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Transport in nearly-free-electron metals. IV. Electromigration in zinc

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The electromigration of a weak scattering impurity in a Bloch electron gas is reconsidered formally while taking into account the conduction-electron screening in the Hartree approximation. Several simplifying approximations are introduced into the formal expressions for the effective charge, and a numerical evaluation of the formulas for Z_a^* and Z_c^* in zinc yields values in good agreement with experiment. Anisotropic relaxation times, resulting from the observed phonon dispersion curves, tend to favor mass transport in the basal plane.

I. INTRODUCTION

The driving force for electromigration, or atomic migration in the presence of electric fields and currents, has been the subject of much theoretical interest. It has been customary to divide the force on the diffusing atom into two parts, the electrostatic force of the applied electric field and the "electron-wind" force, due to collisions between the atom and the current carrying electrons. The early theories of Fiks[1] and Huntington and Grone[2] determine the wind force by calculating the momentum transfer by the electrons per unit time as they are scattered by the atom. Bosvieux and Friedel[3] noted that the electron current induces a dipolarlike distortion in the screening cloud associated with the diffusing atom, resulting in a net electrostatic force. Later, Sorbello[4] extended this viewpoint to a more realistic model of a metal within the framework of pseudopotential theory. More recently, a number of calculations[5-7] have been performed using Kubo's linear-response formalism.[8] A review of the theoretical treatments of electromigration has been written by Sorbello.[9]

We are especially interested in the effective charge of Zn since it is one of the materials in which single-crystal measurements[10] have been made. In his investigation, Routbort found that the driving force was about half as effective along the hexagonal axis as perpendicular to it. In light of the nearly isotropic conductivity of Zn, these results were initially puzzling,[11] which stimulated the work of Chan and Huntington[12,13] on high-temperature conductivity and subsequently the present work.

In order to treat anisotropic effects realistically, the theory must be extended to include band-structure effects. The first efforts in this direction were made by Fiks[14,15] and by Feit and Huntington.[11] In both of these theories, the diffusing atom was considered to be in an extended plane-wave state, an assumption which appears more appropriate for a free particle. In Sec. II the general theory of band-structure effects in electromigration is reconsidered by combining, to a certain extent, the approaches of Feit[11] and Sorbello.[4] The effects of band structure on electron screening are included in a formal way via the "dielectric-matrix" formalism.[16] The dielectric matrix is essentially treated as a scalar in Sec. III, and a semiempirical pseudopotential form factor is used in the numerical computations of the electron wind force. A simplified model of the Fermi surface of Zn is introduced in which the effects of Brillouin-zone plane intersections are considered one pair at a time. Also in this section we summarize the results of Chan and Huntington[13] for the electron mean free path $\vec{\lambda}$ which are used in the calculation. Finally, a discussion of the results is presented in Sec. IV.

II. FORCE ON A DIFFUSING ATOM IN A DRIFTING GAS OF BLOCH ELECTRONS

We calculate here the effects of electric current on an atom diffusing in a crystal lattice. If $\vec{R}$ represents the coordinate of the diffusing particle and $\vec{P}$ its conjugate momentum, we write

$$\frac{d}{dt}\langle \vec{P}\rangle = -\langle\Psi|\frac{\partial H}{\partial \vec{R}}|\Psi\rangle \,, \tag{1}$$

where H is the total Hamiltonian and Ψ the exact wave function of the system, which we treat as having Hermitian properties. Invoking the Born-Oppenheimer approximation, we take the migrating ion to be a heavy classical particle, essentially fixed at each point along its diffusion path as it interacts with the electrons. $d\langle\vec{P}\rangle/dt$ then represents the force on the classical particle and (1) becomes

$$\vec{F} = -\langle\Psi|\frac{\partial H}{\partial \vec{R}}|\Psi\rangle \,. \tag{2}$$

We wish to calculate only the current-dependent part of the driving force so that H may be replaced by the electron-defect interaction potential U. (In the case of interstitial diffusion, neglecting lattice distortion, U may be a single ionic potential. For diffusion by the vacancy mechanism, U must include the potential of the jumping ion as well as the "semivacancies" at either end of the diffusion path.)[11] In terms of the one-electron wave functions ψ, (2) becomes

$$\vec{F} = -\sum_{\vec{k}} f(\vec{k}) \langle \psi_{\vec{k}} | \frac{\partial U}{\partial \vec{R}} | \psi_{\vec{k}} \rangle . \tag{3}$$

In Eq. (3), $f(\vec{k})$ represents the electron-distribution function in the presence of the applied electric field. It, of course, must be perturbed from the Fermi-Dirac function f^0 in order to reflect the presence of current. In what follows, we will assume that $f(\vec{k})$ is a known function, having been determined from an independent solution of the Boltzmann equation in the high-temperature range. In our numerical computations, the actual solution of Chan and Huntington[13] for the electron mean free path $\vec{\lambda}$ will be used.

