\cdot[A]\cdot[\xi] \\ +\{\text{anharmonic terms}\}. \tag{5}$$

In this expression N is the total number of particles of the perfect lattice, ϵ_L the rigid lattice energy per atom, and $\Delta\Phi^*$ the lattice energy change for the formation of the initial configuration; $[\xi]$ is the column matrix

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[5] G. Nardelli and A. Repanai-Chiarotti, Nuovo cimento **18**, 1053 (1960).

[6] R. Fieschi, G. Nardelli, and A. Repanai, Suppl. Nuovo cimento No. 3, 463 (1959).

[7] D. Lazarus, in *Solid-State Physics* edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960), Vol. 10.

[8] C. Zener, *Imperfections in Nearly Perfect Crystals* (John Wiley & Sons, Inc., New York, 1952).

[9] This condition, very crude in principle, should not affect drastically the numerical results because of the high quantum numbers involved in the diffusive motion, and the high atomic mass of the particle.

[10] H. Kanzaki, J. Phys. Chem. Solids **2**, 24 (1957).

whose elements are the vector displacements of all the atoms in the crystal from the (*) configuration; the elements of the column matrix $[f]$ are the first-order derivatives of the potential energy, and those of the square matrix $[A]$ are the second-order derivatives, both evaluated in the (*) configuration; by $[\cdots]^{\dagger}$ we mean the adjoint to $[\cdots]$.

If the initial deformed configuration is sufficiently close to the true equilibrium configuration, in the expansion (5) the anharmonic terms can be neglected. As the (*) configuration we assume that for which only the four nearest neighbors $B_1, \cdots, B_4$ of the particle at the saddle point are displaced from the regular lattice site B_i to the new position $B_i^* = B_i + \mathbf{v}_i$, every other atom being undisplaced (Fig. 1); $\mathbf{v}_i$ is chosen in such a way that the potential energy is a minimum when region (II) is unrelaxed. Therefore region (I) includes the atom at the saddle point 0 (the origin of the coordinate axes), its four nearest neighbors $(B_1 \cdots B_4)$, and the two holes (h_1, h_2).

The coefficients $[f]$ of the linear term in the above expansion may be regarded as external forces exerted on the system[10,11]; owing to the present choice of the displacements $\mathbf{v}_i$, the forces on the atoms of region (I) vanish.

The condition of elastic equilibrium for the saddle-point configuration is then

$$[A]\cdot[\xi] = -[f]. \tag{6}$$

The reliability of the harmonic approximation is proved *a posteriori*. The solution is formally given by

$$[\xi] = -[A]^{-1}\cdot[f]. \tag{7}$$

The first term in the right-hand member of (4), that is the static contribution to the Helmholtz free energy for activation of the transition state, is finally

$$\Delta\Phi = \Delta\Phi^* - \tfrac{1}{2}[f]^{\dagger}\cdot[A]^{-1}\cdot[f]. \tag{8}$$

We call the second term in the right-hand member the relaxation energy, $\Delta\Phi_{\text{relax}}$.

The main difficulties in the evaluation of the relaxation energy are given by the inversion of the matrix $[A]$. We can try to achieve this through a perturbative expansion, splitting $[A]$ into the sum of two terms,

$$[A] = [A_0] + [A_1], \tag{9}$$

so that

$$[A]^{-1} = \sum_{n=0}^{\infty} (-1)^n ([A_0]^{-1}\cdot[A_1])^n \cdot [A_0]^{-1}. \tag{10}$$

This expansion converges to the true inverse matrix, provided each eigenvalue of $[A_0]^{-1}\cdot[A_1]$ is smaller than unity in absolute value. For the evaluation of each term of (10) we need the knowledge of the inverse unperturbed matrix $[A_0]^{-1}$.

