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Theory of electromigration in noble and transition metals

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We have used the scattering theory and the muffin-tin approximation to evaluate the electron wind force acting on an atom in an electric field. Within the relaxation-time approximation, the force depends in an intricate manner on the nature of the Fermi surface, the electronic wave functions, the Fermi velocities, and the host- and the solute-metal phase shifts. The formalism is general and applicable to both simple and transition metals. The effective valences for several solutes in noble-metal hosts have been evaluated. It is shown that in general the effective valence cannot be related to the residual resistivity of a solute, even for host metals which have nearly spherical Fermi surfaces but nonnegligible phase shifts at the Fermi energy. However, for a jellium matrix, the electron wind force is directly proportional to the residual resistivity; this is a result which has been obtained here, within the framework of the Boltzmann equation, from a nonlinear calculation of the impurity potential.

I. INTRODUCTION

When a constant electric field is applied to a solid there is a force exerted on the atoms by the electric field which causes the transport of atoms. This force is in addition to the one which already exists in the absence of the electric field due to the concentration gradient of point defects. The electric field exerts the force on the ions in two ways: First, there is a direct electrostatic force on the ions. Second, the electric field causes a slight change in the distribution function of the Fermi electrons. This is proportional to the electric field and exerts an indirect electronic or polarization force on the moving atom. In most cases this is the dominant contribution to the driving force for electromigration. The contribution of this electronic term was first calculated by Bosvieux and Friedel[1] within the Born approximation in a pioneering work some 20 years ago. They also calculated the residual resistivity of the solute within the same approximation and showed that the electronic contribution to the driving force could be related directly to the residual resistivity of the solute. Sorbello[2] and Genoni and Huntington[3] have recently used the pseudopotential method [within the one and two orthogonalized-plane-wave (OPW) framework, respectively] to estimate this contribution in simple metals. We remark in this connection that in the cases where the perturbation created by an impurity or a defect is not weak, the screening of the defect is unlikely to be treated properly within the linear-screening approximation.

In this paper we propose a new method, based on the muffin-tin approximation,[4] which allows the calculation of the effective valence for simple as well as transition metals. Section II is devoted to the calculation of the force on the moving atom and it is shown that, except for a free-electron metal, the force cannot be expressed in terms of its residual resistivity. In Sec. III numerical calculations for noble-metal-based alloys are presented and concluding remarks are given in Sec. IV.

II. FORCE ON THE MOVING ATOM

Within the Born-Oppenheimer approximation, the force, $\vec{F}(\vec{R})$, exerted by the electron gas on an atom situated at $\vec{R}$, may be written as[5–7]

$$\vec{F}(\vec{R}) = -\sum_k f(k) \left\langle \psi_k \left| \frac{\partial V(|\vec{r}-\vec{R}|)}{\partial \vec{R}} \right| \psi_k \right\rangle , \quad (1)$$

where ψ_k is the Bloch function of an electron with wave vector $\vec{k}$ and band index n ($k \equiv \vec{k}, n$), $V(r)$ the screened potential at r, and $f(k)$ the Fermi distribution function which in the presence of an electric field, $\vec{E}$, may be written, within the linearized Boltzmann-equation approximation[8] as

$$f(k)=f_0(k)+g(k)\ , \tag{2}$$

$$g(k)=-e\tau(k)\vec{V}_k\cdot\vec{E}\frac{\partial f_0(k)}{\partial E}\ , \tag{3}$$

where $f_0(k)$ is the Fermi distribution function in the absence of the electric field, $\tau(k)$ is the relaxation time due to scattering by phonons, and $\vec{V}_k$ is the electron group velocity. The force due to the electric field is governed by the function $g(k)$ in the Fermi distribution function. At low temperatures when the Fermi surface is well defined, $\partial f_0/\partial E$ is a δ function and the component of the force exerted by the electric field in the direction of the electric field at an atom situated at the origin may be written as

$$F=\frac{2\Omega_0}{8\pi 3}\int_{\mathrm{FS}}\frac{dS_k}{|\nabla_k E_k|}e\tau(k)\vec{V}_k\cdot\vec{E} \times\int d^3r\,\psi_k^*(r)\psi_k(r) \times(\hat{r}\cdot\vec{E})\frac{dV(r)}{dr}\ , \tag{4}$$

where Ω_0 is the unit-cell volume and the integration in Eq. (4) is over the Fermi surface. Hereafter, Rydberg atomic units ($e^2=2$, $\hbar=1$, $m=\frac{1}{2}$) will be used.

