Now take the ratio of Eqs. (7) and (8). The result is

$$\frac{\Gamma(\epsilon_{\alpha\beta})}{\Gamma_0} = \left\langle \exp\left(-\frac{1}{kT}\sum_{\alpha,\beta}C_{\alpha\beta}\epsilon_{\alpha\beta}\right)\right\rangle_\sigma \Big/$$

$$\left\langle \exp\left(-\frac{1}{kT}\sum_{\alpha,\beta}C_{\alpha\beta}\epsilon_{\alpha\beta}\right)\right\rangle_A. \quad (9)$$

The angular brackets indicate that a statistical average has been taken of the quantity within the brackets, and the subscripts σ and A indicate that the averages are taken over the regions of configuration space σ and A, respectively. The explicit expressions for these averages are

$$\left\langle \exp\left(-\frac{1}{kT}\sum_{\alpha,\beta}C_{\alpha\beta}\epsilon_{\alpha\beta}\right)\right\rangle_\sigma$$

$$= \int_\sigma e^{-\varphi(q_j,0)/kT}\exp\left(-\frac{1}{kT}\sum_{\alpha,\beta}C_{\alpha\beta}\epsilon_{\alpha\beta}\right)d\sigma \Big/$$

$$\int_\sigma e^{-\varphi(q_j,0)/kT}d\sigma, \quad (10)$$

$$\left\langle \exp\left(-\frac{1}{kT}\sum_{\alpha,\beta}C_{\alpha\beta}\epsilon_{\alpha\beta}\right)\right\rangle_A$$

$$= \int_A e^{-\varphi(q_j,0)/kT}\exp\left(-\frac{1}{kT}\sum_{\alpha,\beta}C_{\alpha\beta}\epsilon_{\alpha\beta}\right)dA \Big/$$

$$\int_A e^{-\varphi(q_j,0)/kT}dA. \quad (11a)$$

For small strains and high temperatures, the conditions under which the experimental effects of strain on diffusion are usually determined, the exponents in Eq. (9) can be expanded into a series, and only the first two terms need be retained. Thus, Eq. (9) can be written as

$$\frac{\Gamma(\epsilon_{\alpha\beta})}{\Gamma_0} = \left(1-\frac{1}{kT}\sum_{\alpha,\beta}\langle C_{\alpha\beta}\rangle_\sigma \epsilon_{\alpha\beta}\right)\Big/$$

$$\left(1-\frac{1}{kT}\sum_{\alpha,\beta}\langle C_{\alpha\beta}\rangle_A \epsilon_{\alpha\beta}\right), \quad (11b)$$

where $\langle C_{\alpha\beta}\rangle_\sigma$ and $\langle C_{\alpha\beta}\rangle_A$ are given by

$$\langle C_{\alpha\beta}\rangle_\sigma = \int_\sigma \left(\frac{\partial\varphi}{\partial\epsilon_{\alpha\beta}}\right)_{q_j,0} e^{-\varphi(q_j,0)/kT}d\sigma \Big/$$

$$\int_\sigma e^{-\varphi(q_j,0)/kT}d\sigma, \quad (12)$$

$$\langle C_{\alpha\beta}\rangle_A = \int_A \left(\frac{\partial\varphi}{\partial\epsilon_{\alpha\beta}}\right)_{q_j,0} e^{-\varphi(q_j,0)/kT}dA \Big/$$

$$\int_A e^{-\varphi(q_j,0)/kT}dA. \quad (13)$$

Taking logarithms of Eq. (11) and utilizing the fact that $\ln(1-x)\approx -x$ for small x, gives

$$\ln\frac{\Gamma(\epsilon_{\alpha\beta})}{\Gamma_0} = \frac{1}{kT}\{\sum_{\alpha,\beta}[\langle C_{\alpha\beta}\rangle_A - \langle C_{\alpha\beta}\rangle_\sigma]\epsilon_{\alpha\beta}\}, \quad (14)$$

or, defining a parameter $m_{\alpha\beta}$ by

$$m_{\alpha\beta} = \langle C_{\alpha\beta}\rangle_A - \langle C_{\alpha\beta}\rangle_\sigma. \quad (15)$$