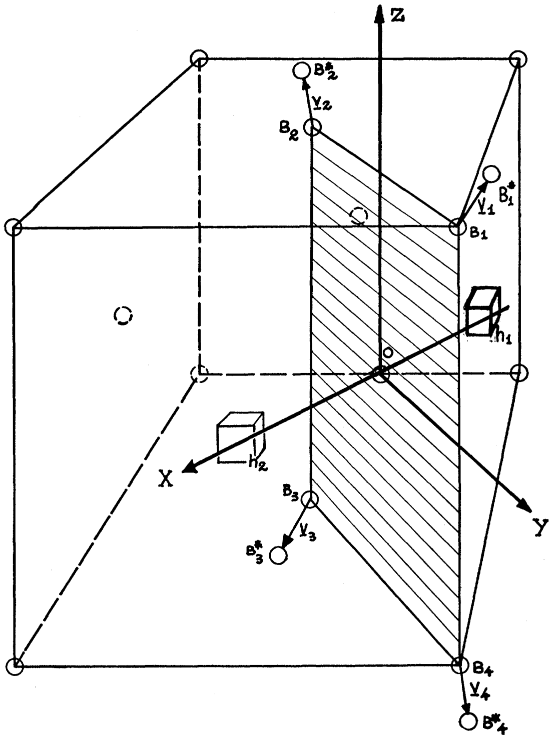

FIG 1. Initial deformed configuration around the atom at the saddle point.

The above choice of the initial deformed configuration suggests the following decomposition:

$$[A_0] \equiv \begin{pmatrix} [A^{\mathrm{I}}] & 0 \\ 0 & [A^{\mathrm{II}}] \end{pmatrix}, \qquad [A_1] \equiv \begin{pmatrix} 0 & [A^{\mathrm{I\cdot II}}] \\ [A^{\mathrm{I\cdot II}}]^{\dagger} & 0 \end{pmatrix}, \tag{11}$$

where the square submatrix $[A^{\mathrm{I}}]$ contains the elements of $[A]$ which refer only to the atoms B^* of region (I) (the diffusing particle is considered as a fixed potential source), $[A^{\mathrm{II}}]$ contains the elements connected with the atoms of region (II), while $[A^{\mathrm{I\cdot II}}]$ is the rectangular submatrix representing the coupling between the sets $\{B^*\}$ and (II) of atoms.

From the above considerations it follows that the relaxation energy can be expanded in powers of the perturbation $[A_1]$:

$$\Delta\Phi_{\text{relax}} = -\tfrac{1}{2}\sum_{n=0}^{\infty} \Delta\Phi_{\text{relax}}^{(n)}, \tag{12}$$

where

$$\Delta\Phi_{\text{relax}}^{(n)} = (-1)^n [f]^{\dagger}\cdot([A_0]^{-1}\cdot[A_1])^n \cdot[A_0]^{-1}\cdot[f]. \tag{13}$$

The first contribution $(n=0)$ represents the elastic work done by the "forces" exerted by region (I) on the atoms of region (II). The first power of the pertur-

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[11] J. D. Eshelby, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3.

bation ($n=1$) gives no contribution, so that the submatrix $[A^{\mathrm{I}}]^{-1}$ plays its role in the third ($n=2$) and following terms only.

(b) Zero-Point Energy and Thermal Free Energy

In order to evaluate the vibrational contribution to the Helmholtz free energy for the activation of self-diffusion we should employ the "trace formula" given by Lifshitz, Montroll, and others.[12,13] Unfortunately, the perturbation operator corresponding to a hole or to the saddle point configuration is not sufficiently simple to employ the trace formula for numerical applications. Alternatively, we could use the perturbative techniques suggested by Stripp and Kirkwood[14] some years ago, but at the present time we do not know any proof for the convergence of this perturbative expansion.[15] Huntington and co-workers[16] tried to justify the Einstein model for the self-entropy of a vacancy in fcc metals; however, in the light of more rigorous theory, their proof does not seem to be generally valid.

Nevertheless, the Einstein scheme should give the correct order of magnitude of the perturbation on the vibrational properties; hence we follow this scheme in view of its simplicity.