For an isolated interstitial, take U to be of the form $u(\vec{r}-\vec{R})$, $\vec{r}$ being the electron coordinate and $\vec{R}$ the coordinate of the diffusing ion. [In the case of diffusion by the vacancy mechanism, we would take

$$U = u(\vec{r}-\vec{R}) - u(\vec{r}-\vec{R}_1) - u(\vec{r}-\vec{R}_2) , \tag{4}$$

$\vec{R}_1$ and $\vec{R}_2$ denoting the positions of the semivacancies.] Fourier expanding u and substituting in (3) gives

$$\vec{F} = \sum_{\vec{k}} \sum_{\vec{q}} f(\vec{k})\, i\vec{q}\, u(\vec{q})\, e^{-i\vec{q}\cdot\vec{R}} \langle \psi_{\vec{k}} | e^{i\vec{q}\cdot\vec{r}} | \psi_{\vec{k}} \rangle . \tag{5}$$

At this point in his formal development, Feit[11] replaced u everywhere by a potential screened as it would be in a free electron gas without current flow. He then calculated the electron wave functions ψ, using first-order perturbation theory, neglecting other contributions to screening. We depart from that approach here and proceed as in Sorbello,[4] treating U as an unscreened potential in (3), but accounting for the electron-electron interactions by calculating the ψ's self-consistently (in the Hartree approximation) to first order in the defect potential. Unlike the Sorbello treatment, we assume a weak, *local* potential for the ions, and treat the case of Bloch electrons. Our zero-order wave functions, therefore, will have a spatially varying part of the form

$$\phi_{\vec{k}} = \sum_{\vec{G}} a_{\vec{G}}(\vec{k})\, e^{i(\vec{k}+\vec{G})\cdot\vec{r}} , \tag{6}$$

where the sum is, in general, over the set of all reciprocal-lattice vectors. From first-order perturbation theory, we can write the wave function $\psi_{\vec{k}}$ as

$$\psi_{\vec{k}} = |\phi_{\vec{k}}\rangle + \sum_{\vec{k}'} \frac{|\phi_{\vec{k}'}\rangle \langle \phi_{\vec{k}'} | W | \phi_{\vec{k}} \rangle}{\epsilon(\vec{k}) - \epsilon(\vec{k}') + i\alpha} . \tag{7}$$

In Eq. (7), the potential W must be self-consistently determined. The Bloch functions ϕ are the self-consistent eigenstates of the crystal-lattice potential. W, therefore, includes the defect potential, as well as the change in the screening potential of the conduction electrons due to the presence of the defect. In order to determine the latter, we need an expression for the total conduction-electron charge density, which may be written

$$n(\vec{r}) = \sum_{\vec{k}} f(\vec{k})\, \psi^*_{\vec{k}} \psi_{\vec{k}} . \tag{8}$$

Fourier transforming Eq. (2.12) gives

$$n(\vec{q}) = \frac{1}{\Omega} \int \sum_{\vec{k}} f(\vec{k})\, \psi^*_{\vec{k}} \psi_{\vec{k}}\, e^{-i\vec{q}\cdot\vec{r}}\, d\vec{r} , \tag{9}$$

Ω being the crystal volume. In terms of the Bloch functions ϕ,

$$n(\vec{q}) = \frac{1}{\Omega} \sum_{\vec{k}} f(\vec{k}) \langle \phi_{\vec{k}} | e^{-i\vec{q}\cdot\vec{r}} | \phi_{\vec{k}} \rangle + \frac{1}{\Omega} \sum_{\vec{k},\vec{k}'} f(\vec{k}) \frac{\langle \phi_{\vec{k}} | e^{-i\vec{q}\cdot\vec{r}} | \phi_{\vec{k}'} \rangle \langle \phi_{\vec{k}'} | W | \phi_{\vec{k}} \rangle}{\epsilon(\vec{k}) - \epsilon(\vec{k}') + i\alpha} . \tag{10}$$

The first term on the right-hand side of Eq. (10) represents the zero-order charge density, i.e., the charge density in the absence of the impurity, depending only on the Bloch wave functions ϕ. We need an expression for the change in charge density due to the presence of the defect, which we call Δn. After some algebra, we arrive at the following expression for $\Delta n(\vec{q})$:

$$\Delta n(\vec{q}) = \frac{1}{\Omega} \sum_{\vec{k},\vec{k}'} \langle \phi_{\vec{k}} | e^{-i\vec{q}\cdot\vec{r}} | \phi_{\vec{k}'} \rangle \langle \phi_{\vec{k}'} | W | \phi_{\vec{k}} \rangle \times \left(\frac{2 f^0(\vec{k})}{\epsilon(\vec{k}) - \epsilon(\vec{k}')} - 2 i \pi g(\vec{k})\, \delta(\epsilon(\vec{k}) - \epsilon(\vec{k}')) \right) , \tag{11}$$

where $g(\vec{k}) = f(\vec{k}) - f^0(\vec{k})$. Next we explicitly divide the potential W into two parts

$$W = U + \Delta V_s , \tag{12}$$

where ΔV_s means the change in the screening potential due to the defect. ΔV_s can be further broken up into $\Delta V_s^0 + \Delta V_s^c$, where the superscript zero denotes that part of V_s independent of the current, and V_s^c is the current-dependent part. With this notation,

$$W = U + \Delta V_s^0 + \Delta V_s^c . \tag{13}$$

Now write

$$W^0 = U + \Delta V_s^0 , \tag{14}$$

so that W^0 represents the defect potential screened as it would be in a stationary gas of Bloch electrons. From (11), we get for the change in charge density in the zero current case the expression

$$\Delta n^0(\vec{q}) = \frac{1}{\Omega} \sum_{\vec{k}, \vec{k}'} \langle \phi_{\vec{k}} | e^{-i\vec{q}\cdot\vec{r}} | \phi_{\vec{k}'} \rangle \langle \phi_{\vec{k}'} | W^0 | \phi_{\vec{k}} \rangle \frac{2f^0(\vec{k})}{\epsilon(\vec{k}) - \epsilon(\vec{k}')} , \tag{15}$$

which is consistent with an expression derived by Stoddart *et al.*[17] [their Eq. (3.10)].

