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Anisotropic diffusion in stress fields

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The effects of external fields on the diffusion of particles in crystals is discussed. Emphasis is put on the anisotropy of drift diffusion due to elastic strain fields in cubic crystals. The continuum equation of diffusion is derived microscopically from lattice theory. It is shown that in an elastic strain field the anisotropy of the saddle-point configuration leads to an anisotropic diffusion, whereas the possible anisotropy of the equilibrium configuration is unimportant. In an homogeneous strain field the diffusion is characterized by three independent "elasto-diffusion constants," the measurements of which yield direct information about the symmetry and strength of the dipole tensor of the saddle-point configuration. Possible applications to other problems are discussed briefly.

I. INTRODUCTION

In continuum theory of particle diffusion, the current density $\vec{j}$ is proportional to the gradient of the particle density ρ

$$j_i(\vec{R}) = -\sum_j D_{ij}\, \partial_{R_j} \rho(\vec{R}, t) . \tag{1}$$

The connecting quantity D_{ij}, the diffusion tensor, is diagonal in cubic crystals, i.e., $D_{ij} = D_0 \delta_{ij}$, where D_0 is the diffusion constant. D_0 usually obeys an Arrhenius law: $D_0 = D^0 \exp(-E_0/kT)$ with the migration energy E_0. In the presence of external fields, like, stress fields or electric fields, one obtains, in addition to the above diffusion current, a drift current which is set proportional to the gradient of the interaction energy $E(\vec{R})$ of the particle in the external field, so that for cubic crystals

$$j_i(\vec{R}, t) = -D_0 \partial_{R_i} \rho(\vec{R}, t) - D_0 \beta \rho(\vec{R}, t) \partial_{R_i} E(\vec{R}). \tag{2}$$

Here $D_0\beta = D_0/kT$ is the mobility of the particle.

In this continuum description of diffusion three effects have been neglected. This can be shown by a microscopic derivation of the continuum diffusion starting from lattice diffusion which will be given in Sec. II.

(i) The symmetry of the diffusion tensor is not only determined by the symmetry of the host lattice, but can be strongly affected by the symmetry and the elementary-jump mechanism of the defect itself. For instance, one can have one- or two-dimensional diffusion processes which means an extremely strong anisotropy of the diffusion.

(ii) For drift diffusion one has to distinguish between the interaction energies in the equilibrium configuration $E_e(\vec{R})$ and in the saddle-point configuration $E_s(\vec{R})$. *A priori* it is not clear in which way these two energies enter in Eq. (2). One is inclined to think that one has to identify $E(\vec{R})$ in Eq. (2) with the interaction in the equilibrium position, which turns out to be the case. However, in addition the diffusion constant becomes $\vec{R}$ dependent, namely, $D(\vec{R}) = D_0 \exp\{-\beta[E_s(\vec{R}) - E_e(\vec{R})]\}$. This has drastic consequences: in the stationary state the current $\vec{j}$ turns out to be independent of the interaction $E_e(\vec{R})$, so that for $E_s \equiv 0$ the current is the same as in an unperturbed crystal, however large E_e! This effect has already been pointed out previously by other authors, e.g., Wolfer and Ashkin[1] and Schroeder and Dettmann.[2]

(iii) The external field effectively lowers the cubic symmetry of the crystal so that one expects the diffusion tensor to become anisotropic. This is the topic of the present paper. We will see that it is the anisotropy of the saddle-point configuration, e.g., in an elastic stress field the anisotropy of its dipole tensor, which determines the symmetry of the diffusion tensor. The simplest case is the diffusion in a homogeneously deformed cubic crystal with strain field ϵ_{kl}, where, as has been pointed out by Flynn,[3] one obtains an additional contribution proportional to ϵ_{kl} to the diffusion tensor of a cubic defect

$$D_{ij} = D_0 \delta_{ij} + \sum_{kl} d_{ijkl} \epsilon_{kl} .$$

As will be discussed in Sec. III, the symmetry of the "elastodiffusion tensor" d_{ijkl} is determined by the symmetry of the saddle-point configuration, so that a measurement of the elastodiffusion constants allows the determination of the symmetry and strength of the dipole tensor of the saddle-point configuration.

The importance of the anisotropy of the saddle point has first been pointed out by Koehler.[4] Kronmüller, Frank, and Hornung[5] have also discussed the effects due to the saddle-point interaction. However, they obtain an isotropic-diffusion tensor which may be regarded as a first approximation to the anisotropic one. The importance of the anisotropic diffusion for various experiments will be discussed in Sec. V. Independently, Savino[6] has recently also given a derivation of diffusion anisotropy. Ingle and Crocker[7] have studied the anisotropic diffusion of vacancies in bcc by computer simulation.

II. DERIVATION OF CONTINUUM THEORY OF DIFFUSION FROM LATTICE THEORY

First we treat defects with cubic symmetry only; a generalization to defects with lower symmetry is given in Sec. III. As an example, we consider a hydrogen atom on octahedral sites in an fcc metal. Figure 1(a) shows the host atoms in a (100) plane. The hydrogen atom may occupy one of the octahedral positions (marked by the small dots). If the particle density at site $\vec{n}$ is $\rho_{\vec{n}}(t)$, then the particle current from $\vec{n}$ to $\vec{m}$ is given by[8]

$$j_{\vec{m}\vec{n}}(t) = \nu e^{-\beta E_0} s_{(\vec{m}-\vec{n})}\, e^{-\beta(E_s^{(\vec{m},\vec{n})} - E_e^{(\vec{n})})}\, \rho_{\vec{n}}(t)$$
$$= \lambda_{\vec{m}\vec{n}}\, \rho_{\vec{n}}(t). \tag{3}$$

Here ν is an attempt frequency assumed to be the same for all sites. The energies are counted from the equilibrium energy in the ideal lattice which is set equal to zero. E_0 is the saddle-point energy in the ideal lattice. The potential energy in the saddle point $(\vec{m}\vec{n})$ which connects the equilibrium positions $\vec{n}$ and $\vec{m}$ deviates from this ideal value by $E_s^{(\vec{m},\vec{n})}$, and the energies in the equilibrium positions $\vec{n}$ and $\vec{m}$ are $E_e^{(\vec{n})}$ and $E_e^{(\vec{m})}$, respectively [see Fig. 1(b)]. The change of the density at site $\vec{m}$ is then

$$\dot{\rho}_{\vec{m}}(t) = \sum_{\vec{n}} [\lambda_{\vec{m}\vec{n}}\, \rho_{\vec{n}}(t) - \lambda_{\vec{n}\vec{m}}\, \rho_{\vec{m}}(t)] + p_{\vec{m}}(t)\,, \tag{4}$$

where the first term represents the increase of $\rho_{\vec{m}}(t)$ due to particles jumping from a neighboring site to $\vec{m}$, the second term the decrease due to particles jumping away from $\vec{m}$, and the last term the increase due to particle production $p_{\vec{m}}(t)$ at $\vec{m}$.

In *thermal equilibrium* $[p_{\vec{m}}(t) = 0 = \dot{\rho}_{\vec{m}}(t)]$ the particle density is given by $(\sum_{\vec{m}} \rho_{\vec{m}}(t) = 1)$

$$\rho_{\vec{m}} = \frac{\exp(-\beta E_e^{(\vec{m})})}{\sum_{\vec{m}'} \exp(-\beta E_e^{(\vec{m}')})} \tag{5}$$

as can be verified by inserting into Eq. (4). Thus the equilibrium density is independent of the interaction E_s in the saddle point (however, the time needed to obtain thermal equilibrium depends strongly on E_s!). A more general formula for the transition probability $\lambda_{\vec{m}\vec{n}}$ is due to Vineyard.[9] For its validity see the discussion in the book of Flynn.[3]

$$\lambda_{\vec{m}\vec{n}} = \frac{\prod_{i=1}^{3N} \nu_i^{(\vec{n})}}{\prod_{j=1}^{3N-1} \nu_j^{(\vec{m},\vec{n})}}\, e^{-\beta E_0}\, e^{-\beta(E_s^{(\vec{m},\vec{n})} - E_e^{(\vec{n})})}\,. \tag{6}$$

Here $\nu_i^{(\vec{n})}$, $i = 1, \ldots, 3N$, are the eigenfrequencies of the whole crystal if the defect is localized at the position $\vec{n}$, whereas $\nu_j^{(\vec{m},\vec{n})}$, $j = 1, \ldots, 3N-1$ are the eigenfrequencies of the crystal if the defect is at the saddle point $(\vec{m}, \vec{n})$. Since this configuration is unstable, the (imaginary) frequency $\nu_{3N}^{(\vec{m},\vec{n})}$ corresponding to the decay of this configuration has to be left out in the product over j. In the following we will always assume the more simple form of Eq. (3) for $\lambda_{\vec{m}\vec{n}}$. However, all subsequent equations can easily be modified for the more general expression (6). For instance, the equilibrium density is instead of Eq. (5) given by

$$\rho_{\vec{m}} = \frac{\prod_{i=1}^{3N} \nu_i^{(\vec{m})} \exp(-\beta E_e^{(\vec{m})})}{\sum_{\vec{m}'} \prod_{j=1}^{3N} \nu_j^{(\vec{m}')} \exp(-\beta E_e^{(\vec{m}')})}\,. \tag{7}$$

In most cases the exponential dependence on the energy $E_e^{(\vec{m})}$ is much more important than the frequency factors, so that Eq. (3) represents a satisfactory approximation.