The Einstein frequencies of the atoms in region (II) are slightly affected by the distortion of region (I), so that the change of phonon free energy in region (II) may be evaluated by a perturbative expansion. Then, if we define

$$\varphi(z)\equiv\hbar(z)^{\frac{1}{2}}/2+\beta^{-1}\ln[1-\exp(-\beta\hbar z^{\frac{1}{2}})], \qquad (14)$$

we can write, remembering (3),

$$\begin{aligned}\Delta E_{\mathrm{zpe}}+\Delta F_{\mathrm{th}}=4\sum_{\alpha=1}^{3}\{\varphi(\omega_\alpha{}^2(B^*))-\varphi(\omega_E{}^2)\}\\ +\sum_{\alpha=2,3}\{\varphi(\omega_\alpha{}^2(0))-\varphi(\omega_E{}^2)\}+\varphi(\omega_1{}^2(h))\\ -\varphi(\omega_E{}^2)+\sum_{n=1}^{\infty}\frac{-1}{n!}\varphi^{(n)}\frac{\mathrm{Sp}[\delta A^{\mathrm{II}}]^n}{M^n}, \qquad (15)\end{aligned}$$

where M is the atomic mass; $\omega_E=2\pi\nu_E$ is the Einstein frequency for the perfect lattice; $\omega_\alpha(B^*)$ are the Einstein frequencies ($\alpha=1, 2, 3$) of the atom B^*, and $\omega_\alpha(0)$ are the transverse Einstein frequencies ($\alpha=2, 3$) of the diffusing atom, both in the saddle-point configuration; $\omega_1(h)$ is the Einstein frequency, in the hole direction, of a nearest neighbor of the hole before diffusion. By $\varphi^{(n)}(\omega_E{}^2)$ we mean the nth-order derivative of $\varphi(z)$ evaluated at $z=\omega_E{}^2$. We note that the first term in the right-hand member of (14) represents the zero-point energy while the second term represents the thermal free energy.

4. NUMERICAL RESULTS

The Helmholtz free energy per atom for the activation of the "transition state" is evaluated at the temperature of 80°K. We use the following Lennard-Jones interatomic potential,

$$\phi(r)=\mathcal{A}r^{-12}-\mathcal{B}r^{-6}, \qquad (16)$$

where $\mathcal{A}=1.63\times10^{-7}$ erg$\times$A^{12} and $\mathcal{B}=1.05\times10^{-10}$ erg $\times$A^{6}.[17] For the sake of consistency, we choose for the lattice constant the equilibrium value calculated by means of the above potential; at $T=80$°K, Zucker[18] gives the value $a=5.45$ A.

(a) Change of Lattice Energy

(a-1) Energy Change for the Formation of the (*) Configuration

Remembering its definition [Sec. 3 (a)], $\Delta\Phi^*$ is given by

$$\begin{aligned}\Delta\Phi^*=3\epsilon_L+\phi(|\mathbf{r}_{h1}-\mathbf{r}_{h2}|)+\textstyle\sum_j{}^{(B^*)}\phi(|\mathbf{r}_j|)\\ +\textstyle\sum_l{}^{(\mathrm{II})}\phi(|\mathbf{r}_l{}^0|)-\sum_j{}^{(B)}\sum_l{}^{(\mathrm{II})}\phi(|\mathbf{r}_j-\mathbf{r}_l{}^0|)\\ +\textstyle\sum_j{}^{(B^*)}\sum_l{}^{(\mathrm{II})}\phi(|\mathbf{r}_j-\mathbf{r}_l{}^0|)-\frac{1}{2}\sum_j{}^{(B)}\sum_{j'}{}^{(B)}\\ +\phi(|\mathbf{r}_j-\mathbf{r}_{j'}|)\tfrac{1}{2}\textstyle\sum_j{}^{(B^*)}\sum_{j'}{}^{(B^*)}\phi(|\mathbf{r}_j-\mathbf{r}_{j'}|), \qquad (17)\end{aligned}$$

where $\mathbf{r}_l{}^0$ is the position vector of the lth lattice site of region (II), and by $\sum_j{}^{(\cdots)}\sum_l{}^{(\mathrm{II})}\phi(\cdots)$ we mean the double summation of the interatomic potential for the indicated sets of atoms when region (II) is in the unrelaxed configuration. The summations are performed including contributions up to third neighbors. Owing to the short-range character of the interatomic potential, this limitation seems to be a reliable approximation for argon crystals. The rigid lattice energy per atom in the perfect crystal $\epsilon_L>0$ is evaluated by the lattice sums of Jones and Ingham.