Poisson's equation can now be used to relate Δn and ΔV_s. Specifically,

$$\Delta V_s(\vec{q}) = (4\pi e^2/q^2)\, \Delta n(\vec{q}) . \tag{16}$$

Using (16) and recalling that $\Delta V_s^0 = W^0 - U$, Eq. (11) yields

$$U(\vec{q}) = \sum_{\vec{G}} \epsilon(\vec{q}, \vec{q} + \vec{G})\, W^0(\vec{q} + \vec{G}) . \tag{17}$$

Here ϵ is the dielectric matrix whose rows and columns are labeled by reciprocal-lattice vectors and its elements are given by

$$\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{H}) = \delta_{\vec{G},\vec{H}} - \frac{4\pi e^2}{\Omega |\vec{q} + \vec{G}|^2} \sum_{\vec{k}, \vec{L}} \frac{2f^0(k)}{\epsilon(\vec{k}) - \epsilon(\vec{k} + \vec{q} + \vec{L})} \langle \phi_{\vec{k}} | e^{-i(\vec{q}+\vec{G})\cdot\vec{r}} | \phi_{\vec{k}+\vec{q}+\vec{L}} \rangle \langle \phi_{\vec{k}+\vec{q}+\vec{L}} | e^{i(\vec{q}+\vec{H})\cdot\vec{r}} | \phi_{\vec{k}} \rangle , \tag{18}$$

where $\vec{L}$, $\vec{G}$, and $\vec{H}$ are reciprocal-lattice vectors. In Eq. (18), we have used the notation of Sham and Ziman.[18] Equation (17) resembles the scalar equation $U(\vec{q}) = \epsilon(\vec{q})\, W^0(\vec{q})$ which relates the screened and unscreened potentials in the free-electron gas. The relationship between these potentials in the presence of the crystal lattice (Bloch electrons) is much more complicated. In order to proceed, we assume that Eq. (17) can be inverted, and formally write

$$W^0(\vec{q}) = \sum_{\vec{G}} \epsilon^{-1}(\vec{q}, \vec{q} + \vec{G})\, U(\vec{q} + \vec{G}) . \tag{19}$$

We can now use Eqs. (11) and (16) to derive an expression for $\Delta n^c(\vec{q})$, the current-dependent change in the charge density, in terms of ϵ and ϵ^{-1}. We get

$$\begin{aligned} \Delta n^c(\vec{q}) = -2\pi i \sum_{\vec{G}, \vec{L}, \vec{M}} & B(\vec{q} + \vec{L}, \vec{q} + \vec{M}) \\ & \times \epsilon^{-1*}(\vec{q} + \vec{L}, \vec{q}) \\ & \times \epsilon^{-1} (\vec{q} + \vec{M}, \vec{q} + \vec{G})\, U(\vec{q} + \vec{G}) , \end{aligned} \tag{20}$$

where the matrix B is given by

$$\begin{aligned} B(\vec{q} + \vec{G}, \vec{q} + \vec{H}) = \sum_{\vec{k}, \vec{L}} & g(\vec{k})\, \delta(\epsilon(\vec{k}) - \epsilon(\vec{k} + \vec{q} + \vec{L})) \\ & \times \langle \phi_{\vec{k}} | e^{-i(\vec{q}+\vec{G})\cdot\vec{r}} | \phi_{\vec{k}+\vec{q}+\vec{L}} \rangle \\ & \times \langle \phi_{\vec{k}+\vec{q}+\vec{L}} | e^{i(\vec{q}+\vec{H})\cdot\vec{r}} | \phi_{\vec{k}} \rangle . \end{aligned} \tag{21}$$

Equation (20) is the central result of this section; it represents the distortion of the screening cloud around the defect in the presence of the current. We are now ready to return to the expression for the force, Eq. (5), and substitute our result from Eq. (20). The complete expression for the current-dependent force becomes

$$\begin{aligned} \vec{F} = -2\pi \sum_{\vec{q}} \vec{q} e^{i\vec{q}\cdot\vec{R}} \sum_{\vec{G}, \vec{L}, \vec{M}} & B(\vec{q} + \vec{L}, \vec{q} + \vec{M}) \\ & \times \epsilon^{-1}(\vec{q} + \vec{M}, \vec{q} + \vec{G})\, U(\vec{q} + \vec{G}) \\ & \times \epsilon^{-1*}(\vec{q} + \vec{L}, \vec{q})\, u^*(\vec{q}) . \end{aligned} \tag{22}$$

