Calculation of the Force Acting on an Impurity in a Metal Submitted to an Electric Field or a Temperature Gradient *

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Using the Bosvieux-Friedel polarization model, the charge carrier induced force on an impurity in a normal metal submitted to a temperature gradient or an electric field is calculated, and a connection is made between the two phenomena. The results are interpreted in terms of the specific resistivity and thermoelectric power of the impurity in the matrix.

A crude estimation of the force due to phonon scattering on an impurity in a temperature gradient is given.

Introduction

In this paper we will discuss the main features of the BOSVIEUX-FRIEDEL type calculation [1] and its advantages with respect to the FIKS-HUNTINGTON type [2, 3]. It seems that the former treatment is better for

(i) it allows us to calculate the force acting on the solute ion itself, without considering the scattering of the conduction electrons on the neighbouring ions;

(ii) it enables us to give an estimation of the contribution of the screening charge polarization of a vacancy to the force acting on a neighbouring impurity ion;

(iii) it is more versatile than the F-H treatment as it may be applied in principle to more complicated situations than the free electron case. For example, it should permit to determine the polarization of the screening charge of an impurity in a tight-binding approximation, as in the case of a d-band in a transitional metal, and to deduce the contribution of the d-band to the force on the impurity ion.

BOSVIEUX and FRIEDEL have shown [1] that an isolated impurity in a metal subjected to an electric field is submitted to a total force arising from three contributions:

- an electrostatic force $Z' \boldsymbol{\epsilon}$ acting on the ion of valency Z';
- a so-called direct polarization force:
$$-(Z'-Z)\,\boldsymbol{\epsilon} = -z\,\boldsymbol{\epsilon} \qquad (1)$$
acting on the electron cloud of the impurity. The sum of these two contributions is simply $Z\boldsymbol{\epsilon}$, showing that an impurity ion feels the same electrostatic force as do the solvent ions;
- finally there exists an "indirect polarization force" due to the existence of an electric current in the system. The quantum mechanical calculation of this force leads to a result which is very easily interpretable in terms of the specific resistivity of the impurity ion in the matrix.

The main aim of this paper is to analyse this force due to the modification of the Fermi distribution of the carriers in the matrix, caused by an external perturbation such as an electric field or a temperature gradient. We will not follow exactly the calculation of BOSVIEUX and FRIEDEL, although the method is in principle the same.

After having shown that the force acting on the impurity ion follows directly from the knowledge of the electronic spatial distribution $\delta\varrho(\boldsymbol{r})$, we calculate explicitly $\delta\varrho(\boldsymbol{r})$ in the Born approximation and in the free electron case.

I. Expression of $\boldsymbol{F}(\boldsymbol{b})$ **

a) Due to the external perturbation $(\boldsymbol{\epsilon}, \nabla T)$, the distribution function $f(\boldsymbol{k})$ of the electrons of wave vector $\boldsymbol{k}$ is given by the Boltzmann linearized equation:

$$f(\boldsymbol{k}) = f_0(\boldsymbol{k}) + g(\boldsymbol{k}) \qquad (2)$$

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[1] C. BOSVIEUX and J. FRIEDEL, J. Phys. Chem. Solids **23**, 123 [1962].

[2] V. B. FIKS, Sov. Phys. Solid State **5**, 2549 [1964].

[3] H. B. HUNTINGTON and A. R. GRONE, J. Phys. Chem. Solids **20**, 76 [1960].

** $\boldsymbol{F}(\boldsymbol{b})$ is the force acting on a charge z' located at site $\boldsymbol{b}$ with respect to the impurity at the origin.

where [***]

$$g(\boldsymbol{k}) = -\left(-\frac{\partial f_0}{\partial E}\right)\tau(\boldsymbol{k})\;\boldsymbol{k}\cdot\boldsymbol{a}(k) \tag{3}$$

and
$$\boldsymbol{a}(k) = \boldsymbol{\epsilon} + \nabla T\left(\frac{\mathrm{d}E_{\mathrm{F}}}{\mathrm{d}T} + \frac{E-E_{\mathrm{F}}}{T}\right).$$

The distribution function $g(\boldsymbol{k})$ is simply the deviation of the perturbed distribution $f(\boldsymbol{k})$ from the isothermal, electric field free distribution function $f_0(\boldsymbol{k})$.

b) The perturbing potential $V(\boldsymbol{r})$ due to the impurity may be expressed as a sum of the self consistent potential $V_0(\boldsymbol{r})$ of the impurity in a field-free matrix, and a potential $V_1(\boldsymbol{r})$ which represents the modification of $V_0(\boldsymbol{r})$ due to the fields:

$$V(\boldsymbol{r}) = V_0(\boldsymbol{r}) + V_1(\boldsymbol{r}). \tag{4}$$

c) In a first order calculation, the electronic charge deviation from the free electron density in the vicinity of the impurity will be then written as a sum of three contributions:

$$\delta\varrho(\boldsymbol{r}) = \delta\varrho_0(\boldsymbol{r}) + \delta\varrho_1(\boldsymbol{r}) + \delta\varrho_2(\boldsymbol{r}) \tag{5}$$

where:

- $\delta\varrho_0$ is the screening charge at point $\boldsymbol{r}$ in the absence of external perturbation;
- $\delta\varrho_1$ is the modification of this screening charge arising from the scattering of the displaced electrons [$g(\boldsymbol{k})$ distribution] on the impurity potential $V_0(\boldsymbol{r})$;
- $\delta\varrho_2$ is the contribution to the screening charge of the scattering of the non displaced electrons [$f_0(\boldsymbol{k})$ distribution] on the modification $V_1(\boldsymbol{r})$ of the potential due to the fields. In this approximation, second order effects arising from the scattering of the displaced electrons on the $V_1(\boldsymbol{r})$ potential are neglected.