(a-2) Relaxation Energy

The relaxation energy is given by the perturbative expansion (12). The "forces" $[f]$ are defined as

$$[f]\equiv\{(\partial\Phi/\partial\mathbf{r}_l)_*\}; \qquad (18)$$

$\mathbf{r}_l$ indicates the position vector of the lth atom, and the derivative is evaluated at the (*) configuration. With the adopted convention, we may write

$$[f]=\begin{pmatrix}[f^{\mathrm{I}}]\\ [f^{\mathrm{II}}]\end{pmatrix}, \qquad (19)$$

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[12] M. Lifshitz, Suppl. Nuovo cimento **3**, 716 (1956).

[13] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955); **102**, 72 (1956); A. A. Maradudin, P. Mazur, E. W. Montroll, and G. H. Weiss, Revs. Modern Phys. **30**, 175 (1958); J. Mahanty, A. A. Maradudin, and G. H. Weiss, Progr. Theoret. Phys. (Kyoto) **20**, 369 (1958).

[14] K. F. Stripp and J. G. Kirkwood, J. Chem. Phys. **22**, 1579 (1954).

[15] G. Nardelli and N. Tettamanzi, Nuovo cimento (to be published); preliminary communication at the XLVI Conference of the Italian Physical Society.

[16] H. B. Huntington, G. A. Schirn, and E. S. Wajda, Phys. Rev. **99**, 1085 (1955).

[17] C. Domb and J. Zucker, Nature **178**, 484 (1956).

[18] J. Zucker, J. Chem. Phys. **25**, 915 (1954).

where

$$\mathbf{f}_j^{\mathrm{I}}=0,\quad (j=1\cdots 4)$$

$$\mathbf{f}_l^{\mathrm{II}}=\left\{\frac{\partial}{\partial\mathbf{r}}\left[\phi(|\mathbf{r}|)+\sum_j^{(B)}\phi(|\mathbf{r}-\mathbf{r}_j|)-\sum_j^{(B)}\phi(|\mathbf{r}-\mathbf{r}_j|)-\sum_h^{(h_1,h_2)}\phi(|\mathbf{r}-\mathbf{r}_h|)\right]\right\}_{\mathbf{r}=\mathbf{r}_l^0}. \quad (20)$$

The matrix $[A]$ is defined in a similar way as

$$[A]\equiv\{(\partial^2\Phi/\partial\mathbf{r}_l\partial\mathbf{r}_{l'})_*\}. \quad (21)$$

The elements of the submatrix $[A^{\mathrm{I}}]$ are

$$\mathbf{A}_{jj'}^{\mathrm{I}}=\left\{\frac{\partial}{\partial\mathbf{r}_j}\frac{\partial}{\partial\mathbf{r}_{j'}}\left[\frac{1}{2}\sum_j^{(B)}\sum_{j'}^{(B)}{}'\phi(|\mathbf{r}_j-\mathbf{r}_{j'}|)+\sum_j^{(B)}\phi(|\mathbf{r}_j|)+\sum_j^{(B)}\sum_l^{(\mathrm{II})}\phi(|\mathbf{r}_j-\mathbf{r}_l^0|)\right]\right\}_{\mathbf{r}_j=\mathbf{r}_j^*,\mathbf{r}_{j'}=\mathbf{r}_{j'}^*}; \quad (22)$$

$\mathbf{r}_j^*$ is the position vector of the atom B_j^*.