Equation (22) can be made more explicit by substituting for B from its definition. Also, we can make the complete $\vec{R}$ dependence of the expression explicit by substituting for $U(\vec{q} + \vec{G})$, the defect potential. In our later computations, we will be interested in self-diffusion in Zn single crystals (via the vacancy mechanism). Therefore, for $U(\vec{q} + \vec{G})$ we use

$$\begin{aligned} U(\vec{q} + \vec{G}) = u(\vec{q} + \vec{G}) (e^{-i(\vec{q}+\vec{G})\cdot\vec{R}} & - e^{-i(\vec{q}+\vec{G})\cdot\vec{R}_1} \\ & - e^{-i(\vec{q}+\vec{G})\cdot\vec{R}_2}) \end{aligned} \tag{23}$$

which follows from Eq. (4). Making these two substitutions in Eq. (22) results in

$$\begin{aligned} \vec{F} = -\frac{2\pi}{\hbar} \sum_{\vec{k}, \vec{k}'} & g(\vec{k})\, \delta(\epsilon(\vec{k}) - \epsilon(\vec{k}')) \\ & \times \sum_{\vec{q}} \hbar \vec{q} \sum_{\vec{G}, \vec{L}, \vec{M}} \langle \phi_{\vec{k}} | e^{-i(\vec{q}+\vec{L})\cdot\vec{r}} | \phi_{\vec{k}'} \rangle \\ & \times \langle \phi_{\vec{k}'} | e^{i(\vec{q}+\vec{M})\cdot\vec{r}} | \phi_{\vec{k}} \rangle \epsilon^{-1}(\vec{q} + \vec{M}, \vec{q} + \vec{G}) \\ & \times u(\vec{q} + \vec{G})\, \epsilon^{-1*}(\vec{q} + \vec{L}, \vec{q}) \\ & \times u^*(\vec{q})\, S(\vec{q}, \vec{G}, \vec{R}) , \end{aligned} \tag{24}$$

where we have collected the $\vec{R}$ dependence of the expression into the term

$$S(\vec{q},\vec{G},\vec{R})=e^{i\vec{q}\cdot\vec{R}}\left(e^{-i(\vec{q}+\vec{G})\cdot\vec{R}}-e^{-i(\vec{q}+\vec{G})\cdot\vec{R}_1}-e^{-i(\vec{q}+\vec{G})\cdot\vec{R}_2}\right). \tag{25}$$

For purposes of comparison, it is instructive to consider the form of Eq. (24) in the free-electron-gas limit. Taking the matrix ϵ over into a scalar function, and replacing the Bloch functions by plane waves, we get

$$\vec{F}_{(\mathrm{FE})}=-\frac{2\pi}{\hbar}\sum_{\vec{k},\vec{k}'}g(\vec{k})\hbar(\vec{k}'-\vec{k})\,|w^0(\vec{k}'-\vec{k})|^2\times S(\vec{k}'-\vec{k},\vec{O},\vec{R})\,\delta(\epsilon(\vec{k})-\epsilon(\vec{k}')). \tag{26}$$

As pointed out by Sorbello,[4] Eq. (26) resembles the sum of momentum transfers for transitions between states on the Fermi sphere, multiplied by the corresponding transition probability. For the vacancy case, the formula is complicated by the appearance of the factor S, which accounts for the more complex defect structure involved in vacancy diffusion.

Equation (24), however, is not subject to such a simple interpretation. Self-consistent screening of the potentials in the Bloch electron gas is accounted for formally by the appearance of elements of the inverse dielectric matrix. In simple terms, the screening cloud surrounding the diffusing particle is distorted by the presence of the lattice, even the zero-current case, its distortion depending on the position $\vec{R}$ of the particle relative to the perfect lattice. The factor $-\hbar\vec{q}$ in Eq. (24) also deserves some comment. It apparently plays a role analogous to $\hbar(\vec{k}-\vec{k}')$, or momentum transfer, in the free-electron case [Eq. (26)]. From the form of the matrix elements in Eq. (24), we see that in the summation $\vec{q}$ is restricted to take on values of the form

$$\vec{q}=\vec{k}'-\vec{k}+\vec{N}, \tag{27}$$

where $\vec{N}$ is a reciprocal-lattice vector. In terms of plane waves, this is suggestive of simultaneous scattering by the defect and Bragg reflection by the crystal lattice, resulting in a momentum transfer $\hbar(\vec{k}-\vec{k}'-\vec{N})$. As previously noted,[9] however, we know that the electron wind force cannot be analyzed in terms of momentum transfer on a per collision basis, since the Bloch wave functions are not momentum eigenstates.

III. APPLICATION TO ZINC

A. Nearly-free-electron model

In applying Eq. (24), by far the most serious complications would arise in attempting to calculate $\epsilon(\vec{q},\vec{q}+\vec{G})$ and $\epsilon^{-1}(\vec{q},\vec{q}+\vec{G})$. Although ϵ has been the topic of considerable general discussion in the literature,[19] little attention has been paid to actual numerical computations, particularly of off-diagonal terms. Some approximate calculations relevant to insulators and semiconductors are discussed by Sinha[20] in his review article. For metals, directional effects in screening have been largely ignored. In applying our nearly-free-electron (NFE) model to Zn, we will follow the latter course and replace $\epsilon(\vec{q},\vec{q}+\vec{G})$ with the free-electron scalar form. We will, however, account for the Bloch nature of the zero-order states in Eq. (24) with a two-orthogonalized-plane-wave (2-OPW) model. We should warn that the consistency of this procedure is not clear; the directional effects being ignored are not estimable in any obvious way. Arguments that they are small for a NFE metal would seem to apply equally well to the band-structure effects being retained. We will see that those which are included in the computations do affect the quantitative results without significantly altering the overall qualitative picture.