We now make the muffin-tin (MT) approximation in which the whole crystal is divided into touching spheres (muffin tins) and the potential outside these spheres (the interstitial region) is assumed constant. Within the augmented-plane-wave (APW) formalism,[9] the wave function inside a MT sphere can be written as

$$\psi_k(\vec{r})=\frac{4\pi}{(\Omega_0)^{1/2}}\sum_{lm}i^l A_{lm}(k)\,Y_{lm}(\hat{r})R_l(k,r)\ , \tag{5}$$

where

$$A_{lm}(k)=\sum_{\vec{g}}j_l(k_gR)Y_{lm}^*(\hat{k}_g) \tag{6}$$

with $\vec{k}_g=\vec{k}+\vec{g}$. Here $a_g(k)$ are the coefficients of expansion of the wave function which can be readily obtained in an APW calculation, j_l is the spherical Bessel function, Y_{lm} the spherical harmonics, and R_l the radial wave function which, of course, depends on k only through the energy E_k. R_l is normalized so that at the MT radius R, $R_l(k,R)=1$. $\vec{g}$ denotes a reciprocal-lattice vector.

The form of the wave function given in Eq. (5) results in a considerable simplification of the integrals occurring in Eq. (4), and one finds

$$F=\int_{\mathrm{FS}}\frac{dS_k}{|\nabla_k E_k|}e\tau(k)\vec{V}_k\cdot\vec{E}\ I(k)\ , \tag{7}$$

where

$$I(k)=\frac{4}{\pi}\sum_{lm}\sum_{l'm'}i^{-l+l'}A_{lm}^*(k)A_{l'm'}(k)\int_0^R dr\,r^2R_l(k,r)R_{l'}(k,r)\frac{dV(r)}{dr}\int d\hat{r}\,Y_{lm}^*(\hat{r})Y_{l'm'}(\hat{r})\cos\theta\ , \tag{8}$$

where we have assumed the field E to be in Z direction and $\cos\theta=\hat{r}\cdot\hat{E}$. The integral over the solid angle, $d\hat{r}$, can be easily evaluated using the Clebsch-Gordan coefficients,[10] and is given by

$$\int d\hat{r}\,Y_{lm}^*(\hat{r})Y_{l'm'}(\hat{r})\cos\theta=\left[\frac{(l-m)(l+m)}{(2l+1)(2l'+1)}\right]^{1/2}\delta_{l',l-1}\delta_{m'm}+\left[\frac{(l-m+1)(l+m+1)}{(2l+1)(2l'+1)}\right]^{1/2}\delta_{l',l+1}\delta_{m'm}\ . \tag{9}$$

Since the potential outside the muffin-tin sphere is constant the radial wave function in the interstitial region may be expanded in terms of the spherical Bessel (j_l) and Neumann (n_l) functions,

$$R_l(k,r)=\frac{1}{N_l(K,R)}[j_l(kR)\cos\delta_l(E)-n_l(KR)\sin\delta_l(E)]\ , \tag{10}$$

where

$$N_l(K,R)=j_l(KR)\cos\delta_l(E)-n_l(KR)\sin\delta_l(E)\ , \tag{11}$$

$K=\sqrt{E}$, and $\delta_l(E)$ is the phase shift of the muffin-tin potential $V(r)$ evaluated at the energy E. With this it is easy to show using the Schrödinger equation (see Appendix A for the derivation) that

$$\int_0^R r^2 R_l(k,r) R_{l+1}(k,r)\frac{dV}{dr}=\frac{\sin[\delta_{l+1}(E)-\delta_l(E)]}{N_l(K,R)N_{l+1}(K,R)} . \tag{12}$$

We thus find that

$$I(k)=-\frac{8}{\pi}\sum_{lm}\left[\frac{(l-m+1))l+m+1)}{(2l+1)(2l+3)}\right]^{1/2}\left[\frac{1}{N_lN_{l+1}}\right]\sin(\delta_{l+1}-\delta_l)\mathrm{Im}[A_{lm}^{*}(k)A_{l+1,m}(k)] , \tag{13}$$

where N_l and N_{l+1} are the values of $N_l(K,R)$ and $N_{l+1}(K,R)$, respectively, evaluated at the Fermi energy E_F, and Im denotes the imaginary part of the function. Equation (7) in conjunction with Eq. (13) thus gives the electronic contribution to the force on an atom of the matrix in its normal stable position. By using the properties of spherical harmonics it is easy to show that this force vanishes.