d) For the purpose of a self consistent calculation, let us write that the perturbing potential $V(\boldsymbol{r})$ and the electronic density are related by the Poisson equation:

$$\Delta V(\boldsymbol{r}) = -4\pi\,\delta\varrho(\boldsymbol{r}) + 4\pi z\,\delta(\boldsymbol{r}) \tag{6}$$

where $z\,\delta(\boldsymbol{r})$ is the bare perturbing charge due to the impurity ion of excess valency z. Taking account of the consistency of the potential $V_0(\boldsymbol{r})$ with $\delta\varrho_0(\boldsymbol{r})$, one obtains:

$$\Delta V_1(\boldsymbol{r}) = -4\pi(\delta\varrho_1 + \delta\varrho_2)\,, \tag{7}$$

which reads, after Fourier transformation [†]:

$$-K^2 V_1(\mathbf{K}) = -4\pi\big(\delta\varrho_1(\mathbf{K}) + \delta\varrho_2(\mathbf{K})\big)\,. \tag{8}$$

e) The expression $\boldsymbol{F}(\boldsymbol{b})$ of the force on an impurity ion of excess charge z' at site $\boldsymbol{b}$ with respect to the impurity ion of excess valency z located at site $\boldsymbol{O}$ is then given by the coulombic force due to the electron screening charge:

$$\boldsymbol{F}(\boldsymbol{b}) = z'\int\frac{\delta\varrho(\boldsymbol{r})\,(\boldsymbol{r}-\boldsymbol{b})}{|\,\boldsymbol{r}-\boldsymbol{b}\,|^3}\,\mathrm{d}_3r\,. \tag{9}$$

If $\delta\varrho(\boldsymbol{r})$ is known by its Fourier transform, it is easy to show that:

$$\boldsymbol{F}(\boldsymbol{b}) = 4\pi i z'\int \mathrm{d}_3K\,\delta\varrho(\mathbf{K})\,\exp\{i\,\mathbf{K}\cdot\boldsymbol{b}\}\cos\Theta_K/K \tag{10}$$

where Θ_K is the angle between $\mathbf{K}$ and the direction of the fields $\boldsymbol{\epsilon}$ and ∇T. In particular, the force acting on the impurity ion itself is:

$$\boldsymbol{F}(0) = 4\pi i z\int d_3K\,\delta\varrho(\mathbf{K})\cos\Theta_K/K\,. \tag{11}$$

The value of $\boldsymbol{F}(\boldsymbol{b})$ hinges then on the calculation of $\delta\varrho(\mathbf{K})$, which is contained in the following section.

II. Calculation of $\delta\varrho(\mathbf{K})$

The perturbing potential $V(\boldsymbol{r})$ scatters the free electron wave functions $\varphi_k(\boldsymbol{r})$ to the new states $\psi_k(\boldsymbol{r})$:

$$\psi_k = \varphi_k + G^0\,V\,\psi_k \tag{12}$$

where G^0 is the free electron Green function. In the Born approximation, one assumes that the perturbing potential V is so small that it is valid to make $\psi_k \sim \varphi_k$ in the preceding equation, which becomes:

$$\psi_k = \varphi_k + G^0\,V\,\varphi_k$$

so that:

$$\psi_k(\boldsymbol{r}) = \varphi_k(\boldsymbol{r}) - \frac{1}{2\pi}\int\frac{\exp\{i\,k\,|\,\boldsymbol{r}-\boldsymbol{r}'\,|\}}{|\,\boldsymbol{r}-\boldsymbol{r}'\,|}\,V(\boldsymbol{r}')\,\varphi_k(\boldsymbol{r}')\,\mathrm{d}_3r'. \tag{13}$$

[***] Throughout this paper, atomic units are used: $|\,e\,| = \hbar = m = 1$.

[†] Throughout this paper, the following definition of the Fourier transform is used:

$$V(\boldsymbol{r}) = \int V(\mathbf{K})\,\exp\{i\,\mathbf{K}\cdot\boldsymbol{r}\}\,\mathrm{d}_3K;$$
$$V(\mathbf{K}) = \int V(\boldsymbol{r})\,\exp\{-i\,\mathbf{K}\cdot\boldsymbol{r}\}\,\mathrm{d}_3r/(2\pi)^3.$$

Taking a unit volume of the crystal, the normalized wave functions are simply $\varphi_k(\mathbf{r}) = \exp\{i\,\mathbf{k}\cdot\mathbf{r}\}$ and the first order contribution of the $\mathbf{k}$ electrons to the screening charge is:

$$\begin{aligned}\delta\varrho_k(\mathbf{r}) &= \psi_k^*(\mathbf{r})\,\psi_k(\mathbf{r}) - \varphi_k^*(\mathbf{r})\,\varphi_k(\mathbf{r})\\ &\sim -\frac{1}{2\pi}\int \mathrm{d}_3r'\,V(\mathbf{r}')\\ &\quad\cdot\exp\{i\,\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})\}\,\frac{\exp\{i\,k\,|\mathbf{r}-\mathbf{r}'|\}}{|\mathbf{r}-\mathbf{r}'|} + \text{C. C.}\end{aligned}$$

The total electronic density is then the sum of the contributions of all the $\mathbf{k}$ electrons:

$$\delta\varrho(\mathbf{r}) = \sum_{\mathbf{k}} f(\mathbf{k})\,\delta\varrho(\mathbf{k}) = \frac{1}{4\pi^3}\int \mathrm{d}_3k\,f(\mathbf{k})\,\delta\varrho_k(\mathbf{r}). \tag{14}$$

a) Calculation of $\delta\varrho_0(\mathbf{r})$ *and* $\delta\varrho_2(\mathbf{r})$