In Eq. (24), the above approximation results in the expression

$$\vec{F}=-2\pi\sum_{\vec{k},\vec{k}'}g(\vec{k})\,\delta(\epsilon(\vec{k})-\epsilon(\vec{k}'))\times\sum_{\vec{q}}\vec{q}\sum_{\vec{M}}\langle\phi_{\vec{k}}|e^{-i\vec{q}\cdot\vec{r}}|\phi_{\vec{k}'}\rangle\times\langle\phi_{\vec{k}'}|e^{i(\vec{q}+\vec{M})\cdot\vec{r}}|\phi_{\vec{k}}\rangle\times w^0(\vec{q}+\vec{M})\,w^{0*}(\vec{q})\,S(\vec{q},\vec{M},\vec{R}), \tag{28}$$

w^0 being a screened potential ($w^0=u/\epsilon$). This formula is similar to those derived by Feit[11] and Fiks,[15] except that it contains "cross terms" of the form $w^0(\vec{q}+\vec{M})w^{0*}(\vec{q})$, $\vec{M}\neq\vec{0}$. Such terms were absent from the above mentioned formulas because the authors both assumed a plane-wave state for the diffusing particle, resulting in a sort of "pseudomomentum-conservation" condition. As pointed out earlier, the diffusing particle is treated here as a heavy classical particle.

In Fig. 1, we display the semiempirical form factor $F(q)$ which was substituted for the spherically symmetric ionic potential w^0 in Eq. (28). The form factor was determined by interpolation between points determined by Stark and Falicov.[21] A recent form factor calculation by Greenfield and Wiser[22] agrees quite well with the values which we used.

$F(q)$ was also used to construct our Fermi surface model, approximated by considering distortions arising from one pair of Brillouin-zone walls at a time. The Fermi surface of Zn is distorted

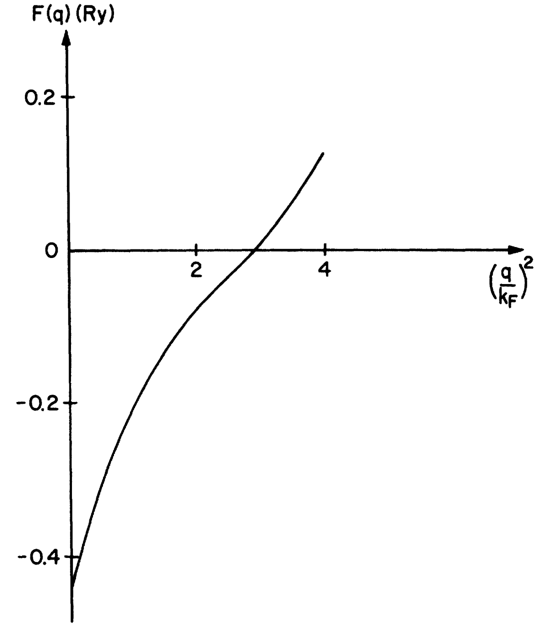

FIG. 1. Semiempirical form factor for Zn.

TABLE I. Reciprocal-lattice vectors which intersect the Fermi surface of Zn and associated coupling strength parameters g.

	$\lvert\vec{K}\rvert$ (k_F)	g
$\vec{K}_1$	1.596	0.023
$\vec{K}_2$	1.740	0.001
$\vec{K}_3$	1.914	0.047

by three sets of planes whose reciprocal-lattice vectors (RLV's) are the vectors $\vec{K}_1$, $\vec{K}_2$, and $\vec{K}_3$ listed in Table I. The amount of distortion caused by each plane is determined by the coupling strength parameter, $g = k_F|F(K)|/\epsilon_F K$. The relevant g values for Zn at 650 K are also shown in Table I. Since the K_2 RLV falls very near the zero of $F(q)$, we therefore ignore the distortion caused by this set of planes, which results in considerable simplification. The remaining RLV's were considered one pair at a time, as illustrated in Fig. 2. In this 2-OPW model, the standard equation

$$\epsilon/\epsilon_F = (k/k_F)^2 + 2\gamma\{(\gamma-\mu) \pm [(\gamma-\mu)^2 + g^2]^{1/2}\}, \quad (29)$$

gives the electron mean energy near the Kth zone. In Eq. (29), $\gamma = K/2k_F$, $\mu = k_{\parallel}/k_F$, as in Fig. 2. The plus sign in Eq. (29) goes with $\mu > \gamma$. Equation (29) reveals that for the slanting, or K_3 RLV's, the values of γ and g are such that the region corresponding to $\mu > \gamma$ is not occupied. This results in a considerable amount of missing free area from the Fermi surface in this simple model, as illustrated by the shaded areas of Fig. 3. Figure 3 also illustrates the division of the surface into regions in which the effect of a single pair of planes is con-

