The potential-energy functions $\varphi_v(q_j,\epsilon_{\alpha\beta})$ and $\varphi_0(q,\epsilon_{\alpha\beta})$ can be expanded as Taylor series in the strain just as in the development beginning with Eq. (4) and leading to Eq. (16). The result is

$$\frac{n_v(\epsilon_{\alpha\beta})}{n_v}=\exp\left(\frac{1}{kT}\sum_{\alpha,\beta}w_{\alpha\beta}\epsilon_{\alpha\beta}\right), \tag{40}$$

where

$$w_{\alpha\beta}=\left\langle\left(\frac{\partial\varphi_0}{\partial\epsilon_{\alpha\beta}}\right)_{q_j,0}\right\rangle-\left\langle\left(\frac{\partial\varphi_v}{\partial\epsilon_{\alpha\beta}}\right)_{q_j,0}\right\rangle. \tag{41}$$

For the special case of uniform compression or expansion, Eqs. (40) and (41) become

$$\frac{n_v(\epsilon)}{n_v^0}=e^{(3w/kT)\epsilon}, \tag{42}$$

$$w=\left\langle\left(\frac{\partial\varphi_0}{\partial\epsilon}\right)_{q_j,0}\right\rangle-\left\langle\left(\frac{\partial\varphi_v}{\partial\epsilon}\right)_{q_j,0}\right\rangle, \tag{43}$$

where ϵ is the volume strain.

IV. PROOF THAT THE STATISTICAL AVERAGES $\langle(\partial\varphi/\partial\epsilon)_{qj,0}\rangle$ DO NOT VANISH

The preceding theory depends on the statistical averages of the derivatives of the potential energy of the crystal with respect to strain. It has been assumed that these averages are not zero, and that a first-order expansion in the strains is therefore adequate for small strains. This assumption can be justified by expanding the crystal energy in normal coordinates. The statistical averages of interest all have the form

$$\left\langle\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0\right\rangle=\int\cdots\int\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0 e^{-\varphi/kT}\prod_j dq_j \Big/ \int\cdots\int e^{-\varphi/kT}\prod_j dq_j, \tag{44}$$

where φ is the total potential energy of the crystal as a function of all the coordinates q_j, and the subscript zero means that the derivative is evaluated at zero strain. If the q_j are taken to be the normal coordinates, φ can be written to the second order as

$$\varphi=\varphi(0)+\tfrac{1}{2}\textstyle\sum_j\omega_j^2q_j^2, \tag{45}$$

where $\varphi(0)$ is the potential energy when all the atoms are at their mean positions, and the ω_j are the normal mode frequencies. Differentiating Eq. (45) with respect to strain gives

$$\frac{\partial\varphi}{\partial\epsilon}=\frac{\partial\varphi(0)}{\partial\epsilon}+\sum_j\omega_j\frac{d\omega_j}{d\epsilon}q_j^2, \tag{46}$$

and, since at zero strain the first term on the right is zero,

$$\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0=\sum_j\omega_j\frac{d\omega_j}{d\epsilon}q_j^2. \tag{47}$$

For the purposes of this discussion, ϵ will be taken to be the strain corresponding to uniform compression or expansion, so that for small strains the volume is given by

$$V=V_0(1+3\epsilon), \tag{48}$$

V_0 being the volume at zero strain. Introducing the Grüneisen parameter γ_j by the relation

$$d\ln\omega_j/d\ln V=-\gamma_j, \tag{49}$$

where the γ_j are a set of positive constants, and using Eq. (48), Eq. (47) becomes

$$\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0=-3\sum_j\gamma_j\omega_j^2q_j^2. \tag{50}$$

Substituting Eqs. (45) and (50) into Eq. (44) gives

$$\left\langle\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0\right\rangle=-3\int\cdots\int\left(\sum_j\gamma_j\omega_j^2q_j^2\exp\left(-\frac{1}{2kT}\sum_j\omega_j^2q_j^2\right)\right)\prod dq_j \Big/ \int\cdots\int\exp\left(-\frac{1}{2kT}\sum_j\omega_j^2q_j^2\right)\prod dq_j. \tag{51}$$

Now perform a coordinate transformation according to the following definition:

$$u_j\equiv\omega_jq_j. \tag{52}$$

Then, after a few simple algebraic manipulations, Eq. (51) becomes

$$\left\langle\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0\right\rangle=-3\sum_j\gamma_j\int_{-\infty}^{\infty}u_j^2\exp\left(-\frac{u_j^2}{2kT}\right)du_j \Big/ \int_{-\infty}^{\infty}\exp(-u_j^2/2kT)du_j \tag{53}$$

and performing the integrations gives

$$\left\langle\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0\right\rangle=-3kT\sum_j\gamma_j. \tag{54}$$

Equation (54) shows that the averages of the first derivatives are never zero and that these averages are proportional to the temperature.

It is extremely difficult to make any *a priori* decisions concerning the signs of $m_{\alpha\beta}$ and $w_{\alpha\beta}$ defined by Eqs. (15) and (41). Such a decision requires a detailed investigation of the variation of localized normal mode vibrations with strain in the vicinity of a defect. However, on the basis of general physical considerations, it is to be expected that both $m_{\alpha\beta}$ and $w_{\alpha\beta}$ are positive.