To calculate the force F^S on an impurity atom in substitutional position one needs to calculate the electron wave functions in the presence of the solute potential $V^S(r)$. We neglect here the size effect of the solute and assume the potential to be zero outside the muffin-tin sphere. Following ordinary scattering theory[11,12] the wave function ψ_K^S inside the muffin-tin sphere can be written as a sum of two terms, the wave function ψ_k of the unperturbed lattice and an outgoing spherical wave ψ_{out}^S,

$$\psi_k^S=\psi_k+\psi_{\mathrm{out}}^S . \tag{14}$$

The scattered wave can be expressed in terms of Henkel functions $h_l=j_l+in_l$,

$$\psi_k^S(\vec{r})=\sum_{lm} i^l B_{lm}^S h_l(Kr)Y_{lm}(\hat{r}) , \quad r>R . \tag{15}$$

Inside the muffin-tin spheres, ψ_k^S may also be written as a linear combination of the solutions R_l^S of the radial Schrödinger equation for impurity potential

$$\psi_k^S=\sum_{lm} i^l A_{lm}^S(k)R_l^S(k,r)Y_{lm}(\hat{r}) , \tag{16}$$

where, again R_l^S is normalized to unity at $r=R$. Outside the muffin-tin sphere, R_l^S may be written in terms of the phase shifts δ_l^S of the impurity potential

$$R_l^S(k,r)=\frac{1}{N_l^S(K,R)}[j_l(Kr)\cos\delta_l^S(E) -n_l(Kr)\sin\delta_l^S(E)] , \tag{17}$$

with

$$N_l^S(K,R)=j_l(KR)\cos\delta_l^S(E)-n_l(KR)\sin\delta_l^S(E) . \tag{18}$$

The requirement that the wave function and its radial derivative determined from Eq. (14) be continuous to those from Eq. (16) determines both A_{lm}^S and B_{lm}^S. In particular, we have

$$A_{lm}^S(k)=e^{i(\delta_l^S-\delta_l)}\frac{N_l^S(K,R)}{N_l(K,R)}A_{lm}(k) . \tag{19}$$

Proceeding as before for the calculation of F, we may now calculate the force F^S on the impurity atom in its substitutional position:

$$F^S=\int_{\mathrm{FS}}\frac{dS_k}{|\nabla_k E_k|}e\tau(k)\vec{V}_k\cdot\vec{E}I^S(k) , \tag{20}$$

where

$$I^S(k)=-\frac{8}{\pi}\sum_{lm}\left[\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}\right]^{1/2}\sin(\delta_{l+1}^S-\delta_l^S)\sin(\Delta_{l+1}-\Delta_l)\left[\frac{1}{N_lN_l+1}\right] \times\mathrm{Re}[A_{lm}^{*}(k)A_{l+1,m}(k)] , \tag{21}$$

and $\Delta_l=\delta_l^S-\delta_l$. Re denotes the real part of the function.

Equations (20) and (21) are the main results of this paper and show that the force exerted by the electron gas on an impurity atom depends on the nature of the Fermi surface, the electron group velocities at the Fermi surface, the solute phase shifts δ_l^S, the excess solute phase shifts Δ_l, and the wave-function character $A_{lm}(k)$ at the Fermi surface. It also depends on the details of the electronic relaxation time $\tau(k)$, due to phonon and impurity scattering at the Fermi surface. Equation (20) also shows that the force on an atom of the solvent vanishes since $\Delta_l=0$ as was found from Eq. (7).