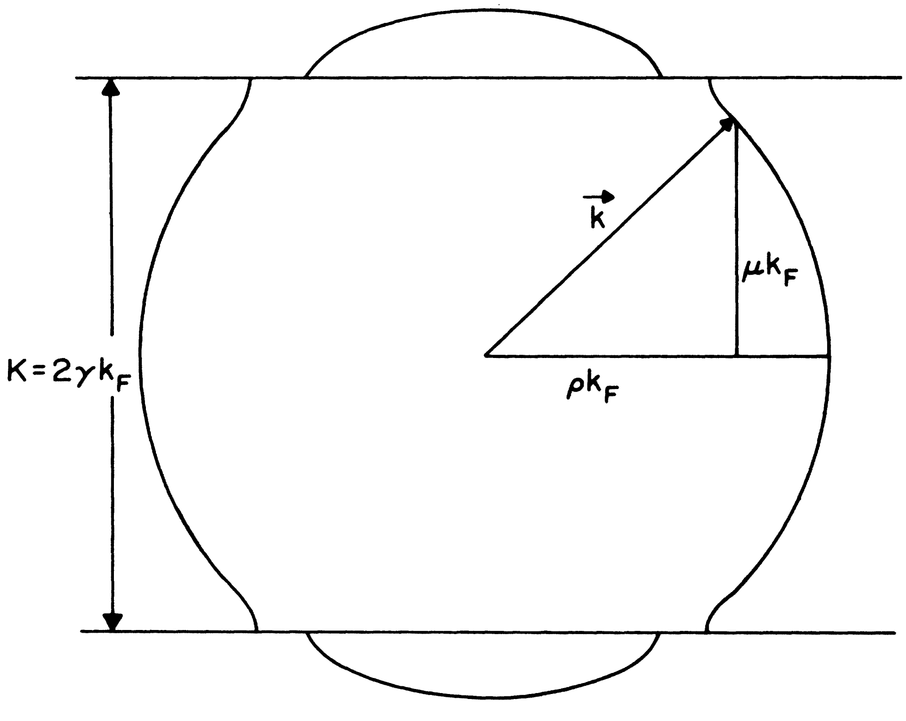

FIG. 2. Distortion of Fermi sphere by a single pair of Brillouin zone planes.

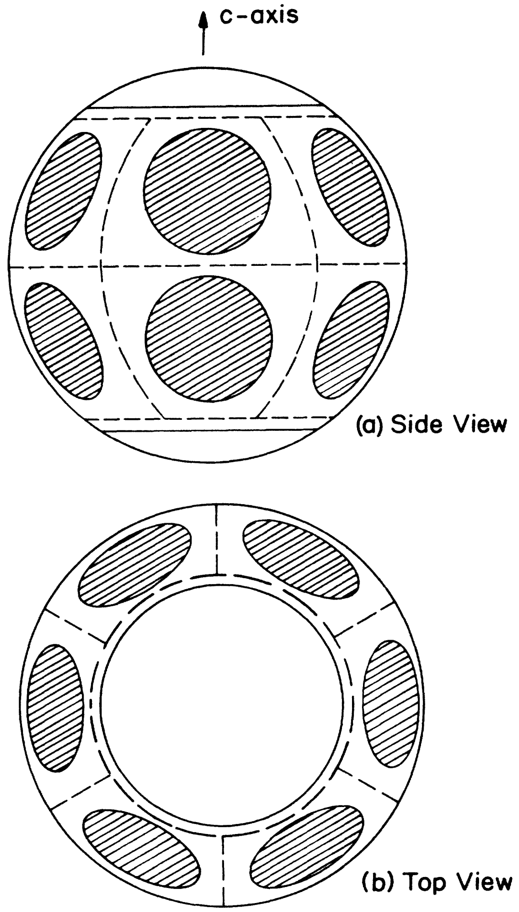

FIG. 3. Division of Fermi surface into regions. Missing area shown shaded.

sidered. The two plane-wave wave-functions consistent with this model have the standard form

$$\phi_{\vec{k}} = \alpha(\mu)\, e^{i\vec{k}\cdot\vec{r}} + \beta(\mu)\, e^{i(\vec{k}+\vec{K})\cdot\vec{r}}\,, \tag{30}$$

where α and β are given by

$$\alpha(\mu) = \tfrac{1}{2}\{1 + |\gamma-\mu| / [(\gamma-\mu)^2 + g^2]^{1/2}\}^{1/2}, \tag{31}$$

$$\beta(\mu) = \pm\tfrac{1}{2}\{1 - |\gamma-\mu| / [(\gamma-\mu)^2 + g^2]^{1/2}\}^{1/2}. \tag{32}$$

This form for the wave functions allows explicit evaluation of the matrix elements in Eq. (28).

Following Chan and Huntington[13] we take the perturbed part of the electron-distribution function to be

$$g(\vec{k}) = e\vec{E}\cdot\vec{\lambda}(\vec{k})\,\delta(\epsilon(\vec{k}) - \epsilon_F)\,, \tag{33}$$

where

$$\lambda_{a,c} = \tau_{a,c}(\vec{k})\, v_{a,c}(\vec{k})\,, \tag{34}$$

the subscripts referring to the direction of the applied electric field, either in the basal plane a or along the hexagonal axis c. The $\vec{k}$ dependence of τ turns out to be weak, therefore we replace $\tau_{a,c}(\vec{k})$ by the appropriate average value. This was the procedure followed by Chan and Huntington in their conductivity calculations. The relevant numerical values are $\langle\tau_a\rangle = 0.47\times10^{-14}$ sec and $\langle\tau_c\rangle = 0.28\times10^{-14}$ sec. The $\vec{k}$ dependence of the velocity factor in Eq. (34) is included as prescribed by our 2-OPW model of the Fermi surface, i.e.,

$$v_{\parallel} \simeq (\hbar k_F \mu/m)[1 - 2\beta^2(\mu)]$$

and

$$v_{\perp}(\mu) = \hbar k_F \rho/m\,,$$

where the subscripts refer to the reciprocal-lattice vector which defines the axis of cylindrical symmetry for each particular region. The a and c components of $\vec{v}$ are then obtained from $v_{\parallel}$ and $v_{\perp}$ by a straightforward coordinate transformation.