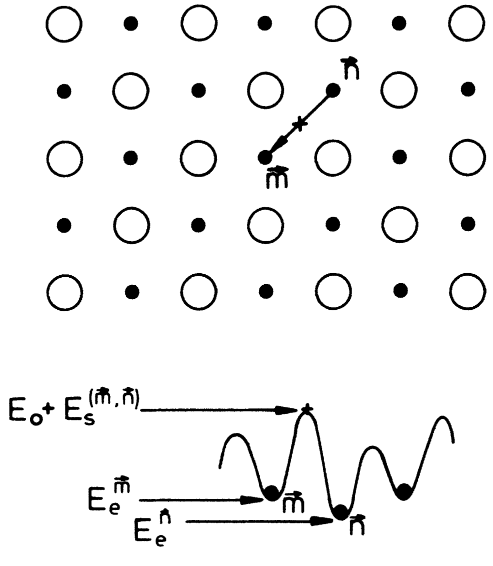

FIG. 1. (a) Octahedral sites (●) in a (100) plane of an fcc host lattice (large circles). The arrow indicates a jump path of a hydrogen atom with a saddle point (×). (b) Sketch of the energy profile for a defect (●) in a distorted crystal. $E_e^{(\vec{m})}$ is the energy in the equilibrium site $\vec{m}$; $E_0 + E_s^{(\vec{m},\vec{n})}$ the energy in the saddle point $(\vec{m}, \vec{n})$ between the equilibrium sites $\vec{m}$ and $\vec{n}$.

For a time-independent production the system achieves a *stationary state* for which

$$\sum_{\vec{n}} (\lambda_{\vec{m}\vec{n}}\rho_{\vec{n}} - \lambda_{\vec{n}\vec{m}}\rho_{\vec{m}}) + p_{\vec{m}} = 0. \tag{8}$$

By introducing a renormalized density $W_{\vec{m}} = \rho_{\vec{m}} \exp(\beta E_e^{(\vec{m})})$, which according to Eq. (5) describes the deviation from the thermal distribution; this equation can also be written in the form

$$\sum_{\vec{n}} \tilde{\lambda}_{\vec{m}\vec{n}}(W_{\vec{n}} - W_{\vec{m}}) + p_{\vec{m}} = 0;$$

$$\tilde{\lambda}_{\vec{m}\vec{n}} = \tilde{\lambda}_{\vec{n}\vec{m}} = \nu \exp[-\beta(E_0 + E_s^{(\vec{m},\vec{n})})], \tag{9}$$

where $\tilde{\lambda}_{\vec{m}\vec{n}}$ depend only on the saddle point, but not on the equilibrium interaction. Thus for given production $p_{\vec{m}}$ and given interaction $E_s^{(\vec{m},\vec{n})}$ these equations determine the renormalized density $W_{\vec{m}}$ uniquely, which is consequently independent of the interactions $E_e^{(\vec{m})}$ at the equilibrium positions! Further also the microscopic currents

$$j_{\vec{m}\vec{n}} = \lambda_{\vec{m}\vec{n}}\rho_{\vec{n}} = \tilde{\lambda}_{\vec{m}\vec{n}}W_{\vec{n}}; \quad W_{\vec{n}} = \rho_{\vec{n}} \exp(\beta E_e^{(\vec{n})}) \tag{10}$$

are independent of E_e and so is any macroscopic current which is a sum of microscopic $j_{\vec{m}\vec{n}}$. Note, however, that the densities do depend on the equilibrium interaction, since $\rho_{\vec{m}} = \exp(-\beta E_e^{(\vec{m})})\, W_{\vec{m}}$.

The above result can be made plausible by looking at Fig. 1(b). In thermal equilibrium the distribution of particles within a single valley is governed by the barometric-pressure formula. Applying a harmonic expansion around the valley minimum one obtains just the result Eq. (7) for the total density within valley m. However the current across the saddle $j_{\vec{m}\vec{n}}$ does not depend on the density at the bottom of the valley, but is determined by the density at the saddle itself which depends critically on the energy of the saddle point, i.e., on $E_s^{(\vec{m},\vec{n})}$. Thus the above result, Eq. (10), for the current in the stationary state is not unplausible.

Equation (9) for the stationary state can also be derived from a variational principle. The underlying "Lagrangian" is the lattice equivalent of the one used by Schroeder and Dettmann[2] for continuum diffusion

$$L[W_{\vec{m}}] = \frac{1}{4} \sum_{\vec{m}\vec{n}} \tilde{\lambda}_{\vec{m}\vec{n}}(W_{\vec{n}} - W_{\vec{m}})^2 - \sum_{\vec{m}} p_{\vec{m}} W_{\vec{m}} . \tag{11}$$

The extremal condition $\delta L = 0$ yields directly Eq. (9), and the stationary value L_0 of $L[W_{\vec{m}}]$ is

$$L_0 = -\frac{1}{2} \sum_{\vec{m}} p_{\vec{m}} W_{\vec{m}} .$$

Let us now specify the external field and assume a slowly varying elastic strain field $\epsilon_{ij}(\vec{R})$, e.g., a homogeneous deformation or the longranging strain field of a dislocation. In this case the interactions can be described by the dipole tensors for the equilibrium $\underline{P}^e$ and saddle-point configurations $\underline{P}^s$

$$E_e^{(\vec{m})} = -\sum_{ij} P_{ij}^e \epsilon_{ij}(\vec{R}^{\vec{m}});$$

$$E_s^{(\vec{m},\vec{n})} = -\sum_{ij} P_{ij}^s(\vec{m}\vec{n})\epsilon_{ij}(\vec{R}^{\vec{m},\vec{n}}) . \tag{12}$$

Since in this section we will only consider cubic defects, $\underline{P}^e$ is isotropic ($P_{ij}^e = P_0^e \delta_{ij}$). Contrarily, the saddle-point dipole tensor is anisotropic and moreover depends on the direction of the elementary jump (see Fig. 2). For a jump from $\vec{n}$ to $\vec{m}$ or vice versa, the defect exerts strong forces (dashed arrows in Fig. 2) on the neighboring atoms, so that the dipole tensor has a large component in the direction of the nearest neighbors and two smaller ones for the perpendicular directions. One can see that the dipole tensor $\underline{P}^s(\vec{m}\vec{n})$ for the jump $\vec{m} \leftrightarrow \vec{n}'$ (full lines in Fig. 2) can be obtained from $\underline{P}^s(\vec{m},\vec{n})$ by a rotation by 90°.

The transition to continuum diffusion is most conveniently performed by using the Lagrangian $L[W_{\vec{m}}]$. If $W_{\vec{m}} = W(\vec{R}^{\vec{m}})$ is slowly varying, we expand $W_{\vec{n}}$ in a Taylor series

$$W_{\vec{n}} \cong W(\vec{R}^{\vec{m}}) + \sum_i (R_i^{\vec{n}} - R_i^{\vec{m}})\partial_{R_i^{\vec{m}}} W(\vec{R}^{\vec{m}}) + \cdots .$$

Instead of summing in Eq. (11) over $\vec{m}$ and $\vec{n}$, we may first sum over the difference $\vec{h} = \vec{n} - \vec{m}$, i.e., over all z neighbors of $\vec{m}$ and then perform the sum over $\vec{m}$ by transforming it to an integral over

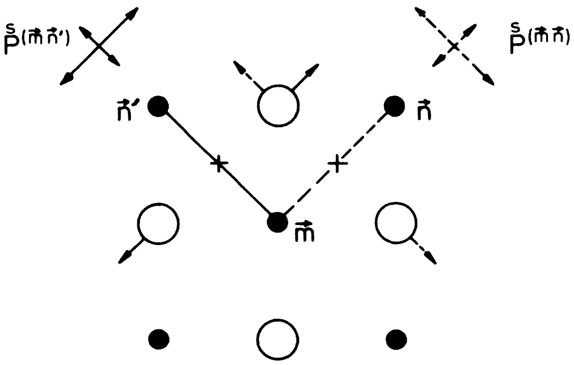

FIG. 2. Dipole tensor $\underline{P}^s$ in the saddle point (✕) between two octahedral sites (●) in an fcc crystal. At the saddle point between sites $\vec{m}$ and $\vec{n}$ the defect exerts strong forces (dashed arrows) on the neighboring host atoms (large circles), thus the dipole tensor $\underline{P}^s$ has a large component in this direction. For a jump between $\vec{m}$ and $\vec{n}'$ the dipole tensor is rotated by 90°.

$\vec{R}^{\vec{m}}=\vec{R}$. The result is

$$L[W]=\int\frac{d^3R}{V}\left(\frac{1}{2}\sum_{ij}\tilde{D}_{ij}(\vec{R})\partial_{R_i}W(\vec{R})\partial_{R_j}W(\vec{R})-p(\vec{R})W(\vec{R})\right), \tag{13}$$

$$\begin{aligned}\tilde{D}_{ij}(\vec{R})&=\frac{1}{2}\sum_{\vec{h}}\lambda^0_{\vec{h}}\,R_i^{\vec{h}}R_j^{\vec{h}}\exp\left(\beta\sum_{kl}\epsilon_{kl}(\vec{R})P^s_{kl}(\vec{h})\right)\\&=D_0\frac{3}{Z}\sum_{\vec{h}=\mathrm{NN}}r_i^{\vec{h}}r_j^{\vec{h}}\exp\left(\beta\sum_{kl}\epsilon_{kl}(\vec{R})P^s_{kl}(\vec{h})\right)\end{aligned} \tag{14}$$

for cubic crystals.