Equation (14) can be written as

$$\Gamma(\epsilon_{\alpha\beta}) = \Gamma_0 \exp\left(\frac{1}{kT}\sum_{\alpha,\beta}m_{\alpha\beta}\epsilon_{\alpha\beta}\right). \quad (16)$$

Since Γ_0 can always be written as[8]

$$\Gamma = \nu^* e^{-\Delta E^*/kT}, \quad (17)$$

where ΔE^* is the energy of activation for the atomic jump and ν^* is an effective frequency, it is evident from Eq. (16) that the strain affects the jump frequency by an effective change in the energy of activation.

Equation (16) shows that the jump frequency has a simple exponential dependence on the strains and that this dependence is controlled by the derivatives of the potential energy with respect to the strains evaluated at the saddle point of the activated state.

Equation (16) gives the general relation between the jump frequency and the strain that will be used in this paper.

To illustrate the application of Eq. (16), three special cases will be considered:

(1) Uniform compression or expansion, in which

$$\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = \epsilon, \quad (18)$$

(all other strains$=0$)

(2) Simple shear, in which

$$\epsilon_{xy} = \epsilon_{yx} = \epsilon_s, \quad (19)$$

(all other strains$=0$)

(3) Simple elastic tension or compression in the x direction, in which

$$\epsilon_{xx} = \epsilon_L,$$
$$\epsilon_{yy} = \epsilon_{zz} = -\mu\epsilon_L, \quad (20)$$

where μ is Poisson's ratio. For these three cases, Eq. (16) gives the following results: For uniform compression or expansion,

$$\Gamma(\epsilon) = \Gamma_0 e^{(3m/kT)\epsilon}, \quad (21)$$

where

$$m = \langle C\rangle_A - \langle C\rangle_\sigma, \quad (22)$$

and

$$\langle C\rangle_\sigma = \int_\sigma \left(\frac{\partial\varphi}{\partial\epsilon}\right)_{q_j,0} e^{-\varphi(q_j,0)/kT}d\sigma \Big/ \int_\sigma e^{-\varphi(q_j,0)/kT}d\sigma, \quad (23)$$

$$\langle C\rangle_A = \int_A \left(\frac{\partial\varphi}{\partial\epsilon}\right)_{q_j,0} e^{-\varphi(q_j,0)/kT}dA \Big/$$

$$\int_A e^{-\varphi(q_j,0)/kT}dA. \quad (24)$$

For simple shear,

$$\Gamma(\epsilon_s) = \Gamma_0 e^{(2m_s/kT)\epsilon_s}, \qquad (25)$$

where

$$m_s = \langle C_s \rangle_A - \langle C_s \rangle_\sigma, \qquad (26)$$

$\langle C_s \rangle_A$ and $\langle C_s \rangle_\sigma$ are given by statistical averages similar to Eqs. (23) and (24), i.e.,

$$\langle C_s \rangle_\sigma = \left\langle \left(\frac{\partial \varphi}{\partial \epsilon_s} \right)_{q_j,0} \right\rangle_\sigma, \qquad (27)$$

$$\langle C_s \rangle_A = \left\langle \left(\frac{\partial \varphi}{\partial \epsilon_s} \right)_{q_j,0} \right\rangle_A. \qquad (28)$$

For simple elastic tension or compression in the x direction,

$$\Gamma(\epsilon_L) = \Gamma_0 e^{(m_l/kT)(1-2\mu)},$$

where

$$m_l = \langle C_l \rangle_A - \langle C_l \rangle_\sigma, \qquad (29)$$

or

$$m_l = \left\langle \left(\frac{\partial \varphi}{\partial \epsilon_L} \right)_{q_j,0} \right\rangle_A - \left\langle \left(\frac{\partial \varphi}{\partial \epsilon_L} \right)_{q_j,0} \right\rangle_\sigma. \qquad (30)$$

III. DEPENDENCE OF VACANCY CONCENTRATION ON STRAIN

The n appearing in Eq. (1) has a different significance for different mechanisms of diffusion. Broadly speaking, n is the probability that a diffusing particle has a site available to jump into. For dilute interstitial diffusion this probability is nearly unity whether or not the system is strained. For diffusion by a vacancy mechanism, however, n is the atomic fraction of vacancies in the crystal, given by

$$n = n_v/N_T, \qquad (31)$$

where n_v is the vacancy concentration, and N_T is the total number of lattice sites per cubic centimeter. It is therefore necessary to investigate the variation of n_v with strain.