V. EFFECT OF PRESSURE ON DIFFUSION CONSTANT

Using Eqs. (1), (21), and (42), and the fact that the lattice parameter in the strained system is $(1+\epsilon)$ times the lattice parameter in the unstrained system, the relation between the diffusion coefficients in the strained and unstrained systems for uniform compression or expansion is

$$D(\epsilon)=D_u(1+\epsilon)^2\exp\left(\frac{M}{kT}3\epsilon\right), \qquad (55)$$

where D_u is the diffusion coefficient in the unstrained system, and M is given by

$$M=m+w \quad \text{(vacancy mechanism)}, \qquad (56)$$

$$M=m \quad \text{(interstitial, ring or exchange mechanism)}. \qquad (57)$$

In terms of the volume strain, $\epsilon=\frac{1}{3}(\Delta V/V_0)$ for small strains, where ΔV is the initial volume, so that Eq. (55) takes the form

$$D\left(\frac{\Delta V}{V_0}\right)=D_u\left(1+\frac{\Delta V}{V_0}\right)^{\frac{2}{3}}\exp\left[\frac{M}{kT}\left(\frac{\Delta V}{V_0}\right)\right]. \qquad (58)$$

Therefore, it is evident that a plot of $\ln[D(\Delta V/V_0)\times(1+\Delta V/V_0)^{-\frac{2}{3}}]$ against $\Delta V/V_0$ should be linear with a slope a given by

$$a=M/kT, \qquad (59)$$

and an intercept given by $\ln D_u$.

Several investigators have obtained data on the variation of the diffusion coefficients with pressure that is suitable for testing Eq. (58). Reference 2 presents data for the self-diffusion coefficient as a function of pressure for sodium, phosphorous, and mercury up to pressures of 12 000, 4000, and 8000 atmospheres, respectively. The self-diffusion coefficient of liquid gallium up to pressures of 10 000 atmospheres is given in reference 3. The self-diffusion coefficient for single-crystal zinc up to pressures of 10 000 atmospheres for diffusion in the directions parallel to and perpendicular to the c axis is given in reference 1. The self-diffusion coefficient of lead up to pressures of 8000 atmospheres at two temperatures is given in reference 5.

The electrical conductivities of silver chloride and silver bromide have been measured as a function of pressure up to 300 atmospheres.[4] Since in these silver halides it has been shown that the conductivity depends almost entirely on the mobility of the silver ion, the conductivity is proportional to the diffusion coefficient of the silver ion by the Nernst-Einstein relation, and the data of reference 4 are suitable for testing Eq. (58).

Plots of the variation of the quantity of $\log[D(\Delta V/V_0)\times(1+\Delta V/V_0)^{-\frac{2}{3}}]$ against $\Delta V/V_0$ for the self-diffusion of sodium, phosphorous, mercury, gallium, and lead are shown in Fig. 1. The quantities $\log[D(\Delta V/V_0)\times(1+\Delta V/V_0)^{-\frac{2}{3}}]$ for single-crystal zinc were plotted against the fractional change in lattice parameter $\Delta\lambda/\lambda$, since this is a more natural unit for discussing diffusion in anisotropic crystals and the linear compressions perpendicular and parallel to the c-axis are available. The zinc data are plotted in Fig. 2.

Figure 3 gives $\log(1/R)$ plotted against $\Delta V/V_0$ for silver chloride and silver bromide, where R is the resistivity. The volume change $\Delta V/V_0$ is small enough for the pressure range considered so that $(1+\Delta V/V_0)^{-\frac{2}{3}}$ does not appreciably affect the results and can be ignored.

Compressibility data[11–16] were used to obtain the appropriate value of $\Delta V/V_0$ for zinc, sodium, mercury, lead, silver chloride, and silver bromide. For gallium, $\Delta V/V_0$ was computed from the data of Richards and Boyer[17] assuming that the form of $\Delta V/V_0$ as a function of pressure is the same as that for mercury. The values of $\Delta V/V_0$ for white phosphorus were computed from data in reference 16 assuming that the variation of the fractional volume change with pressure has the same form as that observed[18] for black and red phosphorus.

In all cases, the available compressibility data were extrapolated to the diffusion temperature.

The linearity of the plots presented in Figs. 1 to 3 shows that the form of Eq. (58) is valid for those systems investigated within the probable inaccuracies of the experiments and the calculations.

The slopes of the plots are given in Table I, where $a=M/kT$ and aT are shown for the various materials.

The fact that aT is so much smaller for the liquid metals than for any of the solids including sodium is indicative of the difference in the mechanism of diffusion in liquids and solids. In a liquid, the atoms are not constrained to remain at lattice positions, so that diffusion occurs by a cooperative process involving the migrating atom and its nearest neighbors. Thus, the change in the interatomic forces can be kept to a minimum throughout the diffusion process, and consequently aT would be very low.

From Eqs. (54) and (59) it is seen that a should be temperature independent. For the self-diffusion of lead for which pressure data are available at two temperatures, the value of a is reasonably constant.

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