To evaluate the elements of the submatrix $[A^{\mathrm{II}}]$ it is convenient to split it into two parts, the first giving the coupling coefficients between the atoms in the perfect lattice, and the second including the perturbation to the former matrix arising from the imperfection of region (I):

$$[A^{\mathrm{II}}]=[A_p^{\mathrm{II}}]+[\delta A^{\mathrm{II}}], \quad (23)$$

where

$$[A_p^{\mathrm{II}}]\equiv\{(\partial^2\Phi/\partial\mathbf{r}_l\partial\mathbf{r}_{l'})_p\}. \quad (24)$$

p indicates that the derivatives of the total potential energy of the lattice are evaluated at the perfect crystal configuration; l and l' range only over the atoms of region (II);

$$\delta\mathbf{A}_{ll'}^{\mathrm{II}}\equiv\delta_{ll'}\left\{\frac{\partial}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{r}}\left[\phi(|\mathbf{r}|)+\sum_j^{(B^*)}\phi(|\mathbf{r}-\mathbf{r}_j|)-\sum_j^{(B)}\phi(|\mathbf{r}-\mathbf{r}_j|)-\sum_h^{(h_1,h_2)}\phi(|\mathbf{r}-\mathbf{r}_h|)\right]\right\}_{\mathbf{r}=\mathbf{r}_l^0}. \quad (25)$$

Finally, the elements of the perturbation matrix $[A_1]$ are

$$\mathbf{A}_{jl}^{\mathrm{I\cdot II}}\equiv\left\{\frac{\partial}{\partial\mathbf{r}_j}\frac{\partial}{\partial\mathbf{r}_l}\phi(|\mathbf{r}_j-\mathbf{r}_l|)\right\}_{\mathbf{r}_j=\mathbf{r}_j^*,\mathbf{r}_l=\mathbf{r}_l^0}. \quad (26)$$

In view of the short-range character of the interatomic potential, the forces and the perturbation matrices $[\delta A^{\mathrm{II}}]$ and $[A^{\mathrm{I\cdot II}}]$ are assumed to have nonvanishing elements only for the first and second neighbors to the holes and to the four atoms B. Provided the perturbative expansion (12) is convergent, the evaluation of the relaxation energy is substantially a problem of numerical inversion of the unperturbed matrix. Only those elements which are connected by the perturbation $[A^{\mathrm{I\cdot II}}]$ are necessary.

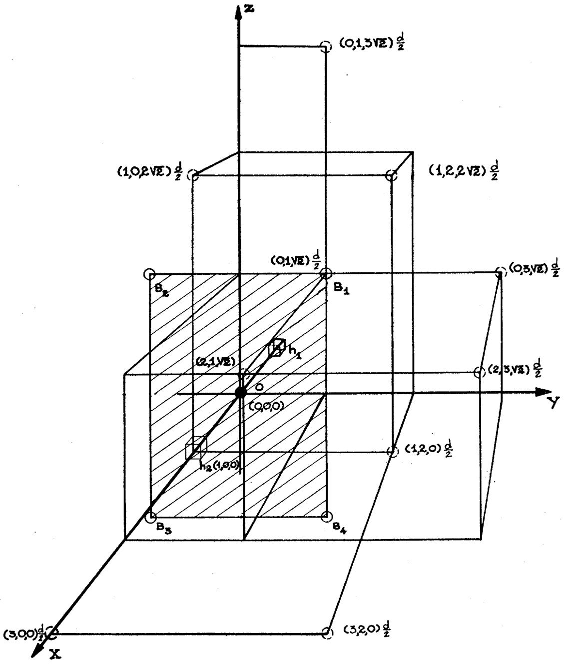

FIG. 2. Atoms of region (I) and of region (II) in the first quadrant. The broken circles indicate points of the set (II*). The components are in units of $d/2$.

We note also that, up to the first-order term, only inversion of the submatrix $[A_p^{\mathrm{II}}+\delta A^{\mathrm{II}}]$ is required. Unfortunately the inversion of $[A_0]$ or $[A_p^{\mathrm{II}}+\delta A^{\mathrm{II}}]$ is too difficult a numerical problem. A rough estimate of the zero-order relaxation energy can be easily obtained if we neglect the influence of the tensors outside the diagonal of the matrix $[A_p^{\mathrm{II}}+\delta A^{\mathrm{II}}]$, i.e., if we neglect the coupling between different atoms of the lattice. The contribution arising from the off-diagonal tensors could be of the same order as that from the diagonal ones; in any case, the Einstein approximation should give the correct order of magnitude of the relaxation energy.