The electronic density $\delta\varrho_0(\mathbf{r})$ in absence of any perturbing field is then given by:

$$\begin{aligned}\delta\varrho_0(\mathbf{r}) &= -\frac{1}{8\pi^4}\int_{|\mathbf{k}|<k_F} \mathrm{d}_3k\,\mathrm{d}_3r'\,V_0(\mathbf{r}')\\ &\quad\cdot\exp\{i\,\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})\}\,\frac{\exp\{i\,k\,|\mathbf{r}-\mathbf{r}'|\}}{|\mathbf{r}-\mathbf{r}'|} + \text{C. C.}\end{aligned}$$

that is:

$$\delta\varrho_0(\mathbf{r}) = \frac{-k_F^2}{2\pi^3}\int \mathrm{d}_3r'\,V_0(\mathbf{r}')\,\frac{j_1(2\,k_F\,|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|^2} \tag{15}$$

where $j_1(x)$ is the first spherical Bessel function:

$$j_1(x) = \frac{\sin x - x\cos x}{x^2}.$$

The result (15) may be found in the paper of Stoddart, March and Stott [4], where the Dirac density matrix is used.

Inserting in (15) a potential $V_0(\mathbf{r}) = \lambda\,\delta(\mathbf{r})$, we get immediately the asymptotic form of the screening charge around the impurity:

$$\delta\varrho_0(\mathbf{r}) \underset{r\to\infty}{\sim} \lambda\,\frac{2\,k_F^4}{\pi^3}\,\frac{\cos(2\,k_F\,r)}{(2\,k_F\,r)^3} \tag{16}$$

a result first obtained by Friedel.

The screening charge $\delta\varrho_2(\mathbf{r})$ may be calculated in the same way as $\delta\varrho_0(\mathbf{r})$ with $V_0(\mathbf{r})$ replaced by $V_1(\mathbf{r})$:

$$\delta\varrho_2(\mathbf{r}) = -\frac{k_F^2}{2\pi^3}\int \mathrm{d}_3r'\,V_1(\mathbf{r}')\,\frac{j_1(2\,k_F\,|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|^2}, \tag{17}$$

but we need the spatial dependence of $V_1(\mathbf{r})$ to obtain the asymptotic form of $\delta\varrho_2(\mathbf{r})$.

Fourier transforming the expression (15) and (17), one obtains:

$$\begin{aligned}\delta\varrho_0(\mathbf{K}) &= -\frac{1}{4\pi}\,g_0(K)\,V_0(\mathbf{K}),\\ \delta\varrho_2(\mathbf{K}) &= -\frac{1}{4\pi}\,g_0(K)\,V_1(\mathbf{K})\end{aligned} \tag{18}$$

where

$$g_0(K) = \frac{2\,k_F}{\pi}\left[1 + \frac{1-x^2}{2\,x}\log\left|\frac{1+x}{1-x}\right|\right] \quad (x = K/2\,k_F). \tag{19}$$

Then it is shown that the oscillatory asymptotic form may be traced to the sharpness of the Fermi distribution at the Fermi level.

b) Calculation of $\delta\varrho_1(\mathbf{r})$

The same method, applied to the calculation of $\delta\varrho_1(\mathbf{r})$, leads to:

$$\begin{aligned}\delta\varrho_1(\mathbf{r}) &= \frac{1}{4\pi^3}\int g(\mathbf{k})\,\delta\varrho_k(\mathbf{r})\,\mathrm{d}_3k\\ \text{or}\quad \delta\varrho_1(\mathbf{r}) &= \frac{1}{\pi^3}\int \mathrm{d}_3R\,V_0(\mathbf{r}+\mathbf{R})\,\frac{\mathbf{R}\cdot\mathbf{I}(\mathbf{R})}{R^2}\,\mathbf{I}(\mathbf{R})\end{aligned} \tag{20}$$

where

$$\mathbf{I}(\mathbf{R}) = -\int k^2\,\mathrm{d}E\left(-\frac{\partial f_0}{\partial E}\right)\tau(k)\,\boldsymbol{\alpha}(\mathbf{k})\,j_1(k\,R)\sin k\,R \tag{21}$$

in the approximation of an isotropic relaxation time.

a) Pure Electric Field Case

In the case where $\nabla T = 0$, $\boldsymbol{\alpha}(k) = \boldsymbol{\epsilon}$ and the calculation of $\mathbf{I}(\mathbf{R})$ is straightforward:

$$\mathbf{I}(\mathbf{R}) = -k_F^2\,\tau_F\,j_1(k_F\,R)\,\sin(k_F\,R)\,\boldsymbol{\epsilon}.$$

The electronic density $\delta\varrho_1(\mathbf{r})$ is then obtained as:

$$\begin{aligned}&\delta\varrho_1(\mathbf{r}) = \\ &-\frac{k_F^2}{\pi^3}\,\tau_F\,\boldsymbol{\epsilon}\cdot\int \mathrm{d}_3R\,V_0(\mathbf{r}+\mathbf{R})\,\frac{\mathbf{R}}{R^2}\,j_1(k_F\,R)\,\sin(k_F\,R),\end{aligned} \tag{22}$$

the Fourier transform of which is:

$$\delta\varrho_1(\mathbf{K}) = -\frac{i}{2\pi}\,\tau_F\,\varepsilon\cos\Theta_K\,V_0(K)\,\Theta(2\,k_F - K) \tag{23}$$

where $\Theta(x)$ is the Heaviside function.

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[4] J. C. Stoddart, N. H. March, and M. J. Stott, Phys. Rev. **186**, 683 [1969].