For a jellium matrix we have

$$\delta_l=0,\ \Delta_l=\delta_l^S,\ N_l=j_l,\ A_{lm}(k)=j_l(kR)Y_{lm}^*(k)\ ,$$

so that

$$I^S(k)=-\frac{8}{\pi}\sum_{lm}\left[\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}\right]^{1/2}\sin^2(\Delta_{l+1}-\Delta_l)\mathrm{Re}[Y_{lm}^*(\hat{k})Y_{l+1,m}(\hat{k})]\ . \tag{22}$$

With this and using Eq. (9) one finds

$$F^S=-eE\left[\frac{4\hbar k_F^2}{3\pi m}\right]\sum_l(l+1)\sin^2(\Delta_{l+1}-\Delta_l) \tag{23}$$

$$=-ZeE(\rho_i/\rho_0) \tag{24}$$

where

$$\rho_i=\frac{4\pi}{Zk_F}\left[\frac{\hbar}{e^2}\right]\sum_l(l+1)\sin^2(\Delta_{l+1}-\Delta_l) \tag{25}$$

is the residual resistivity (per defect) of the solute, and

$$\rho_0=\frac{m}{ne^2\tau_F} \tag{26}$$

is the resistivity of the jellium metal of valence Z and electron density $n=Z/\Omega_0=k_F/3\pi^2$, and τ_F is the relaxation time assumed constant, $\tau_F=\tau(k_F)$. Thus the standard result derived by Bosvieux and Friedel[1] and by Turban *et al.*,[13] and Sham[5] that the force due to electronic polarization in a free-electron gas is directly related to the residual resistivity of the solute, is recovered in our formalism.

Returning to the more general case, Eq. (20) shows that in contrast to the residual resistivity of a solute which, within the relaxation-time approximation, depends only on the excess phase shifts Δ_l of the solute via the term $\sin^2(\Delta_{l+1}-\Delta_l)$, the force F^S depends explicitly on both the solute and the host-metal-atom phase shifts. Thus for host metals whose phase shifts are nonnegligible in comparison to those of the solute, the force on the solute atom cannot be expressed in terms of the residual resistivity of the solute.

It is instructive to see how the expression for the force is modified for a metal whose Fermi surface is nearly spherical. In this case it is easily shown that F^S is given by Eq. (24) with ρ_i replaced by $\bar{\rho}_i$, where

$$\bar{\rho}_i=\frac{4\pi}{Zk_F}\left[\frac{\hbar}{e^2}\right]\sum_l\left[\frac{j_lj_{l+1}}{N_lN_{l+1}}\right](l+1)\sin(\delta_{l+1}^S-\delta_l^S)\sin(\Delta_{l+1}-\Delta_l)\ . \tag{27}$$

The expression for $\bar{\rho}_i$ is thus very similar to that of the residual resistivity ρ_i in a free-electron gas. However, this similarity should not be taken too far since in contrast to ρ_i, which is always positive, $\bar{\rho}_i$ can be positive or negative depending on the values of δ_l^S and δ_l. Equation (27) thus allows the effects associated with the host phase shifts to be accounted for in a simple manner while neglecting the Fermi-surface effects for metals with nearly spherical Fermi surfaces. Such an approximation has been shown to yield residual resistivities in noble metals in good agreement with more precise calculations.[14] However, for matrices where the Fermi surfaces are complicated, as is the case for most of the transition, rare-earth and actinide metals, or where Fermi velocities differ considerably from the free-electron values, Eqs. (20) and (21) will have to be evaluated numerically.

III. APPLICATION TO NOBLE METALS

The use of the formalism presented above requires a detailed knowledge of the electronic structure of the host matrix including the wave functions at the Fermi surface. Such a study is underway and is planned to be reported later for the case of niobium in a separate publication. In this paper we have chosen to present the results for noble metals for two reasons. First, the approximation of the spherical Fermi surface allows the use of Eqs. (23) and (27), and second, the phase shifts for several solutes are available from a fit to the experimental data.[12] These phase shifts are given in Tables I and II. We note here that these phase shifts, and approximations similar to the ones introduced above in deriving Eqs. (23) and (27), yielded a rather good agreement of the calculated resistivity both with the experiment and with the resistivity calculated using more elaborate Fermi-surface integrals.[14] This gives us confidence in our calculation of the effective valences for noble metals using Eq. (27).