Let $[A_p^{\mathrm{II}}+\delta A^{\mathrm{II}}]_E$ be the Einstein part of the matrix; we obtain

$$\Delta\Phi_{\mathrm{relax}}^{(0)}\simeq-\tfrac{1}{2}[f^{\mathrm{II}}]^\dagger\cdot[A_p^{\mathrm{II}}+\delta A^{\mathrm{II}}]_E^{-1}\cdot[f^{\mathrm{II}}]. \quad (26)$$

Further contributions to the relaxation energy should be calculated from the terms $\Delta\Phi_{\mathrm{relax}}^{(n)}$ in (13); even the calculation of $\Delta\Phi_{\mathrm{relax}}^{(2)}$, however, requires a considerable amount of work. We found it more convenient to evaluate the second-order relaxation energy and the displacements of B^* atoms by direct lattice calculations, by minimizing the potential energy of the B atoms when region (II) is relaxed up to first order. The atoms of the reduced set (II)*, on which there are nonvanishing forces, are shown in Fig. 2. The results for the displacements are shown in Table I; the contributions to the activation lattice energies are reported in Table II.

Table I. Displacements at the elastic equilibrium (in units of $10^{-2}d$); the coordinate axes are oriented as in Figs. 1 and 2.

Atoms		ξ_x	ξ_y	ξ_z
$B\equiv(0;\frac{1}{2};\frac{1}{2}\sqrt{2})d$	first approx.[a]	0	2.91	4.70
	second approx.[a]	0	2.30	5.75
$(\frac{1}{2};1;0)d$		−0.738	−1.269	0
$(1;\frac{1}{2};\frac{1}{2}\sqrt{2})d$		−0.236	−0.044	−0.071
$(\frac{1}{2};0;\sqrt{2})d$		0.432	0	0.867
$(\frac{3}{2};0;0)d$		0.119	0	0
$(0;\frac{3}{2};\frac{1}{2}\sqrt{2})d$		0	0.872	0.017
$(\frac{3}{2};1;0)d$		0.229	0.239	0
$(\frac{1}{2};1;\sqrt{2})d$		0.743	0.757	1.069
$(1;\frac{3}{2};\frac{1}{2}\sqrt{2})d$		−0.009	0.046	0.045
$(0;\frac{1}{2};\frac{3}{2}\sqrt{2})d$		0	0.005	−0.078

[a] From lattice calculations.

(b) Change of Phonon Free Energy

The phonon free energy for the activation of self-diffusion has been evaluated by the approximate expression (14). Owing to the limitations implicit in the Einstein approximation we consider only the first-order term of the infinite expansion in the right-hand member of (14). The new frequencies are evaluated for the (*) configuration, since the relaxation of region (II) is small.

The numerical results for $\Delta E_{\rm zpe}$ and $\Delta F_{\rm th}$ at a temperature of 80°K are reported in Table III.

The last term in the right-hand member of (15) gives the change of phonon free energy of region (II), while the others represent the change of phonon free energy of region (I) (always neglecting the degree of freedom associated with the direction of diffusion).

In order to compare the present results with those of Huntington,[16] we split the change of entropy into the contributions of region (I) and region (II); in the classical approximation we have

$$\Delta S^{\rm I}/k=-4\sum_{\alpha=1}^{3}\ln[\omega_\alpha(B^*)/\omega_E]-\sum_{\alpha=2,3}\ln[\omega_\alpha(0)/\omega_E]-\ln[\omega_1(h)/\omega_E], \tag{27}$$

$$\Delta S^{\rm II}/k\simeq-(2\omega_E^2)^{-1}{\rm Sp}[\delta A^{\rm II}]/M. \tag{28}$$

Table II. Change of lattice energy.