The asymptotic form of $\delta\varrho_1(\mathbf{r})$ is easily deduced from (22):

$$\delta\varrho_1(\mathbf{r}) \underset{r\to\infty}{\sim} -\lambda \frac{k_\mathrm{F}}{2\pi^2}\tau_\mathrm{F}\,\boldsymbol{\epsilon}\cdot\frac{\mathbf{r}}{r^3}\sin(2\,k_\mathrm{F}\,r). \qquad (24)$$

Then it is shown that the screening charge $\delta\varrho_1(\mathbf{r})$ is anisotropic and that its asymptotic form is $\sin(2\,k_\mathrm{F}\,r)/r^2$. This peculiar property may be traced to the sharpness of the Fermi surface [which gives an asymptotic form $\cos(2\,k_\mathrm{F}\,r)/r^3$ in the field-free case], and to the anisotropy of the occupation number on the Fermi surface, due to the electric field. We note that the screening charge enclosed by two concentric spheres of radii r and $r+\mathrm{d}r$ gives a uniform electric field inside the sphere r; then it is expected that there is no field gradient at the nucleus, in this first order calculation. From Eq. (22), it may be also noted that $\delta\varrho_1(0)=0$, so we do not expect to see any isomeric effect on the nucleus of the impurity ion itself.

β) $\boldsymbol{\epsilon}$ and ∇T

In the case of superimposed electric field and temperature gradient:

$$\boldsymbol{a}(k) = \boldsymbol{\epsilon} + \nabla T\left(\frac{\mathrm{d}E_\mathrm{F}}{\mathrm{d}T} + \frac{E-E_\mathrm{F}}{T}\right),$$

and the expression of $\boldsymbol{I}(\mathbf{R})$ is:

$$\boldsymbol{I}(\mathbf{R}) = -\int k^2\,\mathrm{d}E\left(-\frac{\partial f_0}{\partial E}\right)\tau(k)\,\boldsymbol{a}(k)\;j_1(k\,R)\,\sin(k\,R). \qquad (25)$$

The expression of $\delta\varrho_1(\mathbf{r})$ is then slightly more complicated than in the pure electric field case, as we must keep the integrals over the $(-\partial f_0/\partial E)$ distribution, which give rise to the thermoelectric effects.

By analogy with Eq. (22), the Fourier transform of $\delta\varrho_1(\mathbf{r})$ is:

$$\delta\varrho_1(\mathbf{K}) = -\frac{i}{2\pi}\,[\,\overline{\tau\,a(k)}\,]\cos\Theta_K\,V_0(K) \qquad (26)$$

where $$\overline{\tau\,a(k)} = \int_{K/2}^{\infty}\mathrm{d}E\left(-\frac{\partial f_0}{\partial E}\right)\tau(k)\;a(k) \qquad (27)$$

is the mean value of $\tau(k)\;a(k)$ taken on the derivative of the Fermi distribution.

III. Calculation of F(0), Z* and q_e*

From the Poisson Eq. (7), we are now able to calculate the screening charge due to the fields:

$$-K^2\,V_1(\mathbf{K}) = -4\,\pi\,\delta\varrho_1(\mathbf{K}) + g_0(K)\;V_1(\mathbf{K}), \quad (28)$$

so that $$V_1(\mathbf{K}) = \frac{4\,\pi\,\delta\varrho_1(\mathbf{K})}{K^2+g_0(K)}$$

and

$$\delta\varrho_1(\mathbf{K}) + \delta\varrho_2(\mathbf{K}) = \delta\varrho_1(\mathbf{K})\,\frac{K^2}{K^2+g_0(K)}\,. \qquad (29)$$

From the Poisson equation in the field free case, we can deduce $V_0(K)$ and then obtain for the total displaced charge:

$$\delta\varrho_1(\mathbf{K}) + \delta\varrho_2(\mathbf{K}) \qquad (30)$$
$$= \frac{i\,z}{4\,\pi^3}\,\frac{K^2}{[K^2+g_0(K)]^2}\cos\Theta_K[\overline{\tau\,a(k)}]\,.$$

The force acting on the impurity ion itself is then:

$$F(0) = -\frac{4\,z^2}{3\,\pi}\int_0^\infty \mathrm{d}K\,\frac{K^3}{[K^2+g_0(K)]^2}\,[\overline{\tau\,a(k)}]\,. \quad (31)$$

In the pure electric field case,

$$\overline{\tau\,a(k)} = \tau_\mathrm{F}\,\varepsilon\;\Theta(2\,k_\mathrm{F}-K)$$

and we obtain the expression of the force given by Bosvieux and Friedel [1]:

$$F_\varepsilon(0) = -\frac{4\,z^2\,\tau_\mathrm{F}}{3\,\pi}\,\varepsilon\int_0^{2\,k_\mathrm{F}}\frac{K^3\,\mathrm{d}K}{[K^2+g_0(K)]^2}\,. \qquad (32)$$

This expression may be easily related to the resistivity cross-section of the impurity. The differential cross-section $\sigma(\Theta)$ is related to the Fourier transform of the perturbing potential:

$$\sigma(\Theta) = |\,4\,\pi^2\,V_0(K)\,|^2 = \frac{4\,z^2}{[K^2+g_0(K)]^2}\,,$$

leading to the resistivity cross-section:

$$A_z(E_\mathrm{F}) = 2\,\pi\int_0^\pi \sigma(\Theta)\,(1-\cos\Theta)\,\sin\Theta\,\mathrm{d}\Theta$$
$$= \frac{4\,\pi\,z^2}{k_\mathrm{F}^4}\int_0^{2\,k_\mathrm{F}}\frac{K^3\,\mathrm{d}K}{[K^2+g_0(K)]^2}$$

and $$F_\varepsilon(0) = -\,\varepsilon\,k_\mathrm{F}\,A_z(E_\mathrm{F})\;\sigma \qquad (33)$$

where σ is the conductivity of the pure matrix.