The calculated values of the effective valence for several solutes are presented in Table III. The values using the resisitivity formula [Eq. (25)] are also given for comparison. In these calculations we have assumed, following Bosvieux and Friedel,[1] that a direct force ZeE ($Z=1$ for noble metals) is exerted in the substitutional position but that no direct force exists in the saddle-point position. The average force during the jump is calculated by assuming a sinusoidal variation of the force,[1] which leads to the following expression for the effective valence Z^*,

$$Z^* = Z[1-(\bar{\rho}_i^S+\bar{\rho}_i^{SP})/\rho_0]/2 \,, \qquad (28)$$

where $\bar{\rho}_i^S$ and $\bar{\rho}_i^{SP}$ are the values of $\bar{\rho}_i$ in the stable and the saddle-point configurations of the moving atom, respectively. We have assumed for the calculation of $\bar{\rho}_i^{SP}$ that when the atom moves to the saddle-point position it rigidly carries its screening charge with it. Further, the contribution due to the vacancies to the driving force has been neglected since numerical calculations[15] have shown it to be rather small. The following values of the metal resistivity ρ_0 (in $\mu\Omega\,\text{cm}$) have been used in calculating Z^* from Eq. (28); these values have been taken from the *Handbook of Chemical Physics*[16]:

$$\rho_0 = 1.673 + 0.0068(T-293) \text{ Cu} \,,$$

$$\rho_0 = 1.590 + 0.0041(T-293) \text{ Ag} \,,$$

$$\rho_0 = 2.350 + 0.0040(T-293) \text{ Au} \,,$$

where the temperature T is in K. We have neglected here the resistivity due to the defect itself in comparison to the phonon resistivity, as the former makes a negligible contribution at elevated temperatures.

We observe that for all the solutes presented in Table III the effective valences are large, in general much larger than the solute-metal valence. Low resistivity of noble metals is an important reason for the high effective valences of solutes in these metals. There is an extremely large dispersion in the measured values of the effective valences of solutes in noble metals in the literature; for example, the experimental value of Z^* of Ag in Cu is quoted[17] to lie between -2 and -32. Further, for most solutes studied here experimental measurements have not been performed. We again emphasize here that the choice of these solutes was dictated by the fact that their phase shifts are available from a fit of the experimental data. We note, however, that Doan[15] has obtained a value of $\sim 9.0\ \mu\Omega\,\text{cm/at.\%}$ for the sum $\bar{\rho}_i^S+\bar{\rho}_i^{SP}$ for Sn in Ag by the tracer-diffusion method. This is in good agreement with our calculated value of 10.13 $\mu\Omega\,\text{cm/at.\%}$. Also, Bocquet[18] has obtained a value of $Z^* = -7.6 \pm 2$ for Ag self-diffusion which is to be compared with our calculated value of $Z^* = -4.6$. We observe that the resistivity formula reproduces quite well the results obtained from Eq. (28) which includes the corrections for the host-metal phase shifts. This is essentially due to the fact that the contribution from the saddle-point position is larger than in the stable position, and further the phase shifts of noble metals at the Fermi energy are quite small. What matters most is the difference $\Delta_{l+1}-\Delta_l$ as compared to

TABLE I. Phase shifts δ_l (in radians) of noble metals at the Fermi energy.

Metal	Lattice parameter a (a.u.)	δ_0	δ_1	δ_2
Cu	6.8090	0.0755	0.1298	−0.1186
Ag	7.6901	0.2097	0.1188	−0.1019
Au	7.6825	0.2496	0.0632	−0.2426

TABLE II. Excess phase shifts Δ_l (in radians) of the solutes in noble metals at the Fermi energy of the host.

Alloy	Δ_0	Δ_1	Δ_2
Cu(Au)	0.1820	−0.0870	−0.1470
Cu(Zn)	0.4935	0.2672	0.1276
Cu(Al)	0.2100	0.4800	0.2800
Cu(Ge)	0.1500	0.7480	0.1800
Cu(Ni)	−0.0690	−0.0380	−0.2580
Ag(Au)	0.1760	0.0870	−0.0850
Ag(Sn)	0.2010	0.7860	0.2230
Au(Cu)	−0.2100	0.0770	0.1030
Au(Ag)	−0.2770	−0.0720	0.0510
Au(Zn)	0.2550	0.1800	0.2370
Au(Ga)	0.9800	0.4100	0.1600

$\delta_{l+1}-\delta_l$. For Cu and Ag one finds for the solutes studied, that $\Delta_{l+1}-\Delta_l >> \delta_{l+1}-\delta_l$, and hence the correction due to δ_l is small. On the other hand, for Au-based alloys, this is not always the case, and thus significant correction to the effective valence is obtained.