$\Delta\Phi^*$	13.85×10^{-2} ev
$\Delta\Phi_{\rm relax}$[a]	-0.50×10^{-2} ev
$\Delta\Phi$(total)	13.12×10^{-2} ev[a]
$(\Delta\Phi)_h$	8.70×10^{-2} ev[b]
$(\Delta\Phi_{\rm relax})_h$	-0.03×10^{-2} ev[b]

[a] From lattice calculations.
[b] See reference 5.

Region (I) gives a decrease of entropy of $+2.68k$; this comes from the increase of the frequencies due to the crowding of the five atoms. The analogous contribution found by Huntington in Cu is smaller ($\Delta S^{\rm I}/k=-1.10$). The difference could be explained in part by the slightly smaller outward relaxation of B atoms in argon [$v({\rm Ar})=0.055d$, $v({\rm Cu})=0.06d$) and in part by the different rate of change of the elastic constants with the change of lattice parameters.

The contribution of region (II) differs considerably from the estimate given by Huntington: $\Delta S^{\rm II}({\rm A})/k=-0.064$, $\Delta S^{\rm II}({\rm Cu})/k=1.97$. The discrepancy is due to the fact that Huntington assumes that every atom of region (II) contributes as much as the neighbors of a vacancy, while direct calculations show that some frequencies increase, others decrease, and their effects partly compensate.

(c) The Vibrational Frequency $\bar{\omega}$

The vibrational frequency $\bar{\omega}$ is easily evaluated if again we employ the Einstein approximation:

$$\bar{\omega}\simeq(\beta\hbar)^{-1}2\sinh[\tfrac{1}{2}\beta\hbar\omega_x(h)], \tag{29}$$

where, as before, $\omega_x(h)$ is the Einstein frequency, in the hole direction, of a nearest neighbor of the hole. The numerical value is reported in Table IV; we note that for $T=80$°K there is no substantial difference between $\bar{\omega}$ and $\omega_x(h)$.

Table III. Zero point energy and thermal free energy for activation of self-diffusion at 80°K.

$\Delta E_{\rm zpe}$	0.72×10^{-2} ev
$(\Delta E_{\rm zpe})_h$	-0.51×10^{-2} ev[a]
$\Delta F_{\rm th}$	1.27×10^{-2} ev
$(\Delta F_{\rm th})_h$	-1.30×10^{-2} ev[a]
$(\Delta S/k)_{\beta\to0}$	-2.74

[a] See reference 5.

Finally the contribution to the self-diffusion coefficients are summarized in Table V, where Q, D_0, and D are given by the usual expressions $D=D_0\exp(-\beta Q)$, $D_0\equiv\bar{\nu}a^2\exp(-\Delta F_{\rm th}/k)$, and $Q\equiv\Delta\Phi+\Delta E_{\rm zpe}$.

5. DISCUSSION

Besides the simplification implicit in the adopted scheme, the reliability of the numerical results is subject also to the validity of the following assumptions: (a) Self-diffusion occurs mainly by a vacancy mechanism; (b) the adiabatic theorem holds even for displacements large enough to describe the atomic jumps in the diffusion process, and the "effective potential" is just $\sum_{ll'}{}'\phi(|\mathbf{r}_l-\mathbf{r}_{l'}|)$, where $\phi(r)$ is a well-defined two-body potential; (c) the harmonic approximation holds, in the Einstein scheme, in evaluating the relaxation energy and the vibrational properties of the

Table IV. Vibrational frequency for self-diffusion at 80°K.

$\bar{\omega}$	0.559×10^{13} sec^{-1}
$(\bar{\omega})_{\beta\to0}=\omega_x(h)$	0.554×10^{13} sec^{-1}

TABLE V. Self-diffusion coefficient ($T=80$°K, $a=5.45$ A).

D_0	4.20×10^{-4} cm^2 sec^{-1}
$(D_0)_{\beta\to0}$	1.69×10^{-4} cm^2 sec^{-1}
Q	13.85×10^{-2} ev
Q_h	8.16×10^{-2} ev[a]
$Q_j=Q-Q_h$	5.69×10^{-2} ev
$(Q)_{\beta\to0}$	13.12×10^{-2} ev$=3026$ cal/mole
D	7.95×10^{-13} cm^2 sec^{-1}

[a] See reference 5.

activated complex; (d) the perturbative expansions are quickly convergent.