Here $\lambda^0(\vec{h})=s_{(\vec{h})}\nu\exp(-\beta E_0)$ is the jump rate in the ideal crystal. $\vec{r}^h$ are unit vectors for the different jump directions. In deriving Eq. (14) we have replaced $\epsilon_{kl}(\vec{R}^{(\vec{m},\vec{n})})$ by $\epsilon(\vec{R}^{\vec{m}})$. However, the orientation dependence of $\underline{P}^s(\vec{m},\vec{n})=\underline{P}^s(\vec{h})$ has been taken into account exactly. (Note that $\underline{P}^s(\vec{h})$ has an essential singularity at $\vec{h}=0$, if $\underline{P}^s_{ij}$ is anisotropic.) This means that the saddle-point energy depends explicitly on the direction of the jump: $E_s^{(\vec{h})}(\vec{R})=\sum_{kl}\epsilon_{kl}(\vec{R})P^s_{kl}(\vec{h})$. Due to this angular dependence, the interaction energy $E_s^{(\vec{m}\vec{n})}$ cannot be expanded in a Taylor series around the point $\vec{m}$, since E_s has an essential singularity at this point. For cubic crystals, this gives direct rise to the anisotropy of $\tilde{D}_{ij}(\vec{R})$ according to Eq. (14). Note that Kronmüller *et al.*[5] obtain an isotropic diffusion tensor by assuming a Taylor series for E_s to be valid.

From Eq. (13) we obtain the differential equation for the renormalized density $W(\vec{R})=\rho(\vec{R})\exp[\beta E_e(\vec{R})]$.

$$\sum_{ij}\partial_{R_i}[\tilde{D}_{ij}(\vec{R})\partial_{R_j}W(\vec{R})]+p(\vec{R})=0. \tag{15}$$

Together with the appropriate boundary condition, e.g., $W(\vec{R})=0$ for $R\to\infty$, this equation determines $W(\vec{R})$ uniquely. As in the lattice case, $W(\vec{R})$ is independent of the interaction in the equilibrium configuration and so is the current

$$j_i(\vec{R})=-\sum_j\tilde{D}_{ij}(\vec{R})\partial_{R_j}W(\vec{R}). \tag{16}$$

This is illustrated in Fig. 3. In a crystal with an arbitrary variation of the potential energy in the equilibrium positions [Fig. 3(b)] we have the same stationary current as in the ideal crystal [Fig. 3(a)].

Exceptions from this rule can only occur, if $E_e(\vec{R})$ enters via the boundary condition: if, e.g., the density $\rho(\vec{R})=\rho(\vec{R}_s)$ is given at the boundary S, then we obtain due to $W(\vec{R}_s)=\rho(\vec{R}_s)\exp[\beta E_e(\vec{R}_s)]$ a dependence of W and $\vec{j}$ upon the interaction $E_e(\vec{R}_s)$ at the boundary. However in many cases $E_e(\vec{R})$ can be assumed to vanish at the boundary, so that $W(\vec{R}_s)=\rho(\vec{R}_s)$. Then W and $\vec{j}$ are again independent of E_e.

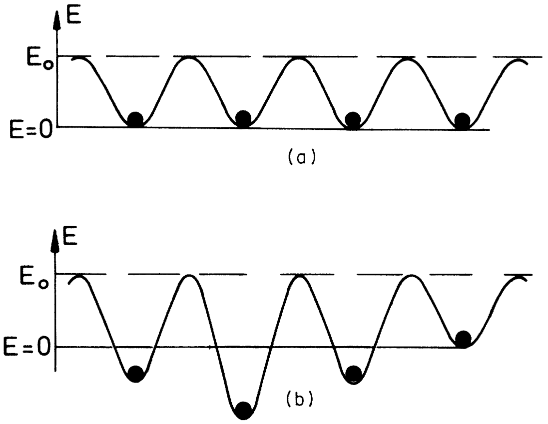

FIG. 3. Energy profiles: (a) ideal lattice; (b) variation of the equilibrium-site energies, saddle-point energies are not changed. For stationary conditions more defects will occupy the deeper valleys, but the jump rate across each saddle point is the same.

Finally we can also reintroduce the density $\rho(\vec{R})$ in Eq. (16) and by differentiation separate $\vec{j}$ into a diffusion current and a drift current.

$$\begin{aligned}j_i=j_i^{\mathrm{diff}}+j_i^{\mathrm{drift}}&=\sum_j D_{ij}(\vec{R})\partial_{R_j}\rho(\vec{R})\\&\quad-\sum_j D_{ij}(\vec{R})\beta\rho(\vec{R})\partial_{R_j}E_e(\vec{R})\end{aligned}$$

with

$$\begin{aligned}D_{ij}(\vec{R})&=\tilde{D}_{ij}(\vec{R})\exp[\beta E_e(\vec{R})]\\&=D_0\frac{3}{Z}\sum_{\vec{h}=\mathrm{NN}}r_i^{\vec{h}}r_j^{\vec{h}}\exp\{-\beta[E_s^{(\vec{h})}(\vec{R})-E_e(\vec{R})]\}.\end{aligned} \tag{17}$$

By comparison with the phenomenological Eq. (2) we see two effects due to the lattice structure which are mentioned in the introduction: the two different interactions E_e, E_s and the anisotropy of D_{ij}.

III. DIFFUSION OF NONCUBIC DEFECTS

So far we assumed cubic symmetry for the defect in its equilibrium configurations. However many defects have lower symmetry than the host lattice. Examples are the tetrahedral and the octahedral interstitial in bcc, where the interstitial site itself has tetragonal symmetry (D_{2d} and D_{4h}, respectively). Figure 4 shows the octahedral sites in the bcc lattice. There are three nonequivalent

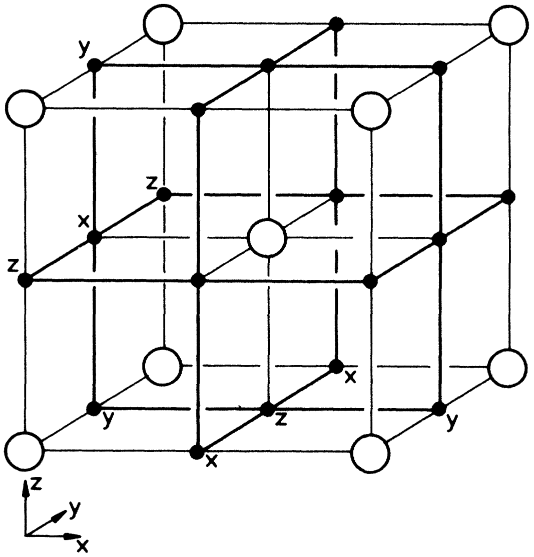

FIG. 4. Octahedral sites (●) in a bcc host lattice (large circles). The host-atom octahedron is not perfect, thus one can distinguish three different site symmetries labelled x, y, z indicating the direction of the closest neighbors.

sites with preferred orientations in x, y, or z direction. Sites with the same orientation form a bcc lattice, the total interstitial lattice is a nonprimitive bcc lattice with three nonequivalent sites.

By denoting the Bravais lattice by vectors $\vec{M}$, $\vec{N}$, and the s nonequivalent sites within the unit cells by $\alpha = 1, \ldots, s$, the equations of motion read

$$\dot{\rho}^{\vec{M}}_{\alpha}(t) = \sum_{\vec{N}\beta}\left[\lambda^{\vec{M}\vec{N}}_{\alpha\beta}\rho^{\vec{N}}_{\beta}(t) - \lambda^{\vec{N}\vec{M}}_{\beta\alpha}\rho^{\vec{M}}_{\alpha}(t)\right] + p^{\vec{M}}_{\alpha}(t)\,, \quad (18)$$

where $\lambda^{\vec{M}\vec{N}}_{\alpha\beta}$ is the transition rate from position $(\vec{N}\beta)$ to $(\vec{M}\alpha)$.

Another example for noncubic defects are self-interstitials in the form of dumbbells, e.g., the ⟨100⟩ dumbbell in fcc with tetragonal symmetry (D_{4h}) as shown in Fig. 5(a) and the ⟨110⟩ dumbbell in fcc with orthorhombic symmetry (D_{2h}) in Fig. 5(b). In such cases we can have different orientations μ on a given site m, e.g., the x, y, or z orientation of the ⟨100⟩ dumbbell or six different ⟨110⟩ orientations for the ⟨110⟩ dumbbell. Thus for each position m we have to introduce partial densities $\rho^{\vec{m}}_{\mu}(t)$ for the different orientations μ, leading to equations of motion similar to Eq. (18)

$$\dot{\rho}^{\vec{m}}_{\mu}(t) = \sum_{\vec{n}\nu}\left[\lambda^{\vec{m}\vec{n}}_{\mu\nu}\rho^{\vec{n}}_{\nu}(t) - \lambda^{\vec{n}\vec{m}}_{\nu\mu}\rho^{\vec{m}}_{\mu}(t)\right] + p^{\vec{m}}_{\mu}(t)\,. \quad (19)$$

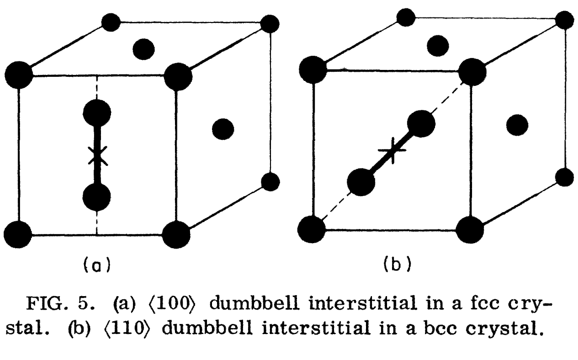

FIG. 5. (a) ⟨100⟩ dumbbell interstitial in a fcc crystal. (b) ⟨110⟩ dumbbell interstitial in a bcc crystal.