If $\varrho_0 = \dfrac{m}{n_0\,e^2\,\tau_\mathrm{F}}$ and $\varrho_i = \dfrac{m\,v_\mathrm{F}\,A_z(E_\mathrm{F})}{Z\,e^2}$

are respectively the resistivity of the pure matrix and the specific resistivity of the solute ion in the matrix, we obtain a very simple relation between the force $F_\varepsilon(0)$ and ϱ_i:

$$F_\varepsilon(0) = -Z\,\varepsilon\left(\frac{\varrho_i}{\varrho_0}\right) = Z^*\,\varepsilon\,. \tag{34}$$

When the matrix is submitted to a temperature gradient, the calculation is slightly more complicated because of the mean value $\overline{\tau\,a(k)}$ taken on the derivative of the Fermi distribution. Letting:

$$\Phi(K) = \frac{K^3}{[K^2 + g_0(K)]^2}$$

we obtain

$$F(0) = -\frac{4\,z^2}{3\,\pi}\int_0^\infty \mathrm{d}K\,\Phi(K)\int_{K/2}^\infty \mathrm{d}E\left(-\frac{\partial f_0}{\partial E}\right)\tau(k)\,a(k)\,. \tag{35}$$

In order to interpret this formula, one notes that the resistivity cross-section of the impurity in an electron gas of Fermi wave vector $k/2$ is:

$$A_z(k/2) = \frac{64\,\pi\,z^2}{k^4}\int_0^k \Phi(x)\,\mathrm{d}x$$

so that $$\frac{\partial}{\partial k}\left(k^4 A_z(k/2)\right) = 64\,\pi\,z^2\,\Phi(k)\,.$$

Integrating by parts the expression of $F(0)$, we obtain simply:

$$F(0) = -\frac{4}{3\,\pi^2}\int_0^\infty E^2 A_z(E)\left(-\frac{\partial f_0}{\partial E}\right)\tau(E)\,a(E)\,\mathrm{d}E\,. \tag{36}$$

As usual, let us define the mean value on the $(-\partial f_0/\partial E)$ distribution as:

$$\langle\tau(E)\,A\,E^n\rangle = \frac{2^{3/2}}{3\,\pi^2\,n_0}\int_0^\infty\left(-\frac{\partial f_0}{\partial E}\right)E^{n+3/2}A(E)\,\tau(E)\,\mathrm{d}E \tag{37}$$

$$= \int_0^\infty\left(\frac{k}{k_\mathrm{F}}\right)^3\left(-\frac{\partial f_0}{\partial E}\right)E^n A(E)\,\tau(E)\,\mathrm{d}E\,.$$

With this notation the thermoelectric field in the pure matrix is:

$$\varepsilon = -\frac{1}{\langle\tau\rangle}\left[\langle\tau\,E\rangle + T^2\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{E_\mathrm{F}}{T}\right)\langle\tau\rangle\right]\frac{\nabla T}{T} \tag{38}$$

and

$$a(E) = \frac{\nabla T}{T}\left[E - \frac{\langle\tau\,E\rangle}{\langle\tau\rangle}\right]. \tag{39}$$

Thus it follows that the force acting on the impurity is given by the expression:

$$F_z(0) = -\sqrt{2}\,\sigma\,\frac{\nabla T}{T}\left[\frac{\langle\tau\rangle\langle\tau\,A\,E^{3/2}\rangle - \langle\tau\,E\rangle\langle\tau\,A\,E^{1/2}\rangle}{\langle\tau\rangle^2}\right] \tag{40}$$

where $\sigma = n_0\,\tau_\mathrm{F}$ is the electrical conductivity of the pure matrix.

Using the well known expansion of $\langle\;\rangle$:

$$\int_0^\infty h(E)\left(-\frac{\partial f_0}{\partial E}\right)\mathrm{d}E = h(E_\mathrm{F}) + \frac{\pi^2}{6}(k\,T)^2\left[\frac{\partial^2 h}{\partial E^2}\right]_{E_\mathrm{F}}, \tag{41}$$

it is straightforward to obtain the force $F_z(0)$ in terms of the derivative of the resistivity cross-section with respect to the energy, at the Fermi level:

$$\frac{F_z(0)}{\nabla T} = -\frac{K_\mathrm{e}}{(2\,E_\mathrm{F})^{1/2}}\,A_z(E_\mathrm{F})\left[1 + 2\left(\frac{\mathrm{d}A/A}{\mathrm{d}E/E}\right)_{E_\mathrm{F}}\right] \tag{42}$$

where the Wiedemann-Franz relation between the thermal conductivity K_e and the electrical conductivity σ has been used.

Using this expression of $F_z(0)$, we can obtain a relation between the force acting on the impurity and the change in the thermoelectric power of the system when impurity ions are dissolved in the matrix. It is well known that at low concentration c_i of the impurity, the thermoelectric power s of the system depends on c_i according to the law [5]:

$$\frac{\Delta s}{s} = -\frac{\varrho_i\,c_i}{c_0}\left(1 - \frac{s_i}{s_0}\right)$$

where $$s_i = \frac{\pi^2}{3}\frac{k^2\,T}{E_\mathrm{F}}\left(\frac{\partial\,\mathrm{Log}\,\varrho_i}{\partial\,\mathrm{Log}\,E}\right)_{E_\mathrm{F}} = -\frac{\pi^2}{3}\frac{k^2\,T}{E_\mathrm{F}}\,\Delta x$$

is the specific thermoelectric power of the impurity ion in the matrix; Δx is the factor defined by Friedel:

$$\Delta x = -\left(\frac{\partial\,\mathrm{Log}\,\varrho_i}{\partial\,\mathrm{Log}\,E}\right)_{E_\mathrm{F}} = -\frac{1}{2}\left[1 + 2\left(\frac{\mathrm{d}A/A}{\mathrm{d}E/E}\right)_{E_\mathrm{F}}\right]. \tag{43}$$

We can then obtain $F_z(0)$ in terms of the factor Δx and the resistivity cross-section $A_z(E_\mathrm{F})$:

$$\frac{F_z(0)}{\nabla T} = \frac{2\,K_\mathrm{e}}{(2\,E_\mathrm{F})^{1/2}}\,A_z(E_\mathrm{F})\,\Delta x\,. \tag{44}$$

This formula has been used in reference [6] to calculate the heat of transport of several impurities in

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[5] J. Friedel, J. Phys. Rad. **14**, 561 [1963].