Point (a) has been already considered; however, it would be worthwhile to consider also crowdion diffusion and the diffusion of a split interstitial.

The adiabatic theorem should hold because of the "closed-shell" structure of atoms in argon crystals. The effective potential could include a many-body component[19] but this term should not appreciably affect the numerical results. Moreover, the present (12–6) Lennard-Jones potential seems to be valid for argon crystals up to a pressure of many thousand atmospheres,[20] where the interatomic distance is of the same order as that between the squeezed atoms in the saddle complex.

The validity of the harmonic approximation for evaluating the relaxation energy is proved *a posteriori* by the weakness of the displacement field; the anharmonicity could still affect to some extent the phonon free energy. Even in the last case, however, its importance is probably negligible.

A critical point is the convergence of the perturbation expansion. In the general case the convergence has not been proven[21]; nevertheless the convergence is easily verified in the Einstein approximation. For the elastic problem, the physical meaning of the Einstein approximation is that of neglecting the transmission of the strain around the point of application of a given force. Therefore this approximation should not be suitable for evaluating the strain itself, but it should give a reasonable estimate of the relaxation energy. More than 90% of the heat of activation, however, is accounted by the energy of region (I) only. The reliability of the Einstein approximation for the vibrational properties of a lattice defect cannot be proven in the general case; however, if there is no impurity frequency associated to the defect itself, it seems that the Einstein approximation can give fairly good numerical results, in the high-temperature limit.[16] We note that in the present scheme there is no relaxation far away from the activated complex, so that any perturbation to the dynamical matrix coming from the relaxation field via the anharmonic terms[5] is completely neglected. In another paper[5] it has been proven that surface effects are not to be taken into account in the evaluation of vibrational changes due to the formation of a lattice defect.

As to the numerical results, it is worth noting (Table III) that the change of zero-point energy gives an appreciable contribution. Hence a poor estimate of the vibrational properties of the activated complex could affect to some extent the activation energy for self-diffusion. The same consideration holds particularly for the pre-exponential factor D_0.

The value we obtain for the heat of activation Q can be compared with the results of the empirical rule of Nachtrieb and co-workers,[22] connecting Q to the latent heat of melting L_m in cubic metals:

$$\begin{aligned} &Q_{80°\mathrm{K}}(\text{atomic theory})=3.210\ \text{cal/mole},\\ &\quad Q_{80°\mathrm{K}}(\text{Nachtrieb})=16.5L_m=4.633\ \text{cal/mole}. \end{aligned} \tag{30}$$

The self-diffusion coefficient has been calculated at $T=80$°K. It is not completely safe to suppose that the temperature dependence of the three contributions $\Delta\Phi$, ΔE_{zpe}, and ΔF_{th} are such that they combine to give a linear temperature dependence of ΔF. It has been shown[5] that for the hole formation the temperature dependence deviates from the linear law, especially at low temperature; hence calculation of D should be repeated at different temperatures. However, in a temperature range of 10° around 75°K, the deviation of ΔF_h from a linear dependence on T is about 2%. This fact suggest that formula (1) can be used with confidence in a small temperature range, such as can be examined experimentally, assuming for Q and D_0 the values at 80°K.

Comparing the present results for the pre-exponential factor D_0 and the heat of activation Q for self-diffusion to the corresponding values in other crystals, we can conclude that transport processes occur in argon at lower rates than in close-packed metals. The pre-exponential factor D_0 is surprisingly small as compared with the experimental results for close-packed metals; this fact cannot be explained on the basis of the present model.

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[19] L. Jansen, thesis, Leiden, 1955 (unpublished).

[20] J. W. Stewardt, J. Phys. Chem. Solids **1**, 146 (1956).

[21] We note that Kanzaki[10] deduced the perturbative expansion for the elastic displacement around a vacancy by an iteration method; he does not prove the convergence of the expansion either.

[22] N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, J. Chem. Phys. **20**, 1189 (1957).