Due to the new orientational degrees of freedom, many new effects can occur. For instance, we can obtain a one- or two-dimensional diffusion process. An example for a linear diffusion is the ⟨110⟩ dumbbell in fcc metals which is supposed to move always along a preferred ⟨110⟩ chain, so that the orientation is not changed during a jump. Thus the different orientations do not couple and for each orientation $\vec{e}$ one can derive a diffusion constant of the form

$$D_{ij} = D_{\parallel} e_i e_j\,, \quad (20)$$

with $\vec{e}$ of ⟨110⟩ type, meaning that we have a constant $D_{\parallel}$ for diffusion along $\vec{e}$, but a constant $D = 0$ for diffusion perpendicular to $\vec{e}$.

An example for a two-dimensional diffusion process is the motion of the di-interstitial in fcc. In Al the stable di-interstitial consists of two parallel ⟨100⟩ dumbbells on nearest-neighbor sites [Fig. 6(a)].[10] The elementary jump of this defect consists of two steps.[11, 12] First one dumbbell jumps to a nearest-neighbor site forming the metastable configuration of Fig. 6(b). From there the dumbbell can proceed to the stable di-interstitial configuration shown in Fig. 6(c). By this elementary jump the dumbbell centers are always restricted to the plane perpendicular to the dumbbell axis.

In most cases, however, one has three-dimensional diffusion. This will be always the case if starting with a given orientation, all others are finally populated with equal probability so that no direction is preferred. An example is the ⟨100⟩ dumbbell in fcc. During the elementary jump one dumbbell atom moves to a nearest neighbor thus forming a new dumbbell on a nearest-neighbor site with the orientation changed by 90°. Figures 7(a)–7(d) illustrate which configurations can transform into each other in this way. For instance, starting with z orientation in the lower right-hand front corner [Fig. 7(a)] we obtain the x or y orientation by jumps to the nearest-neighbor sites. Proceeding this way it can be shown that the orientation is always the same for positions belonging to the same simple cubic (sc)

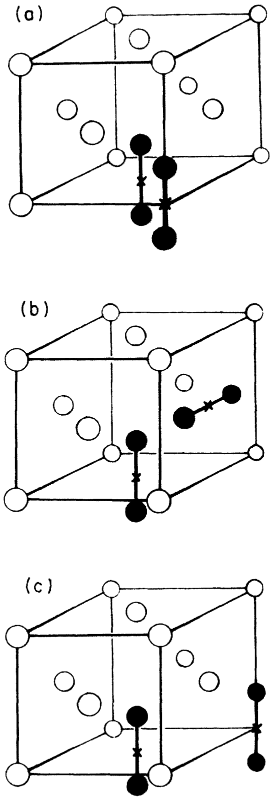

FIG. 6. Diffusion jump of a di-interstitial in fcc crystals (a) equilibrium configuration: two parallel ⟨001⟩ dumbells on nearest-neighbor sites. (b) metastable configuration: the dumbbell in the front corner has performed a regular jump to the nearest-neighbor position on the right-hand face of the cube. (c) equilibrium configuration: after a second jump of the same dumbbell the di-interstitial is in an equilibrium configuration, its center of gravity displaced by half a lattice constant.

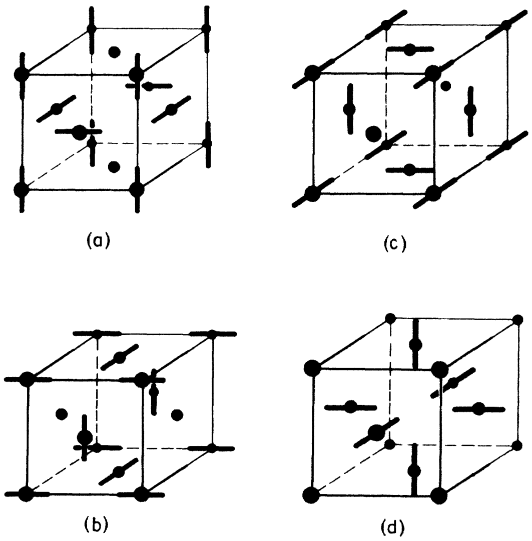

FIG. 7. Four channels for the diffusion of the ⟨100⟩ dumbbell in fcc crystals. The channels are labelled according to the occupation of the lower left-hand front corner of the cube (a) z channel, (b) x channel, (c) y channel, (d) 0 channel.

sublattice. However, when we start with the x orientation on the lower right-hand front corner [Fig. 7(b)], we obtain a quite different set of configurations. In this way all configurations can be classified as belonging to one of the four "migration channels" shown in Figs. 7(a)–7(d). These channels are completely separated and do not mix, as long as the ⟨100⟩ dumbbell does not rotate on its site. According to computer simulations[12] and relaxation measurements in [13]Al and [14]Ni this does not occur at low temperatures.

In bcc, the ⟨110⟩ dumbbell has a very similar migration process: a jump to a neighboring atom with a change of orientation by 60°. In this way we obtain 12 different migration channels. Here however the reorientation on site seems to be much easier, so that channel changes could be very frequent. Below we will see, however, that this does not influence the diffusion constant.

Let us first discuss the lattice and the continuum diffusion for an *ideal lattice* (with orientational degrees of freedom). Equation (19) can be written in the form

$$\dot{\rho}^{\vec{m}}_{\mu}(t)=\sum_{\vec{n}\nu}\lambda^{0\,\vec{m}\vec{n}}_{\mu\nu}[\rho^{\vec{n}}_{\nu}(t)-\rho^{\vec{m}}_{\mu}(t)]+p^{\vec{m}}_{\mu}(t)$$
$$=-\sum_{\vec{n}\nu}\Lambda^{0\,\vec{m}\vec{n}}_{\mu\nu}\rho^{\vec{n}}_{\nu}(t)+p^{\vec{m}}_{\mu}(t)\,, \tag{21}$$

with the ideal jump-frequency matrix

$$\Lambda^{0\,\vec{m}\vec{n}}_{\mu\nu}=\Lambda^{0\,\vec{n}\vec{m}}_{\nu\mu}=-\lambda^{0\,\vec{m}\vec{n}}_{\mu\nu}+\delta^{\vec{m}\vec{n}}_{\mu\nu}\sum_{\vec{n}'\mu'}\lambda^{0\,\vec{m}\vec{n}'}_{\mu\nu'}=\Lambda^{0\,(\vec{m}-\vec{n})}_{\mu\nu}\,. \tag{22}$$

Note that for the ideal crystal the transition probability $\lambda^{0\,\vec{m}\vec{n}}_{\mu\nu}$ is symmetrical in the pairs $\vec{m}\mu$ and $\vec{n}\nu$: $\lambda^{0\,\vec{m}\vec{n}}_{\mu\nu}=\lambda^{0\,\vec{n}\vec{m}}_{\nu\mu}=\lambda^{0\,(\vec{m}-\vec{n})}_{\mu\nu}$. For the solution of Eq. (21) we expand into eigenfunctions of $\Lambda^{0\,\vec{m}\vec{n}}_{\mu\nu}$ which have the form

$$N^{-1/2}a_{\mu}(\vec{q})e^{i\vec{q}\cdot\vec{R}^{\vec{m}}}\ (N=\text{number of sites}). \tag{23}$$

For the amplitudes $a_{\mu}(\vec{q})$ of the s nonequivalent orientations we obtain a system of s-coupled equations

$$\sum_{\nu=1}^{s}\Lambda^{0}_{\mu\nu}(\vec{q})a_{\nu}(\vec{q})=\Omega(\vec{q})a_{\mu}(\vec{q})\,;$$
$$\Lambda^{0}_{\mu\nu}(\vec{q})=\frac{1}{N}\sum_{\vec{m}\vec{n}}\Lambda^{0\,\vec{m}\vec{n}}_{\mu\nu}e^{i\vec{q}(\vec{R}^{\vec{m}}-\vec{R}^{\vec{n}})} \tag{24}$$

which have s orthogonal solutions $a^{(i)}_{\mu}$, $i=1,\ldots,s$. The s eigenvalues $\Omega_i(\vec{q})$ are reciprocal decay constants: the eigensolution $(\vec{q},i)$ decays as $\exp[-\Omega_i(\vec{q})t]$. We have always one "acoustical" solution characterized by $\Omega_1(\vec{q})\to 0$ for $q\to 0$ and $(s-1)$ "optical" ones, with finite relaxation times for $q\to 0$, i.e., $\Omega_i(\vec{q}=0)$ finite. For $q\to 0$ the acoustical mode is determined by the thermal equilibrium $a_\mu^{(1)}(0) = s^{-1/2}$ since all orientations are equivalent.

Contrary, the optical modes represent for $q \to 0$ nonequilibrium distributions of the different orientations in the unit cell. For continuum diffusion only the long-time behavior is important which is determined by the acoustical mode alone.