The atomic fraction of vacancies in a crystal at equilibrium is given by (see Appendix)

$$n_v = \int \cdots \int e^{-\psi_v(p_j,q_j)/kT} \prod_j dp_j dq_j \Big/$$

$$\int \cdots \int e^{-\psi_0(p_j,q_j)/kT} \prod_j dp_j dq_j, \qquad (32)$$

where ψ_v is the energy of the crystal containing a

vacancy and ψ_0 is the energy of the perfect crystal. Performing the integrations over the momenta p_j converts Eq. (32) into

$$n_v = \int \cdots \int e^{-\varphi_v(q_j)/kT} \prod_j dq_j \prod_k (\nu_0)_k \Big/$$

$$\int \cdots \int e^{-\varphi_0(q_j)/kT} \prod_j dq_j \prod_k (\nu_v)_k, \qquad (33)$$

where $\varphi_v(q)$ and $\varphi_0(q)$ are the potential energies in a crystal containing a vacancy and in a perfect crystal, respectively, each taken as a function of all the coordinates; $(\nu_v)_k$ is the frequency of the kth vibrational mode in the crystal containing a vacancy; and $(\nu_0)_k$ is the frequency of the kth normal mode in a perfect crystal. In a strained crystal, the φ and the ν must be written as functions of strain, so that (33) becomes

$$n_v(\epsilon_{\alpha\beta})$$

$$= \int \cdots \int \exp[-\varphi_v(q_j,\epsilon_{\alpha\beta})/kT] \prod_j dq_j \prod_k (\nu_0^\epsilon)_k \Big/$$

$$\int \cdots \int \exp[-\varphi_0(q_j,\epsilon_{\alpha\beta})/kT] \prod_j dq_j \prod_k (\nu_v^\epsilon)_k. \qquad (34)$$

An estimate of the effect of strain on the frequency ratios can be made from Grüneisen's relation[10]

$$d \ln\nu/d \ln V = -\gamma, \qquad (35)$$

where V is the volume and γ is a positive constant. Integrating Eq. (35) for each vibrational mode as the crystal goes from the strained to the unstrained state

$$\frac{(\nu_0^\epsilon)_k}{(\nu_0)_k} = \left(1 + \frac{\delta V}{V}\right)^{-\gamma}, \qquad (36)$$

$$\frac{(\nu_v^\epsilon)_k}{(\nu_v)_k} = \left(1 + \frac{\delta V}{V}\right)^{-\gamma}, \qquad (37)$$

where δV is the volume change arising from the strain. Grüneisen's relation, therefore, leads to an equality of frequency ratios in the strained and unstrained systems:

$$\prod_k (\nu_0^\epsilon)_k \Big/ \prod_k (\nu_v^\epsilon)_k = \prod_k (\nu_0)_k \Big/ \prod_k (\nu_v)_k. \qquad (38)$$

Therefore, the ratio of Eqs. (34) and (33) is

$$\frac{n_v(\epsilon_{\alpha\beta})}{n_v} = \int \cdots \int \exp[-\varphi_v(q_j,\epsilon_{\alpha\beta})/kT] \prod_j dq_j \Big/ \int \cdots \int e^{-\varphi_v(q_j)/kT} \prod_j dq_j$$

$$\times \int \cdots \int e^{-\varphi_0(q_j)/kT} \prod_j dq_j \Big/ \int \cdots \int \exp[-\varphi_0(q_j,\epsilon_{\alpha\beta})/kT] \prod_j dq_j. \qquad (39)$$

[10] John Clarke Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), p. 238.