We turn our attention now to the $\vec{R}$-dependent factor in Eq. (28). Denote the direction of the applied field by the subscript i (i being either a or c in our calculations). The effective force for atomic migration; i.e., $Z_w^i eE_i$, is obtained from the R-dependent force by averaging over the diffusion path. That is,

$$Z_w^i eE_i = \frac{1}{l_i}\int_{\vec{R}_1}^{\vec{R}_2} \vec{F}\cdot d\vec{R}\,, \tag{35}$$

where $l = \vec{R}_2 - \vec{R}_1$ is the vector which defines the diffusion jump, and l_i is its component in the i direction. (For electromigration in the a direction in hcp Zn, we are ignoring here the small contribution of the plane to plane jump to the effective charge in this direction.) Taking the origin of coordinates at the point $\vec{R} = \vec{R}_1$, and using Eqs. (28) and (33)–(35) gives

$$Z_w^i = -2\pi \sum_{\vec{k},\vec{k}'} \tau_i v_i(\vec{k})\,\delta(\epsilon(\vec{k}) - \epsilon_F)\,\delta(\epsilon(\vec{k}) - \epsilon(\vec{k}'))\sum_{\vec{q}}(\vec{q})_l \sum_{\vec{M}} \langle\phi_{\vec{k}}| e^{-i\vec{q}\cdot\vec{r}} |\phi_{\vec{k}'}\rangle$$
$$\times\langle\phi_{\vec{k}'}| e^{i(\vec{q}+\vec{M})\cdot\vec{r}} |\phi_{\vec{k}}\rangle\, w^0(\vec{q}+\vec{M})\, w^{0*}(\vec{q})\,\frac{\int_0^l S(\vec{q},\vec{M},\vec{R})\, dR}{\cos\theta_{l,i}}\,, \tag{36}$$

where we have introduced the notation $l_i = l \cos\theta_{l,i}$. Of course, if the applied field is in the direction of the diffusion jump, then $(\vec{q})_l = (\vec{q})_i$ and $\cos\theta_{l,i} = 1$. We need only consider the real part of the integral in Eq. (36) since all of the other quantities are real in our model. This is explicitly evaluated as

$$\begin{aligned} \mathrm{Re}\left(\frac{1}{l}\int_0^l S(\vec{q},\vec{M},\vec{R})\,dR\right) &\equiv \hat{S}(\vec{q},\vec{M},\vec{l}) \\ &= \frac{\sin(\vec{M}\cdot\vec{l})}{\vec{M}\cdot\vec{l}} \\ &\quad - \frac{\sin(\vec{q}\cdot\vec{l}) - \sin(\vec{M}\cdot\vec{l}) + \sin[(\vec{q}+\vec{M})\cdot\vec{l}]}{\vec{q}\cdot\vec{l}}\,. \end{aligned} \tag{37}$$

B. Calculations and results

For the purpose of numerical computation, the sums over $\vec{k}'$ and $\vec{k}$ in Eq. (36) can be transformed into integrals in the usual way; the δ functions resulting in two surface integrals over the Fermi surface. The result is

$$\begin{aligned} Z_w^i = C \int_{\mathrm{FS}}\int_{\mathrm{FS}} \tau_i v_i(\vec{k}) & \times \sum_{\vec{q},\vec{M}} \frac{(-\vec{q})_l}{\cos\theta_{l,i}} \\ & \times \langle \phi_{\vec{k}} | e^{-i\vec{q}\cdot\vec{r}} | \phi_{\vec{k}'} \rangle \langle \phi_{\vec{k}'} | e^{i(\vec{q}+\vec{M})\cdot\vec{r}} | \phi_{\vec{k}} \rangle \\ & \times F(q) F(|\vec{q}+\vec{M}|)\hat{S}(\vec{q},\vec{M},\vec{l}) \\ & \times \frac{dS}{v(\vec{k})}\frac{dS'}{v(\vec{k}')}\,, \end{aligned} \tag{38}$$

where $C = \Omega_0^2/16\pi^5\hbar^2$. ($\Omega_0$ is the atomic volume.) [Equation (38) is consistent with the expression derived by Sham,[7] except that the latter applies only to an isolated interstitial.] The explicit form of the matrix elements can be seen by substituting from Eq. (6) for the Bloch functions $\phi_{\vec{k}}$. The result is