For small $\vec{q}$, $\Omega_1(\vec{q})$ can then be calculated by perturbation theory

$$\Omega_1(\vec{q}) \cong \sum_{\mu\nu} a_\mu^{(1)}(0)\Lambda^0_{\mu\nu}(\vec{q})a_\nu^{(1)}(0) = \frac{1}{s}\sum_{\mu\nu}\Lambda^0_{\mu\nu}(\vec{q}) . \tag{25}$$

By comparision with the continuum result

$$\Omega_1(\vec{q}) = \sum_{ij} D_{ij}\, q_i q_j , \tag{26}$$

the diffusion tensor D_{ij} follows as

$$D_{ij} = \frac{1}{N}\sum_{\vec{m}\vec{n}} R_i^{\vec{m}} R_j^{\vec{n}} \left(\frac{1}{s}\sum_{\mu\nu}\Lambda^{0\,(\vec{m}-\vec{n})}_{\mu\nu}\right)$$

$$= -\frac{1}{2}\sum_{\vec{h}} R_i^{\vec{h}} R_j^{\vec{h}} \left(\frac{1}{s}\sum_{\mu\nu}\Lambda^{0\,(\vec{h})}_{\mu\nu}\right) . \tag{27a}$$

With Eq. (22) this can be written as

$$D_{ij} = \frac{1}{2}\sum_{\vec{h}} R_i^{\vec{h}} R_j^{\vec{h}} \left(\frac{1}{s}\sum_{\mu\nu}\lambda^{0\,(\vec{h})}_{\mu\nu}\right) . \tag{27b}$$

Thus only the orientational average of $\Lambda^{0\,(\vec{h})}_{\mu\nu}$ enters into the diffusion constant. This is a direct consequence of the equal distribution of all orientations in thermal equilibrium. The resulting effective-jump frequency $\Lambda^{0\,(\vec{h})}_{\mathrm{eff}} = (1/s)\sum_{\mu\nu}\Lambda^{0\,(\vec{h})}_{\mu\nu}$ has therefore the same structure as the jump matrix without orientational degrees of freedom. Furthermore, one can see from Eq. (27) that on-site rotations corresponding to matrix elements $\Lambda^{0\,(\vec{h}=0)}_{\mu\nu}$ do not influence D_{ij} at all.

A similar expression can be derived for cases like the octahedral interstitial in bcc where each interstitial site is connected with a definite symmetry. In this case we have to use the nonprimitive description of Eq. (18). Quite analogous to the above arguments we obtain for the diffusion constant

$$D_{ij} = -\frac{1}{2s}\sum_{\substack{(\vec{M}-\vec{N})\\ \alpha\beta}} (R^{\vec{M}}_{\alpha,i} - R^{\vec{N}}_{\beta,i})(R^{\vec{M}}_{\alpha,j} - R^{\vec{N}}_{\beta,j})\Lambda^{0\,(\vec{M}-\vec{N})}_{\alpha\beta} . \tag{28}$$

Similar to Eq. (27) we can also in this case introduce an effective-jump matrix $\Lambda^{0\,(\vec{h})}_{\mathrm{eff}}$ with the symmetry of the host lattice so that

$$D_{ij} = -\frac{1}{2}\sum_{\vec{h}} R_i^{\vec{h}} R_j^{\vec{h}} \Lambda^{0\,(\vec{h})}_{\mathrm{eff}} ;$$

$$\Lambda^{0\,(\vec{h})}_{\mathrm{eff}} = \frac{1}{s}\sum_{\substack{(\vec{M}-\vec{N})\\ \alpha\beta}} \Lambda^{0\,(\vec{M}-\vec{N})}_{\alpha\beta}\,\delta_{\vec{R}^{\vec{h}},\,\vec{R}^{\vec{M}}_{\alpha}-\vec{R}^{\vec{N}}_{\beta}} . \tag{29}$$

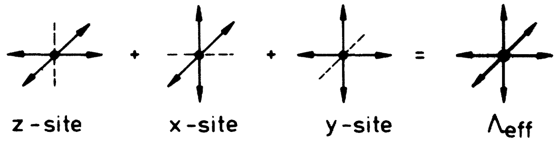

FIG. 8. Structure of the effective jump-frequency matrix for an octahedral interstitial in a bcc crystal: the full star is obtained by adding the planar jump-frequency matrices for the z, x, and y site.

The meaning of this effective-jump matrix is illustrated for the octahedral interstitial in Fig. 8. Whereas for the x, y, and z site we have only planar-jump matrices, the jump directions of which (full lines in Fig. 8) are perpendicular to the preferred axis (dashed line), by averaging over the different sites we obtain a jump matrix Λ^0_{eff} with cubic symmetry.

To derive the analogous expressions for $D_{ij}(\vec{R})$ in a *slightly distorted crystal*, we start as in Sec. II with the Lagrangian for the stationary state, since the gradient expansion is most easily done in this form

$$L[W^{\vec{m}}_\mu] = \frac{1}{4}\sum_{\substack{\vec{m}\vec{n}\\ \mu\nu}} \tilde{\lambda}^{\vec{m}\vec{n}}_{\mu\nu}(W^{\vec{n}}_\nu - W^{\vec{m}}_\mu)^2 - \sum_{\substack{\vec{m}\\ \mu}} p^{\vec{m}}_\mu W^{\vec{m}}_\mu , \tag{30}$$

with

$$W^{\vec{m}}_\mu = \rho^{\vec{m}}_\mu \exp(\beta E_{e\,\mu}^{\;\vec{m}}) ;$$
$$\tilde{\lambda}^{\vec{m}\vec{n}}_{\mu\nu} = \tilde{\lambda}^{\vec{n}\vec{m}}_{\nu\mu} = \nu \exp[-\beta(E_0 + E_s(^{\vec{m}\vec{n}}_{\mu\nu}))] . \tag{31}$$

Here $E_0 + E_s(^{\vec{m}\vec{n}}_{\mu\nu})$ is the energy in the saddle point between the equilibrium configurations $(\vec{m}\mu)$ and $(\vec{n}\nu)$. In the continuum limit we will have a local thermal equilibrium between different orientations on a given site or in a given unit cell. Actually, such a local equilibrium will already be reached after a few jumps, long before any long-range migration process has taken place, as has been pointed out already by Kronmüller *et al.*[5] Thus we have

$$\rho^{\vec{m}}_\mu = \exp(-\beta E_{e\,\mu}^{\;\vec{m}})W^{\vec{m}}_\mu \cong \exp(-\beta E_{e\,\mu}^{\;\vec{m}})W(\vec{R}^{\vec{m}}), \tag{31′}$$

i.e., the renormalized partial density $W^{\vec{m}}_\mu \cong W(\vec{R}^{\vec{m}})$ does not depend on the orientation and is slowly varying. Then we obtain from Eq. (30) for the total renormalized density in the unit cell $W_{\mathrm{tot}}(\vec{R}) = \sum_\mu W(\vec{R}^{\vec{m}}_\mu) = s\,W(\vec{R}^{\vec{m}})$

$$L[W_{\mathrm{tot}}] = \frac{1}{s}\int \frac{d^3R}{V_c}\left(\frac{1}{2}\sum_{ij}\tilde{D}_{ij}(\vec{R})\partial_{R_i}W_{\mathrm{tot}}(\vec{R})\partial_{R_j}W_{\mathrm{tot}}(\vec{R}) - p_{\mathrm{tot}}(\vec{R})W_{\mathrm{tot}}(\vec{R})\right) , \tag{32}$$

with the $\vec{R}$-dependent diffusion constant

$$\tilde{D}_{ij}(\vec{\mathrm{R}}^{\vec{\mathrm{m}}}) = \frac{1}{2}\sum_{\vec{\mathrm{h}}} R_i^{\vec{\mathrm{h}}} R_j^{\vec{\mathrm{h}}} \left(\frac{1}{s}\sum_{\mu\nu} \tilde{\lambda}_{\mu\nu}^{\vec{\mathrm{m}}\vec{\mathrm{m}}+\vec{\mathrm{h}}}\right)$$

$$= \frac{1}{2}\sum_{\vec{\mathrm{h}}} R_i^{\vec{\mathrm{h}}} R_j^{\vec{\mathrm{h}}} \tilde{\lambda}_{\mathrm{eff}}^{(\vec{\mathrm{h}})}(\vec{\mathrm{R}}^{\vec{\mathrm{m}}}) . \qquad (33)$$

A similar result can be obtained for the tetrahedral or octahedral interstitial in bcc [compare Eq. (29)]. Then $\lambda_{\mathrm{eff}}^{(\vec{\mathrm{h}})}$ has the "star structure" of $\Lambda_{\mathrm{eff}}^{0}$ shown in Fig. 8.