[6] M. Gerl, J. Phys. Chem. Solids **28**, 725 [1967].

the noble metals. According to (44) the contribution of the force $F_z(0)$ to the heat of transport of the impurity is given by:

$$q_e^* = -\frac{F_z(0)\,T}{\nabla T} = -\frac{2\,K_e\,T}{k_F}\,A_z(E_F)\,\Delta x$$

which, compared with the definition (34) of the effective valency, leads to the following relationship between q_e^* and Z^*:

$$q_e^* = \frac{\pi^2}{3}\,\frac{(k\,T)^2}{E_F}\,\Delta x\,Z^*. \qquad (45)$$

This relation is easily interpreted: both the heat of transport and the effective valency contain a contribution due to the scattering of the charge carriers on the impurity; both of these contributions are proportional to the resistivity cross-section of the impurity ion and to the local flux of charge carriers. In an isolated metal submitted to a temperature gradient, there is no macroscopic flux of carriers but the thermoelectric phenomena are usually attributed to the existence of two local antiparallel fluxes of carriers and the resistivity cross-section of the impurity is different for these carriers of different energy. The Δx factor being in general positive for solute ions in noble metals, except for a few solute atoms (Mn for example), we expect the contribution q_e^* of the scattering of carriers to the heat of transport to be negative: the "cold carriers" have a larger resistivity cross-section than the "hot carriers" and one gets a force directed to the hot end of the system. For example, in a copper matrix at 1160 K ($k\,T = 0.1$ eV) we expect the approximate relationship:

$$q_e^* = (0.5 \text{ to } 1)\cdot 10^{-2}\,Z^*\ (\text{eV})$$

for normal impurities such as Zn, Ga, Ge, As, . . . , because $\Delta x = 1$ to 2 for these impurities. It is seen thus that the q_e^* contribution to the heat of transport may be important ($q_e^* \sim -0.5$ to -0.25 eV for $Z^* = -50$).

Moreover, the relationship (45) is expected to hold at least approximately along the jump of an ion in a neighbouring vacancy, as the parameter Δx is not strongly dependent on the screening charge of the jumping ion; thus the relation (45) is expected to give a fairly good estimate of the q_e^* contribution to the heat of transport of the impurity.

An interesting advantage of the Bosvieux-Friedel calculation reviewed in this paper is that it is capable of generalization. For example, if one wants to study the force acting on an impurity in a transitional metal one can in principle calculate the polarization of the screening charge an obtain the force. This calculation is somewhat complicated for several reasons:

(i) the conductivity of transitional metals is mainly due to s-electrons, the d-electrons contributing only to about 20%;

(ii) the screening of the impurity is attributed mainly to the d-electrons;

(iii) such a calculation must in principle take into account the hybridization between the s- and d-bands. In a first approximation, this phenomenon may be overlooked if the d-band is filled as in the case of the noble metals, because in the scattering process, the electrons at the Fermi level only are of interest. For transitional metals however, it must be taken account of the hybridization term and, even in this complicated case, the method of Bosvieux and Friedel must lead to the force acting on the impurity.

IV. Phonon Scattering on the Impurity in a Temperature Gradient

The question arises wether, when a phonon of wave vector $\boldsymbol{q}$ is scattered by the impurity to the new state $\boldsymbol{q}'$, the momentum $\hbar(\boldsymbol{q}-\boldsymbol{q}')$ is transferred to the impurity. One may argue that $\hbar\,\boldsymbol{q}$ is not a momentum but a pseudo-momentum; so let us say that the following calculation is made with the approximation of a true momentum transfer process and that it is consequently only a tentative approach to the contribution of phonons to the heat of transport.

Following Fiks[7], it is possible to perform exactly the same calculation as in the case of electrons. We will obtain only a very rough estimate of the contribution to the heat of transport because the Born and adiabatic approximations are very poor for the phonon scattering; in addition, the scattering cross-section of phonons on an impurity is not well known.

However, with these limitations, we can obtain as in the free electron case the force acting on the impurity:

$$\boldsymbol{F}_p = \frac{1}{(2\,\pi)^3}\int \hbar\,\boldsymbol{q}\,g(\boldsymbol{q})\,v(\boldsymbol{q})\,A(q)\,\mathrm{d}_3 q \qquad (46)$$

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[7] V. B. Fiks, Sov. Phys. Solid State **3** (3), 724 [1961].

where $g(\boldsymbol{q})$ is the deviation from the isothermal distribution of the $\boldsymbol{q}$ vector distribution in the temperature gradient, $v(\boldsymbol{q})$ is the group velocity of the phonons $\boldsymbol{q}$ and $A(q)$ is the scattering cross-section of the phonons $\boldsymbol{q}$ on the impurity:

$$A(q) = 2\pi \int \sigma(q,\Theta)\,(1-\cos\Theta)\,\sin\Theta\,\mathrm{d}\Theta\,.$$