$$\begin{aligned} Z_w^i = C \int_{\mathrm{FS}}\int_{\mathrm{FS}} \tau_i v_i(\vec{k}) \sum_{\vec{G},\vec{G}',\vec{K},\vec{K}'} -\frac{(\vec{k}'-\vec{k}+\vec{G}'-\vec{G})}{\cos\theta_{l,i}}\, a^*_{\vec{G}}(\vec{k})\, a_{\vec{G}'}(\vec{k}')\, a^*_{\vec{K}'}(\vec{k}')\, a_{\vec{K}}(\vec{k})\, F(\vec{k}-\vec{k}'+\vec{K}-\vec{K}')F(\vec{k}'-\vec{k}+\vec{G}'-\vec{G}) \\ \times \hat{S}(\vec{k}'-\vec{k}+\vec{G}'-\vec{G}, \vec{G}-\vec{G}'-\vec{K}+\vec{K}', \vec{l})\frac{dS}{v(\vec{k})}\frac{dS'}{v(\vec{k}')}\,. \end{aligned} \tag{39}$$

The integrations in Eq. (39) were carried out numerically and the results are displayed in Table II. The calculated values represent the electron wind contribution to the effective charge. As discussed in Sec. I, we have divided the total effect charge Z^* into an electrostatic contribution from the applied electric field (Z_e) and the electron-wind force, i.e., $Z^* = Z_e + Z_w$. In order to compare the calculated wind force contributions with experimentally determined Z^*, the electrostatic contribution (in our model, $Z_e = +2$) must be added.[23] The calculations were carried out in stages, each feature of the model being introduced separately to assess its quantitative effect. The first calculation was performed using a spherical Fermi surface and 1-OPW wave functions for the electrons. In subsequent calculations, distortion of the Fermi surface and 2-OPW wave functions were added. The experimental results of Routbort[10] are also displayed in Table II.

IV. DISCUSSION

In Sec. II we have reconsidered band-structure effects in electromigration by calculating the force on a weak-scattering impurity in a drifting gas of Bloch electrons. This formal treatment differs from previous treatments in that we explicitly include directional effects in conduction electron screening via self-consistent calculation of the

TABLE II. Calculated values of Z_w.

	Calc. A[a]	Calc. B[b]	Calc. C[c]		Calc. C$-Z_e$	Experiment
Z_w^c:	−6.4	−5.0	−4.2	Z_c^*:	−2.2	−1.95 ± 0.15
Z_w^a:	−9.1	−6.7	−5.7	Z_a^*:	−3.7	−4.4 ± 0.4

[a] Calc. A–1 plane wave, spherical Fermi surface (minus missing cap areas).

[b] Calc. B–1 plane wave, distorted Fermi surface.

[c] Calc. C–2 plane waves, distorted Fermi surface.

scattered electron wave functions. As a result, our formal expression for the driving force, Eq. (24), depends explicitly on the dielectric matrix. Although we introduced $\epsilon(\vec{q},\vec{q}+\vec{G})$ in a formal way, in our numerical computations we did not attempt to go beyond the approximation of treating ϵ as a scalar. In this limit, our formula reduces to those of Feit and Fiks, except for the restriction they impose by treating the migrating atom as if it were in a plane-wave state. In the limit of zero lattice potential, Eq. (24) agrees with the result of Sorbello.

The agreement between our calculated values and experiment must be considered quite good, even though the predicted anisotropy is somewhat low. There is, unfortunately, a certain amount of arbitrariness in some of the factors which contribute to the computed values of Z^*. First, although we calculate Z_w, in order to compare with experiment we assume that $Z_e = +2$, corresponding to the full electrostatic force being present. Although we feel this is essentially correct, it remains a somewhat controversial question. Second, the values of $\langle\tau_i\rangle$ are taken from an independent solution of the Boltzmann equation. However, since they are approximately consistent with the experimental conductivity, they might alternatively be considered as empirically determined parameters. In fact, closer agreement with the experimental anisotropy would have been obtained if the relaxation times had been fitted to the actual experimental conductivity values. Finally, the calculated values of Z_w are of course dependent on choice of pseudopotential form factor.

Despite the qualifications discussed in the previous paragraph, several qualitative conclusions emerge from the numerical computations. Quite clearly, the anisotropy in effective charge is due primarily to the anisotropy in relaxation times. Unlike the conductivity calculation, where Fermi surface distortion compensates the anisotropic relaxation times quite closely, only a slight compensation occurs in the electron wind force. We find that $Z_w^a/Z_w^c = 1.35$, compared to $\langle\tau_a\rangle/\langle\tau_c\rangle = 1.65$. This confirms the suggestion of Chan and Huntington[13] based on rough estimates of the wind forces.

Table II also points out the magnitude of the various band-structure effects which we have considered. The effect of the missing Fermi surface area is quite drastic since the wind-force formula involves two integrations over the Fermi surface. Another result of Fermi surface distortion is the vanishing normal component of electron velocity (and mean free path) at a zone boundary; this tends to reduce transport perpendicular to the zone boundary. There is also the fact that Bloch waves are not momentum eigenfunctions, so that a given scattering event does not give rise to a well-defined momentum transfer. In terms of free electrons, an electron may be simultaneously scattered by the defect and Bragg reflected. We find that this also tends to decrease the effective charge.

We should also comment on the effect of defect structure in the case of vacancy diffusion. Although the full calculations were not repeated for an isolated point defect, some preliminary calculations indicate that the effective charge for the vacancy case is roughly 30% lower than for the interstitial case.

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