IV. DISCUSSION AND CONCLUSION

We have presented a formalism, using scattering-theory approach, which allows the calculation of the force on a moving atom, and hence its effective valence, due to the electronic polarization created by the displacement of the Fermi surface in an electric field. The formalism can be applied to both simple and transition metals. We have shown that the effective valence, within the relaxation-time approximation for the solution of the Boltzmann equation, depends intricately on the electronic structure of the host matrix as well as that of the solute, the nature of the Fermi surface, and a detailed knowledge of the Fermi velocities

TABLE III. Effective valence of solutes in noble metals. Z^* is the value calculated from Eq. (28) using $\bar{\rho}_i^S$ and $\bar{\rho}_i^{SP}$ with the value of ρ_0 at 1000 °C. Z^*_{res} is the value obtained by using the resitivity ρ_i^S in place of $\bar{\rho}_i^S$. ρ_i^S, $\bar{\rho}_i^S$, and $\bar{\rho}_i^{SP}$ are all in $\mu\Omega$ cm/at.%.

Alloy	ρ_i^S	$\bar{\rho}_i^S$	$\bar{\rho}_i^{SP}$	Z^*	Z^*_{res}
Cu(Cu)	0.0	0.0	0.63	−3.2	−3.2
Cu(Au)	0.54	0.79	1.66	−14.0	−12.5
Cu(Zn)	0.52	0.56	1.20	−10.0	−9.6
Cu(Al)	1.44	1.48	2.11	−20.7	−20.5
Cu(Ge)	3.77	4.40	5.48	−57.8	−54.0
Cu(Ni)	1.11	1.83	3.12	−28.7	−24.5
Ag(Ag)	0.0	0.0	0.58	−4.6	−4.6
Ag(Au)	0.38	0.83	1.84	−23.0	−19.0
Ag(Sn)	4.38	4.70	5.43	−88.5	−85.7
Au(Au)	0.0	0.0	1.67	−12.6	−12.6
Au(Cu)	0.49	−0.12	0.95	−6.0	−10.8
Au(Ag)	0.34	−0.30	0.75	−3.0	−8.1
Au(Zn)	0.76	−0.05	0.81	−5.5	−11.9
Au(Ga)	2.10	2.54	4.49	−54.8	−51.4

and the wave-function character at the Fermi surface, and also the phase shifts at the Fermi energy. We have also shown that in the case of host metals whose phase shifts at the Fermi energy are negligible, the effective valence can be related directly to the residual resistivity of the solute in the substitutional and the saddle-point positions. This is a result which was first obtained by Bosvieux and Friedel within the Born approximation, and later more rigorously by Turban, Nozières, and Gerl[13] and by Sham.[5] We have shown here that this is a general result and essentially valid for a jellium matrix within the framework of the linearized Boltzmann equation. However, for simple metals with significant phase shifts at the Fermi energy (for example, Al) the final expression involves not only the excess phase shifts Δ_l of the solute, which determine its residual resistivity, but also the solute-metal phase shifts δ_l^S (or alternatively the host-metal phase shifts δ_l), and in this case the effective valence cannot be reduced to a form resembling the residual resistivity of the solute. Thus the relationship between the effective valence and the residual resistivity is, strictly speaking, valid only for host metals where the jellium approximation can be considered adequate.