The distribution $g(\boldsymbol{q})$ can be deduced from the Boltzmann equation:

$$\boldsymbol{v}(\boldsymbol{q})\cdot\nabla_r f_0 + g(\boldsymbol{q})/\tau(\boldsymbol{q}) = 0 \tag{47}$$

where
$$f_0(\omega) = \frac{1}{e^{\hbar\omega/kT}-1}\,. \tag{48}$$

Similarly the heat flow down the temperature gradient is:

$$W_{\mathrm{p}} = \frac{1}{(2\pi)^3}\int g(\boldsymbol{q})\,\frac{\boldsymbol{q}}{q}\,(\hbar\,\omega)\,v(\boldsymbol{q})\,\mathrm{d}_3 q\,.$$

These expressions are simplified by calculating the specific heat of a system of phonons at temperature T. The internal energy of the system is:

$$E = \int_0^{\omega_{\mathrm{D}}} E(\omega)\,n(\omega)\,f_0(\omega)\,\mathrm{d}\omega$$

where $n(\omega)\,\mathrm{d}\omega = 1/(2\pi)^3\,(4\pi\,q^2\,\mathrm{d}q)$ is the number of phonon states of frequency in the range ω, $\omega+\mathrm{d}\omega$ in the case of an isotropic system where the dispersion curves are the same in all directions. We then obtain:

$$E = \frac{1}{2\pi^2}\int_0^{q_{\mathrm{D}}} \frac{\hbar\,\omega}{e^{\hbar\omega/kT}-1}\,q^2\,\mathrm{d}q \tag{49}$$

and
$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \int_0^{q_{\mathrm{D}}} C_v(q)\,\mathrm{d}q \tag{50}$$

which defines the contribution of the phonons of wave vector q, $q+\mathrm{d}q$ to the specific heat:

$$C_v(q) = \frac{\hbar\,\omega}{2\pi^2}\,q^2\left(\frac{\partial f_0}{\partial T}\right). \tag{51}$$

The deviation $g(\boldsymbol{q})$ o fthe phonon distribution function is then:

$$g(\boldsymbol{q}) = -\frac{2\pi^2}{\hbar\,\omega\,q^2}\,C_v(q)\,\tau(\boldsymbol{q})\,\boldsymbol{v}\cdot\nabla T \tag{52}$$

In the approximation of an isotropic relaxation time, the heat flow in the temperature gradient and the force due to the phonon scattering process on the impurity are then:

$$\left\{\begin{aligned} W_p &= -\tfrac{1}{3}\int_0^{q_{\mathrm{D}}} C_v(q)\,v(q)\,\Lambda(q)\,\mathrm{d}q\,\nabla T, && (53)\\ F_p &= -\tfrac{1}{3}\int_0^{q_{\mathrm{D}}} C_v(q)\,v(q)\,\Lambda(q)\,\frac{A(q)\,q}{\omega(q)}\,\mathrm{d}q\,\nabla T, && (54)\end{aligned}\right.$$

where $\Lambda(q) = v(q)\,\tau(q)$ is the phonon mean free path in the pure matrix. These formulae are simple generalizations of the results obtained in the kinetic theory of gases. Using a Debye approximation with a sound velocity s, it is possible to express $\boldsymbol{F}_p$ in terms of the thermal conductivity coefficient K_p:

$$F_p = -K_p\,\frac{\nabla T}{s}\,\frac{\int_0^{q_{\mathrm{D}}}(C_v\,v\,\Lambda)\,A\,\mathrm{d}q}{\int_0^{q_{\mathrm{D}}}(C_v\,v\,\Lambda)\,\mathrm{d}q}\,. \tag{55}$$

This formula shows clearly that in the formalism used here, the force $\boldsymbol{F}_p$ acting on the impurity is directed toward cold regions, leading to a positive contribution to the heat of transport.

It is possible to obtain a crude estimation of the force F_p in two temperature range:

a) At high temperature ($T \gg \Theta_{\mathrm{D}}$), let us assume that:

$$v\,\Lambda \sim q^n$$

Moreover, in this temperature range, the specific heat $C_v(q)$ is simply:

$$C_v(q) \sim q^2\,k\,.$$

In addition, it is well known that for Rayleigh scattering of phonons the cross-section $A(q)$ is related to the wave number by the expression [8]:

$$A(q) = \beta\,q^4 \tag{56}$$

where β is a coefficient measuring the local perturbation of the lattice by the impurity:

$$\beta = \frac{a^6}{8\pi}\left(\frac{1}{2}\left(\frac{\delta M}{M}\right)^2 + \left[\frac{\delta f}{f} - 12\,\frac{\delta R}{R}\right]^2\right).$$

In this expression $\delta M/M$, $\delta f/f$, $\delta R/R$ are respectively the relative change in the mass at the site of the impurity, the relative change in the force constants and the displacement field around the impurity.

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[8] J. M. ZIMAN, Electrons and Phonons, Oxford University Press 1962.

Using this Rayleigh approximation, which is strictly valuable for low wave numbers, one obtains for F_p:

$$\frac{F_p}{\nabla T} = -\left(\frac{n+3}{n+7}\right) K_p \frac{A(q_{\mathrm{D}})}{s} . \qquad (57)$$

In view of the approximations made in the calculation, the coefficient $[(n+3)/(n+7)]$ appearing in this expression is not of great significance. Nevertheless, one expects a contribution of the phonon scattering to the heat of transport of the following form, in the high temperature range:

$$q_p{}^* = -F_p \frac{T}{\nabla T} \sim 0.5\, K_p\, T \frac{A(q_{\mathrm{D}})}{s} . \qquad (58)$$

In copper for example, for a resistivity cross-section ranging from 10 to 100 Å^2, one obtains values of q^* from 0.3 to 3 eV at a temperature of about 1000 K. This estimation is very crude however principally because of the Born and adiabatic approximations. However it seems that the phonon scattering may be a very important phenomenon which may in fact dominate the electron scattering contribution to the heat of transport.

b) At low temperature, the specific heat $C_v(q)$ is of the form:

$$C_v(q) = \frac{q^2}{2\pi^2}\left(\frac{\hbar\,\omega}{k\,T}\right)^2 k\, e^{-\hbar\omega/kT} \sim q^2\, u^2\, e^{-u} \qquad (59)$$

where $u = \hbar\,\omega/k\,T = \hbar\, s\, q/k\,T$.