As in Sec. II, the tensor $\tilde{D}_{ij}(\vec{\mathrm{R}})$ depends only on the saddle-point properties, in particular on the interaction $E_s\binom{\vec{\mathrm{m}}\vec{\mathrm{n}}}{\mu\nu}$. In the presence of an external strain field $\epsilon_{kl}(\vec{\mathrm{R}})$ we obtain

$$\tilde{D}_{ij}(\vec{\mathrm{R}}) = \frac{1}{2}\sum_{\vec{\mathrm{h}}} R_i^{\vec{\mathrm{h}}} R_j^{\vec{\mathrm{h}}} \left[\frac{1}{s}\sum_{\mu\nu} \lambda^{0}{}_{\mu\nu}^{(\vec{\mathrm{h}})} \times \exp\left(\beta \sum_{kl} \epsilon_{kl}(\vec{\mathrm{R}}) P_{kl}^{s}\binom{\vec{\mathrm{h}}}{\mu\nu}\right)\right] \qquad (34)$$

where $\lambda^{0}{}_{\mu\nu}^{(\vec{\mathrm{h}})}$ is the jump matrix for the ideal crystal and $\underline{P}^{s}\binom{\vec{\mathrm{h}}}{\mu\nu}$ is the dipole tensor for the jump direction $\vec{\mathrm{h}}$. This formula simplifies further, if the dipole tensor $\underline{P}^{s}\binom{\vec{\mathrm{h}}}{\mu\nu}$ is independent of μ and ν, i.e., the same for all jumps with $\vec{\mathrm{h}} = \vec{\mathrm{m}} - \vec{\mathrm{n}}$ irrespective of the orientations. This is, for instance, the case for the saddle-point dipole tensor of the ⟨100⟩ dumbbell which has orthorhombic symmetry[12] and also for the saddle-point dipole tensor of the octahedral and tetrahedral interstitials in bcc. Under these conditions we obtain

$$\tilde{D}_{ij}(\vec{\mathrm{R}}) = \frac{1}{2}\sum_{\vec{\mathrm{h}}} R_i^{\vec{\mathrm{h}}} R_j^{\vec{\mathrm{h}}} \lambda^{0}{}_{\mathrm{eff}}^{(\vec{\mathrm{h}})} \exp\left(\beta \sum_{kl} \epsilon_{kl}(\vec{\mathrm{R}}) P_{kl}^{s}(\vec{\mathrm{h}})\right); \qquad (35)$$

$$\lambda^{0}{}_{\mathrm{eff}}^{(\vec{\mathrm{h}})} = \frac{1}{s}\sum_{\mu\nu} \lambda^{0}{}_{\mu\nu}^{(\vec{\mathrm{h}})} ,$$

i.e., the same result as for defects without preferred orientation [Eq. (14)]. Thus we see that then the anisotropy of the equilibrium configuration is quite unimportant and in a cubic crystal does not lead to anisotropic diffusion. This can only be due to the anisotropy of the dipole tensor $\underline{P}^{s}$ for the saddle-point configuration.

Finally we would like to write the equations of motions in terms of the total density

$$\rho_{\mathrm{tot}}(\vec{\mathrm{R}}^{\vec{\mathrm{m}}}) = \sum_{\mu} \rho_{\mu}^{\vec{\mathrm{m}}} = \frac{1}{s}\sum_{\mu} W_{\mathrm{tot}}(\vec{\mathrm{R}}^{\vec{\mathrm{m}}}) \exp\left(-\beta E_{e}{}_{\mu}^{\vec{\mathrm{m}}}\right)$$

$$\equiv W_{\mathrm{tot}}(\vec{\mathrm{R}}^{\vec{\mathrm{m}}}) \exp[-\beta E_{e}^{\mathrm{eff}}(\vec{\mathrm{R}}^{\vec{\mathrm{m}}})] \qquad (36)$$

Here we have used Eq. (31′). The differential equations for $W_{\mathrm{tot}}(\vec{\mathrm{R}})$ or $\rho_{\mathrm{tot}}(\vec{\mathrm{R}})$, respectively, then take the form

$$\sum_{ij} \partial_{R_i}\left(\tilde{D}_{ij}(\vec{\mathrm{R}})\partial_{R_j}\{\rho_{\mathrm{tot}}(\vec{\mathrm{R}}) \exp[\beta E_{e}^{\mathrm{eff}}(\vec{\mathrm{R}})]\}\right) + P_{\mathrm{tot}}(\vec{\mathrm{R}}) . \qquad (37)$$

By comparison with Eq. (15), we see that the effective interaction E_{e}^{eff}, defined by Eq. (36), replaces the usual interaction in the equilibrium configuration for cubic defects. The diffusion tensor is given by

$$D_{ij}(\vec{\mathrm{R}}) = \frac{1}{2}\sum_{\vec{\mathrm{h}}} R_i^{\vec{\mathrm{h}}} R_j^{\vec{\mathrm{h}}} \lambda^{0}{}_{\mathrm{eff}}^{(\vec{\mathrm{h}})} \exp\{-\beta[E_{s}^{(\vec{\mathrm{h}})}(\vec{\mathrm{R}}) - E_{e}^{\mathrm{eff}}(\vec{\mathrm{R}})]\} . \qquad (38)$$

IV. DIFFUSION IN A HOMOGENEOUSLY DEFORMED CRYSTAL

The simplest deformation state is a homogeneous strain ϵ_{kl}. Since then all interactions are constant throughout the crystal, D_{ij} is independent of $\vec{\mathrm{R}}$. For the density $\rho(\vec{\mathrm{R}})$ we have the usual diffusion equation

$$\sum_{ij} D_{ij}\,\partial_{R_i}\partial_{R_j}\,\rho(\vec{\mathrm{R}}) + p(\vec{\mathrm{R}}) = 0 . \qquad (39)$$

Under normal conditions the external strain ϵ is small, typically 10^{-4}, so that we can expand D_{ij} linearly in ϵ

$$D_{ij} = D_{ij}^{0} + \sum_{kl} d_{ijkl}\epsilon_{kl} ; \quad D_{ij}^{0} = D_0 \delta_{ij} \qquad (40)$$

for cubic crystals.

The "elastodiffusion" tensor d_{ijkl} describes the influence of the homogeneous strain on the diffusion. It has the symmetries

$$d_{ijkl} = d_{jikl} = d_{ijlk} , \qquad (41)$$

and, for cubic crystals, in addition the symmetry against change of the pairs ij and kl. Thus, d_{ijkl} has the same symmetry as the elasticity tensor C_{ijkl} and therefore in cubic crystals three independent constants d_{11}, d_{12}, and d_{44} (in Voigt's notation) corresponding to the elastic constants c_{11}, c_{12}, and c_{44}.

Most conveniently, d_{ijkl} can be written with the help of six orthonormalized basis tensors $\underline{b}^{(\lambda)}$, which form the space of all symmetrical 3 × 3 matrices[15] (like ϵ_{kl} and D_{ij})

$$d_{ijkl} = \sum_{\lambda=1}^{6} d^{(\lambda)} b_{ij}^{(\lambda)} b_{kl}^{(\lambda)}$$

with

$$\sum_{ij} b_{ij}^{(\lambda)} b_{ij}^{(\lambda')} = \delta_{\lambda\lambda'}$$

$$\underline{b}^{(1)} = \frac{1}{\sqrt{3}}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}; \quad \underline{b}^{(2)} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 0 \end{bmatrix};$$

$$\underline{b}^{(3)} = \frac{1}{\sqrt{6}}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{2} \end{bmatrix} \quad \underline{b}^{(4)} = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}; \tag{42}$$

$$\underline{b}^{(5)} = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}; \quad \underline{b}^{(6)} = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

$$d^{(1)} = d_{11} + 2d_{12}; \quad d^{(2)} = d^{(3)} = d_{11} - d_{12};$$
$$d^{(4)} = d^{(5)} = d^{(6)} = 2d_{44}.$$

The physical meaning of the $\underline{b}^{(\lambda)}$ is that they are eigenstates to any fourth-rank tensor of cubic symmetry like d_{ijkl} or C_{ijkl} with eigenvalues $d^{(\lambda)}$ or $c^{(\lambda)}$. $\underline{b}^{(1)}$ describes a homogeneous deformation which couples to the constant $d^{(1)} = d_{11} + 2d_{12}$ or to the compression modulus $c^{(1)} = c_{11} + 2c_{12}$, respectively. $\underline{b}^{(2)}$ and $\underline{b}^{(3)}$ are [110] shear deformations giving rise to the constant $d^{(2)} = d_{11} - d_{12}(c^{(2)} = c_{11} - c_{12})$, whereas for the [100] shear deformations $\underline{b}^{(4)}$, $\underline{b}^{(5)}$, and $\underline{b}^{(6)}$ the constant $d^{(4)} = 2d_{44}(c^{(4)} = 2c_{44})$ enters.

By expanding the diffusion tensor D_{ij} of Eq. (38) with E_e^{eff} from Eq. (36) linear in the strain ϵ_{kl}, we obtain

$$d_{ijkl} = \frac{\beta}{2} \sum_{\vec{h}} R_i^{\vec{h}} R_j^{\vec{h}} \lambda^{0\,(\vec{h})}[P_{kl}^s(\vec{h}) - P_0^e \delta_{kl}]$$

with

$$P_0^e = \tfrac{1}{3}\,\mathrm{Tr}\,\underline{P}^e. \tag{43}$$

Here P_{ij}^e is the dipole tensor in the equilibrium configuration, which is isotropic for cubic defects $(P_{ij}^e = P_0^e \delta_{ij})$. For noncubic defects we have, according to Eq. (36), to average over all equivalent orientations, so that only the invariant $P_0^e = \frac{1}{3}\,\mathrm{Tr}\,\underline{P}^e$ enters. Thus the anisotropy of the noncubic defect does not influence d_{ijkl}.