The calculations for the transition metal Nb are in progress, but are necessarily complicated since detailed Fermi-surface integrations requiring knowledge of the electronic wave functions need to be performed. We have first applied it to the case of noble metals where considerable simplifications can be achieved by assuming a spherical shape for the Fermi surface, an approximation which is not too bad since it has already yielded residual resistivities in good agreement with both the experiment and those calculated by evaluating much more involved Fermi-surface integrals.[14] We have found that the effective valences for solutes in noble metals are, generally speaking, much larger than the solute-metal valence. Even for the atoms of the matrix Z^* is significantly larger than Z, the solvent-atom valence. Among all the cases listed in Table III, Z^* is smallest for the case of *Cu*(Cu) with a value $Z^* = -3.2$, which is more than 3 times the valence of Cu. We believe that these large values of the effective valences (as compared to the solute- or the host-metal-atom valence, whichever may be the case), which are in part due to the low phonon resistivities of noble metals, render the much controversial problem of the direct force rather academic in these cases. Note that a complete neglect of the direct force in the worst case of *Cu*(Cu) will change Z^* from -3.2 to -3.7, while its full inclusion, including the contribution also from the saddle-point position, will result in a Z^* of -2.7. (We recall that the Bosvieux-Friedel model allows the direct force contribution in the substitutional position and is equal to the valence of the host-metal atom.) In our view either value of Z^* is large as compared to the valence of Cu and the difference between them falls within the precision of the experimental measurements.

In the present calculation, the contribution due to a single vacancy adjacent to the solute in the substitutional position and the two half-vacancies in the saddle-point position has been neglected. This contribution cannot be easily calculated. A partial correction can, however, be made by including their contribution via the potential and hence the phase shifts of the solute since the presence of these vacancies does somewhat change the potential of the solute. Bosvieux and Friedel also neglected in their model the contribution from the two half-vacancies in the saddle-point configuration, but calculate the contribution from the vacancy adjacent to the substitutional atom. Doan,[15] following this prescription, has evaluated this contribution in Ag. He finds that it lowers all the effective valences by approximately 2 at 800 °C (i.e., Z^* is changed to $Z^* - 2$). Thus according to this calculation, the effect will be the largest where Z^* is small. The formulation presented here also neglects the backscattering from the host lattice. This is a rather complex problem and not easily treated. Coleridge, Holzwarth, and Lee[12] have, however, suggested a procedure to include the backscattering effects via a suitable modification of the solute-atom phase shifts. The phase shifts given in Table II include these effects since they have been determined from a fit to the experimental data.[12]

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APPENDIX

We have

$$I=\int_0^R R_l R_{l+1}\frac{dV}{dr}r^2dr=\int_0^R u_l u_{l+1}\frac{dV}{dr},\quad u_l=rR_l\ . \tag{A1}$$

The radial wave equations for u_l and u_{l+1} at energy E are

$$-\ddot{u}_l+\left[\frac{l(l+1)}{r^2}+V\right]u_l=Eu_l\ , \tag{A2}$$

$$-\ddot{u}_{l+1}+\left[\frac{(l+1)(l+2)}{r^2}+V\right]u_{l+1}=Eu_{l+1}\ , \tag{A3}$$

where $\dot{u}_l=du_l/dr$, $\ddot{u}_l=d^2u_l/dr^2$, etc. Differentiating (A2) and (A3) with respect to r, multiplying them, respectively, by u_{l+1} and u_l, and then summing them up, one obtains

$$\begin{aligned}u_l u_{l+1}\frac{dV}{dr}&=\frac{1}{2}\left[\left[E-V-\frac{l(l+1)}{r^2}\right]\dot{u}_l u_{l+1}+\left[E-V-\frac{(l+1)(l+2)}{r^2}\right]\dot{u}_{l+1}u_l+\dddot{u}_l u_{l+1}+\dddot{u}_{l+1}u_l\right.\\&\qquad\left.+\frac{4(l+1)^2}{r^3}u_l u_{l+1}\right]\\&=\frac{1}{2}\left[-\ddot{u}_{l+1}\dot{u}_l+\frac{2(l+1)}{r^2}\dot{u}_l u_{l+1}-\ddot{u}_l\dot{u}_{l+1}-\frac{2(l+1)}{r^2}\dot{u}_{l+1}u_l+\dddot{u}_l u_{l+1}+\dddot{u}_{l+1}u_l\right.\\&\qquad\left.+\frac{4(l+1)^2}{r^3}u_l u_{l+1}\right]\\&=\frac{1}{2}\left[\frac{d}{dr}(\ddot{u}_l u_{l+1}+\ddot{u}_{l+1}u_l-2\dot{u}_l\dot{u}_{l+1})+\frac{2(l+1)}{r^2}(\dot{u}_l u_{l+1}-\dot{u}_{l+1}u_l)+\frac{4(l+1)^2}{r^3}u_l u_{l+1}\right]\ .\end{aligned} \tag{A4}$$