For a nearest-neighbor jump matrix $\lambda^{0\,(\vec{h})}$, we can extract the "ideal" diffusion constant D_0 from Eq. (43), so

$$d_{ijkl} = 3D_0\beta \langle r_i^{(\vec{h})} r_j^{(\vec{h})} [P_{kl}^s(\vec{h}) - P_0^e \delta_{kl}] \rangle, \tag{44}$$

where $\langle\ \rangle$ means an average over all jump directions $\vec{R}^{\vec{h}}$. With this formula the constants $d^{(1)}$, $d^{(2)}$, and $d^{(3)}$ can be easily calculated. The results are

$$d^{(1)} = (\underline{b}^{(1)}, \underline{d}\,\underline{b}^{(1)}) = D_0\beta\,\mathrm{Tr}(\underline{P}^s - \underline{P}^e)$$

$$\begin{aligned} d^{(2)} &= \tfrac{1}{2}(\underline{b}^{(2)}, \underline{d}\,\underline{b}^{(2)}) + \tfrac{1}{2}(\underline{b}^{(3)}, \underline{d}\,\underline{b}^{(3)}) \\ &= \tfrac{1}{2} D_0\beta[(r_1^2 - r_2^2)(P_{11}^s - P_{22}^s) \\ &\qquad + (r_2^2 - r_3^2)(P_{22}^s - P_{33}^s) \\ &\qquad + (r_3^2 - r_1^2)(P_{33}^s - P_{11}^s)] \end{aligned}$$

$$\begin{aligned} d^{(4)} &= \frac{1}{3} \sum_{\lambda=4}^{6} (\underline{b}^{(\lambda)}, \underline{d}\,\underline{b}^{(\lambda)}) \\ &= D_0\beta(r_1 r_2 P_{12}^s + r_2 r_3 P_{23}^s + r_3 r_1 P_{13}^s). \end{aligned}$$

In this form $\vec{r} = \vec{r}^{\vec{h}}$ and $\underline{P}^s = \underline{P}^s(\vec{h})$ refer to an arbitrary jump direction $\vec{h}$. One does not have to average over all cubic equivalent directions, since the expressions are already invariant against cubic-symmetry operations.

Note that only the elastodiffusion constant $d^{(1)}$, coupling to a uniform compression, depends on the dipole tensor $\underline{P}^e$ of the equilibrium configuration, and only on its trace. This is a consequence of averaging over all equivalent orientations. Since a compression does not break the cubic symmetry, the change ΔD of the diffusions constant D is given by

$$\Delta D = \tfrac{1}{3} D_0\beta\,\mathrm{Tr}(\underline{P}^s - \underline{P}^e)\,\mathrm{Tr}\,\epsilon = -\beta p(\Delta V^s - \Delta V^e), \tag{46}$$

where p is the corresponding pressure and $\Delta V^s - \Delta V^e$ is the activation volume for diffusion $\mathrm{Tr}\,\underline{P} = (c_{11} + 2c_{12})\Delta V$. This result is well known.[3,16]

By measuring all three constants $d^{(1)}$, $d^{(2)}$, and $d^{(4)}$, one can get very useful information about the symmetry of the saddle-point configuration. For the most important symmetries, $\underline{P}^s$ has the following form

$$\underline{P} = \begin{bmatrix} P_{11} & 0 & 0 \\ 0 & P_{11} & 0 \\ 0 & 0 & P_{11} \end{bmatrix}, \quad \begin{bmatrix} P_{11} & 0 & 0 \\ 0 & P_{22} & 0 \\ 0 & 0 & P_{22} \end{bmatrix},$$

$$\begin{bmatrix} P_{11} & P_{12} & P_{12} \\ P_{12} & P_{11} & P_{12} \\ P_{12} & P_{12} & P_{11} \end{bmatrix}, \quad \begin{bmatrix} P_{11} & P_{12} & 0 \\ P_{12} & P_{11} & 0 \\ 0 & 0 & P_{33} \end{bmatrix}, \tag{47}$$

for cubic, tetragonal, trigonal, and orthorhombic symmetry, respectively.

Now, depending on the geometries, the constants $d^{(\lambda)}$ are proportional to the combinations of P_{ij} elements listed in Table I. Thus, as long as one restricts oneself to these relatively high symmetries, a measurement of $d^{(1)}$, $d^{(2)}$, and $d^{(4)}$ allows a complete determination of the symmetry and strength of $\underline{P}^s$: the vanishing constant determines

TABLE I. Elastodiffusion constants for different saddle-point symmetries.

Symmetry[a]	Cubic	Tetragonal	Trigonal	Orthorhombic
$d^{(1)}$	$P^s_{11}-P^e_0$	$\frac{1}{3}(P^s_{11}+2P^s_{22})-P^e_0$	$P^s_{11}-P^e_0$	$\frac{1}{3}(2P^s_{11}+P^s_{33})-P^e_0$
$d^{(2)}$	0	$P^s_{11}-P^s_{22}$	0	$P^s_{11}-P^s_{33}$
$d^{(4)}$	0	0	P^s_{12}	P^s_{12}

[a] Note that the $\vec{R}^{\vec{h}}$ are jump vectors, i.e., differences between neighboring equilibrium positions. Therefore they are not necessarily connected with the symmetry of the saddle point, even if in most cases $\frac{1}{2}\vec{R}^{\vec{h}}$ is the distance to the saddle point.

the symmetry, the other ones determine the nonzero elements of the dipole tensor $\underline{P}^s$, provided that $\underline{P}^e$ or ΔV^e, the volume change for the equilibrium position, is known. However, this statement is no longer valid, if the saddle-point symmetry is lower or if $\underline{P}^s(\vec{h}_{\mu\nu})$ depends explicitly on the orientations of the defect, as discussed in Sec. III. The whole scheme is quite analogous to the one derived by Trinkaus[17] and Nowick *et al.*[18] for the dipole tensor of the equilibrium configuration: elastodiffusion gives the equivalent information about the dipole tensor of the saddle point as Huang scattering[19] or mechanical relaxation[18] give for the dipole tensor of the equilibrium position.

V. DISCUSSION AND POSSIBLE APPLICATIONS

We have shown in the preceding sections that external (homogeneous) fields can induce an anisotropy of the diffusion of defects. In anisotropic fields the different jump directions become inequivalent even for cubic defects like vacancies or octahedral interstitials in fcc crystals. This is due to the anisotropy of the saddle-point configuration.

For external elastic fields, the double force tensor $\underline{P}^s$ of the defect in the saddle-point configuration determines the potential energy of the defect in the external field and thus also the anisotropy of the diffusion tensor. As shown in Sec. IV, the elements P^s_{ij} of the double-force tensor can in principle be determined by measuring in a single crystal the change of the diffusion constant $\Delta\underline{D}$ induced by applying uniaxial stresses in different crystallographic directions. From Eq. (46) one can easily estimate the expected relative change of D. Using an external strain $\epsilon \cong 10^{-4}$ and a value of $\underline{P}^s \cong 10$ eV, which are both rather high values, one obtains at room temperature a value of $\Delta D/D_0 \cong 4\times10^{-2}$, i.e., D changes at most by a few percent. Unfortunately this is just about the accuracy of measuring diffusion constants, and a direct determination is very difficult. But this diffusion anisotropy can play a role in the reaction of defects due to much larger internal strains caused by other defects.

A. Defect reactions

Defect reactions are usually described in terms of rate equations with rate constants K (for a review on the work of irradiation produced defects see Ref. 20). The *rate constants* depend on the diffusivities of the reactants and the range of the interaction. Let us assume one reactant to be immobile (e.g., dislocation loops) and the other one (e.g., vacancies or interstitials) to be mobile with diffusion constant D. A reaction is assumed to take place if the distance between the reactants is less than R_0, the radius of the reaction volume. Outside of this reaction volume one has to take into account the long-range interaction between the defects, e.g., in metals the elastic-dipole interaction[21] is the most important one. For low-defect concentration the reaction constant K is then given by the total flux of mobile defects into the reaction volume if the density is maintained at unit concentration at infinity.[2] To calculate the density distribution and from this the total flux one has to use Eqs. (15) or (37) which include the change of the potential energy of the equilibrium and saddle-point configurations due to the interaction. This introduces a space-dependent diffusion constant which for the case of point defect absorption has previously been discussed (see e.g., Refs. 2 and 22). For angular-dependent interactions these equations cannot be solved analytically but it turns out that a spherically symmetric ansatz for the renormalized density

$$W(\vec{R}) = \rho_{\text{tot}}(\vec{R}) \exp[\beta E_e^{eH}(\vec{R})] \cong n_0(R) \tag{48}$$

yields good results[2] for the rate constant K. If this ansatz is used in the Lagrangian, Eq. (32), one obtains a radial equation for $n_0(R)$

$$\frac{1}{R^2}\partial_R R^2 \tilde{D}_{\text{eff}}(R)\partial_R n_0(R) + p(R) = 0 . \tag{49}$$

Here $\tilde{D}_{\text{eff}}(\mathrm{R})$ is the angular average of the space-dependent diffusion tensor $\tilde{D}_{ij}(\vec{R})$ given in Eqs. (14) or (34)

$$\tilde{D}_{\text{eff}}(R) = \int \frac{d\Omega}{4\pi} \sum_{ij} r_i \tilde{D}_{ij}(\vec{R}) r_j . \tag{50}$$

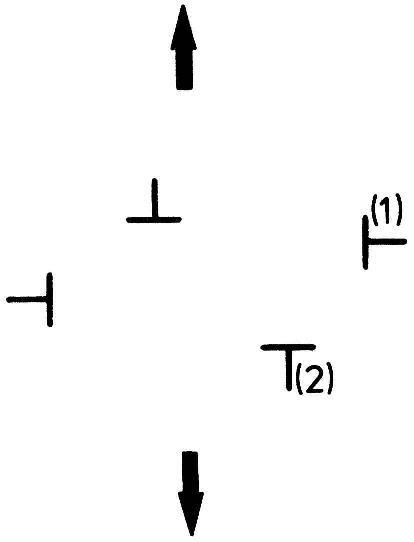

FIG. 9. Dislocations in an external stress (→). (1) extra plane perpendicular to the stress axis terminating in type-1 dislocation; (2) extra plane parallel to the stress axis terminating in type-2 dislocation.

Equation (49) has to be solved with the boundary conditions $p(R)=0$; $n_0(R\to\infty)=1$; $n_0(R-R_0)=0$; the reaction constant K is then given by the total flux through the surface of the reaction volume

$$K=4\pi R_0^2\tilde{D}_{\mathrm{eff}}(R_0)\partial_R n_0(R)\big|_{R_0}\,. \tag{51}$$

As one can see, the interaction enters only via $\tilde{D}_{\mathrm{eff}}(R)$, and thus K, depends only on the interaction in the saddle-point configuration. Due to the influence of the interaction K becomes temperature dependent[2] and for an interaction with attractive directions (like the elastic-dipole interaction in metals) the range which determines the reaction constant is approximately given by the distance at which the potential energy gained by the approaching defect in the saddle-point configuration is equal to the thermal energy kT. The anisotropy of the diffusion does not enter explicitly, of course it determines the value of $\tilde{D}_{\mathrm{eff}}(R)$.

A case where the anisotropy of the diffusion induced by an external stress can enter explicitly is *irradiation creep*. During irradiation under external stress, extra planes perpendicular to the stress axis terminating in type-1 dislocations (see Fig. 9) grow faster than parallel planes terminating in type-2 dislocations. An explanation for this effect, the so-called stress-induced preferred absorption (SIPA) mechanism, has been suggested by Heald and Speight[23] and worked out by several authors.[23-25] In this model the strong elastic polarizability of interstitials by external shears leads to a relatively large and induced change $\Delta P_{ij}(\epsilon)$ of the dipole tensor, resulting in a stronger interaction with dislocations of type 1, and hence in a preferred growth of the corresponding lattice planes. Savino[6] recently suggested that the nonequivalence of the jump directions in external fields due to the anisotropy of the saddle-point configurations could add to the difference in arrival rates. The exponential dependence of $\tilde{D}(R)$ [Eq. (14)] on $\epsilon(R)$ which is the sum of the external strain ϵ_{ext} and the dislocation strain ϵ_{dis} leads to an interference term $\sim\epsilon_{\mathrm{ext}}\epsilon_{\mathrm{dis}}$ due to first-order interaction. Whereas for a configuration with cubic symmetry this leads only to isotropic swelling, the anisotropy of the saddle-point configuration leads to different arrival rates. This has motivated the present paper.

B. Diffusion in homogeneous force fields

Finally we would like to discuss the implication of our results for the measurement of diffusion constants in homogeneous force fields like Gorski effect and electromigration.

Gorski effect[26] is the mechanical relaxation due to the redistribution over macroscopic distances of highly mobile defects (e.g., hydrogen atoms dissolved in bcc metals) under the influence of an inhomogeneous stress. The stress dependence of the diffusion coefficient causes a difference of the relaxation times to reach equilibrium measured when applying and releasing the load, respectively. When a crystal is bent, a dilatational field is produced which depends linearly on the distance across the sample. Due to the interaction with this strain field, the dissolved hydrogen atoms diffuse to the expanded part of the sample. This causes additional anelastic strain whose time development is measured. Since the hydrogen atoms are diffusing under the influence of an external strain, the time for reaching the new (inhomogeneous) equilibrium distribution is determined by the strain-dependent diffusion tensor given in Eq. (38) if one neglects the small difference between the strain field in a saddle point and a neighboring equilibrium site. For crystals with inversion symmetry, the neglected term contributes to the change of the diffusion constant only to second order in the external strain. Thus in principle all stress and anisotropy effects discussed in Sec. IV for homogeneous stresses should show up in the relaxation time. On the other hand, when the load is released the hydrogen atoms relax to the homogeneous equilibrium distribution. This time they only feel the anelastic strain caused by the inhomogeneous defect distribution, which in general is small (except close to phase transitions). The relaxation time in this case is essentially determined by the ideal diffusion constant D_0. Thus, in principle, one can determine the elastodiffusion tensor d_{ijkl}, Eq. (40), by making Gorski effect measurements in differently oriented single crystals, and, in particular, by measuring the difference of the relaxation times between loading and unloading in each case. However, since the estimated change of D is only a few percent, it is clear that in practice this difference is hard to determine. In addition, other effects like irreversible motion of dislocations contribute to the mechanical relaxation when the stress is applied and make an experimental determination of the stress dependence of the diffusion coefficient by Gorski effect even more improbable.

Electromigration[3, 27] can be discussed in close analogy to Gorski effect. Here an external electrical field $\vec{F}$ couples to the effective charge $\underline{q}^*$ of a defect. Two terms can contribute to $\underline{q}^*$: the electrostatic charge and a term arising from the "electron wind force," i.e., from the momentum transfer of the accelerated electrons. The total force on the defect and thus the effective charge can be calculated by linear-response theory.[28] In general, the effective charge $\underline{q}^*$ is a tensor quantity. It depends on the configuration of the defect because of the variation of the scattering power for electrons with the change of configuration. For a diffusing defect this means that during a jump the electrical force can change in magnitude and direction

$$\vec{K}_{\mathrm{electr}}(\vec{x}) = \underline{q}^*(\vec{x})\vec{F}\,. \tag{52}$$

$\underline{q}^*$ must have lattice symmetry, and thus is an oscillating function of $\vec{x}$. As has been argued before[29, 30] $\underline{q}^*$ should have a maximum in the saddle-point configuration. The tensor symmetry of $\underline{q}^*$ is determined by the symmetry of the configurations. In the following we shall restrict to simple defects, like vacancies or hydrogen atoms on octahedral sites in fcc crystals. Then the saddle point is half way between two neighboring equilibrium sites, and along the jump path one can find a common eigenvector representation of the tensor $\underline{q}^*(\vec{x})$ with one eigenvector in the jump direction. For a vacancy jump in fcc crystals, e.g., the symmetry is (110) orthorhombic.

To obtain the change of the potential energy due to the electric field one has to integrate the force along the jump path

$$E(\vec{x}) - E(\vec{x}_0) = \int_{\vec{x}_0}^{\vec{x}} (d\vec{x}', \underline{q}^*(\vec{x}')\vec{F})\,. \tag{53}$$

The jump rates, Eq. (6), and the diffusion tensor, Eq. (17), only contain energy differences between equilibrium sites and saddle points. If $\vec{x}$ and $\vec{x}_0$ are both equilibrium sites we can decompose the integral in Eq. (53) into path integrals along individual jump paths characterized by jump vectors $\vec{R}^{\vec{h}}$

$$E_e(\vec{x}) - E_e(\vec{x}_0) = \sum_{\vec{h}} n_{\vec{h}}\, \Delta E^{\vec{h}}\,, \tag{54}$$

with $n_{\vec{h}}$ the number of jumps with jump vector $\vec{R}^{\vec{h}}$ and

$$\Delta E^{\vec{h}} = \int_0^{\vec{R}^{\vec{h}}} (d\vec{x}', \underline{q}^*(\vec{x}')\vec{F})\,, \tag{55}$$

the potential-energy difference between two equilibrium sites separated by a jump vector $\vec{R}^{\vec{h}}$. To calculate $\Delta E^{\vec{h}}$ we use the eigenvector representation of the (symmetric) effective charge tensor $\underline{q}^*$ along the jump path $\vec{R}^{\vec{h}}$

$$q^*_{ij}(\vec{x}) = \sum_\sigma e_i^\sigma Q^\sigma(\vec{x}) e_j^\sigma\,. \tag{56}$$

Because one of the eigenvectors is parallel to $\vec{R}^{\vec{h}}$, only the longitudinal eigenvalue $Q^l(\vec{x})$ belonging to this eigenvector enters in $\Delta E^{\vec{h}}$. For the cases considered $Q^l(\vec{x})$ is independent of the jump direction and one obtains

$$\Delta E^{\vec{h}} = (\vec{F}, \vec{R}^{\vec{h}})\langle Q^l \rangle\,, \tag{57}$$

with the average longitudinal eigenvalue

$$\langle Q^l \rangle = |\vec{R}^{\vec{h}}|^{-1} \int_0^{\vec{R}^{\vec{h}}} dx'\, Q^l(x')\,. \tag{58}$$

The energy difference between an equilibrium site and a neighboring saddle point can be calculated by the same method yielding[31]

$$E_s(\vec{R} + \tfrac{1}{2}\vec{R}^{\vec{h}}) - E_e(\vec{R}) = \tfrac{1}{2}(\vec{R}^{\vec{h}}, \vec{F})\langle Q^l \rangle\,. \tag{59}$$

One sees that only the average longitudinal eigenvalue $\langle Q^l \rangle$ enters into the diffusion constant. Because of the smallness of the energy differences (typically 10^{-12} eV per jump distance for a metal) one can expand the effective diffusion constant, Eq. (17), in powers of the external field $\vec{F}$

$$D_{ij}(\vec{R}) = D_0\delta_{ij} - \tfrac{1}{4}\beta\,\langle Q^l \rangle \sum_{\vec{h}} R_i^{\vec{h}} R_j^{\vec{h}} (\vec{R}^{\vec{h}}, \vec{F})\lambda^{0\,(\vec{h})} + O(F^2)\,. \tag{60}$$

Due to the particular form of the energy differences, Eqs. (57) and (59), being proportional to the jump vector $\vec{R}^{\vec{h}}$, the effective-diffusion constant does not change in first order in the electrical field for crystals with inversion symmetry. This can easily be seen from Eq. (60). The sum over $\vec{h}$ of an odd power of $\vec{R}^{\vec{h}}$ is zero. Thus electromigration is determined by the ideal diffusion constant and no anisotropy effects, similar to the ones discussed in this paper for "elastomigration," occur.

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