Multiplying (A2) by u_{l+1} and (A3) by u_l and subtracting we have

$$\frac{2(l+1)}{r^2}u_l u_{l+1}=\ddot{u}_{l+1}u_l-\ddot{u}_l u_{l+1}\ . \tag{A5}$$

Substituting (A5) in (A4) one has

$$u_l u_{l+1}\frac{dV}{dr}=\frac{1}{2}\frac{d}{dr}\left[\ddot{u}_l u_{l+1}+\ddot{u}_{l+1}u_l-2\dot{u}_l\dot{u}_{l+1}+\frac{2(l+1)}{r}(\dot{u}_{l+1}u_l-\dot{u}_l u_{l+1})\right]\ . \tag{A6}$$

Hence, from (A1)

$$\begin{aligned}I&=\frac{1}{2}\left[\ddot{u}_l u_{l+1}+\ddot{u}_{l+1}u_l-2\dot{u}_l\dot{u}_{l+1}+\frac{2(l+1)}{r}(\dot{u}_{l+1}u_l-\dot{u}_l u_{l+1})\right]_0^R\\&=\tfrac{1}{2}[r^2(\ddot{R}_{l+1}R_l+\ddot{R}_l R_{l+1}-2\dot{R}_l\dot{R}_{l+1})-2R_l R_{l+1}+2(l+1)r(\dot{R}_{l+1}R_l-\dot{R}_l R_{l+1})]_{r=R}\ .\end{aligned} \tag{A7}$$

Substituting for R_l and R_{l+1} from Eq. (10) in Eq. (A7), and using the properties of spherical Bessel and Neumann functions, it is easily verified that

$$I=\frac{\sin(\delta_{l+1}-\delta_l)}{N_l N_{l+1}}\ , \tag{A8}$$

where N_l and δ_l are evaluated at energy E.

[1] C. Bosvieux and J. Friedel, J. Phys. Chem. Solids 23, 123 (1962).

[2] R. S. Sorbello, J. Phys. Chem. Solids 34, 937 (1973).

[3] T. C. Genoni and H. B. Huntington, Phys. Rev. B 16, 1344 (1977).

[4] J. M. Ziman, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1971), Vol. 26, p. 1.

[5] L. J. Sham, Phys. Rev. B 12, 3142 (1975).

[6] W. L. Schaich, Phys. Rev. B 13, 3350 (1976).

[7] R. S. Sorbello, Phys. Rev. B 23, 5119 (1981).

[8] J. M. Ziman, *Principles of the Theory of Solids* (Clarendon, Oxford, England, 1965).

[9] T. L. Loucks, *Augmented Plane Wave Method* (Benjamin, New York, 1967).

[10] M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[11] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon, Oxford, England, 1965).

[12] G. J. Morgan, Proc. Phys. Soc. London 89, 365 (1966); P. T. Coleridge, N. A. W. Holzwarth, and M. J. G. Lee, Phys. Rev. B 10, 1213 (1974).

[13] L. Turban, P. Nozières, and M. Gerl, J. Phys. (Paris) 37, 159 (1976); M. Gerl, Z. Naturforsch. A 26, 1 (1971).

[14] R. P. Gupta and R. Benedek, Phys. Rev. B 19, 583 (1979).

[15] N. V. Doan, Thèse de Docteur es Sciences Physiques, Faculté des Sciences d'Orsay, France, 1970 (unpublished).

[16] *Handbook of Chemical Physics,* 55th ed. (Chemical Rubber Co., Cleveland, Ohio, 1974).

[17] J. N. Pratt and R. G. R. Sellers, in *Electrotransport in Metals and Alloys,* Diffusion Monograph Series, edited by F. H. Wöhlbier, (Trans. Tech. Publications, Cleveland, Ohio, 1973).

[18] J. L. Bocquet, Thèse de Docteur es Sciences Physiques, Faculté des Sciences d'Orsay (France), 1973 (unpublished).