Thus the phonon-induced heat of transport of the impurity becomes:

$$q_p{}^* = -F_p \frac{T}{\nabla T} = -K_p \frac{\beta\, T}{s}\left(\frac{k\,T}{\hbar\, s}\right)^4 \frac{\int_0^{u_{\mathrm{D}}} u^{n+8}\, e^{-u}\, \mathrm{d}u}{\int_0^{u_{\mathrm{D}}} u^{n+4}\, e^{-u}\, \mathrm{d}u} . \qquad (60)$$

At low temperature $u_{\mathrm{D}} = (\hbar\, s/k\,T)\; q_{\mathrm{D}}$ is very high and a good approximation to (60) is:

$$q_p{}^* \sim \frac{(n+8)\,!}{(n+4)\,!}\,\frac{K_p\, T}{s}\, A(q_{\mathrm{D}})\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^4 . \qquad (61)$$

It is then shown that $q_{\mathrm{p}}{}^*$ depends strongly on the temperature in the low temperature range. Calculations of this type may be of interest for low temperature thermotransport in metals having a high Debye temperature, such as Al, Mg, Be.

V. Conclusion

For the experimental determination of the force acting on an impurity in an electric field or a temperature gradient, one usually performs diffusion experiments. Except in the case of interstitial diffusion mechanism, the application of the formulae obtained for the electromigration force is not trivial.

a) Following Bosvieux and Friedel, one can assume that an interstitial ion of excess charge z is completely screened, so that the direct electrostatic force (1) acting on the impurity ion vanishes. The only force on the impurity arises from the "electron wind":

$$F(0) = -Z\,\varepsilon\left(\frac{\varrho_i}{\varrho_0}\right).$$

During the jump of the ion between two neighbouring interstitial sites, its screening charge is essentially unaffected and one expects that the force $F(0)$ remains fairly constant over the jump. The drift velocity of the interstitial ion is then:

$$v_i = D_i\, F(0)/k\,T .$$

Nevertheless, the specific resistivity ϱ_i involved in the expression of $F(0)$ is not exactly the same as the resistivity $(\varrho_i)_{\mathrm{Linde}}$ obtained by a resistivity measurement because $(\varrho_i)_{\mathrm{Linde}}$ includes the scattering of electrons on the interstitial ion and its relaxed neighbours, whereas ϱ_i is only due to the scattering on the interstitial ion itself. One would expect that:

$$\varrho_i \lesssim (\varrho_i)_{\mathrm{Linde}} .$$

This effect may be of importance for big interstitial ions whose neighbourhood relaxation is rather large.

b) In the case of a vacancy diffusion mechanism, the situation is complicated by the presence of a neighbouring vacancy and the change of the screening charge of the ion over the jump.

The calculation of Bosvieux and Friedel provides a crude estimation of the force acting on the impurity ion, due to the polarization of the screening charge of the neighbouring vacancy. This force is usually referred to by a f_0 term in the expression of $F^z(0)$ at the stable position [9]:

$$F^z(0) = Z\,\varepsilon\left[(1+f_0) - \left(\frac{\varrho_i^z}{\varrho_0}\right)\right]$$

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[9] N. V. Doan and G. Brebec, J. Phys. Chem. Solids **31**, 475 [1970].

the subscript z indicating that the screening charge of the ion is $z = Z' - Z$ at the stable position.

The f_0 term of Bosvieux and Friedel is usually calculated in an approximation where the screening charges of the two defects (impurity and vacancy) are assumed to be independent of each other. In fact, there are interference effects between the two charge clouds and the screening charge density of the complex (ion + vacancy) is not simply the sum of the two screening charges of the individual defects. A better calculation of the force acting on an impurity ion neighbouring a vacancy should involve the determination of the screening charge of the impurity-vacancy complex, according to the general method of Bosvieux and Friedel; but as the f_0 term is not very large however, the approximation of independent screening seems justified.

Nevertheless, it must be emphasized that the expression of f_0 contains the factor $1/\varrho_0$ as in Equation (33). Then a plot of $F(0)$ versus $1/\varrho_0$ is a straight line (assuming that ϱ_i is temperature independent) which intersects the axis $1/\varrho_0 = 0$ at $Z\,\varepsilon$ [and not $Z(1+f_0)\,\varepsilon$]. The value of f_0 affects the slope of the curve and an experimental determination of f_0 is then very difficult.

During the jump, the screening charge of the impurity ion changes and if one assumes [1] that the ion is completely screened at the saddle point, the direct electrostatic force vanishes. Neglecting the f_0 term arising from the polarization of the two half-vacancies, one obtains for the force at the saddle point:

$$F^{z+Z}(0) = -Z\,\varepsilon\left(\frac{\varrho_i^{z+Z}}{\varrho_0}\right).$$

The average force along the jump is then:

$$F = \tfrac{1}{2}\,[F^z(0) + F^{z+Z}(0)] = \tfrac{1}{2}\,Z\,\varepsilon\left[1 + f_0 - \frac{\bar\varrho_i}{\varrho_0}\right]$$

where $$\bar\varrho_i = \varrho_i^z + \varrho_i^{z+Z}.$$

It is reasonable to expect that, following the arguments already given in the case of an interstitial mechanism:

$$\varrho_i^z \lesssim (\varrho_i^z)_{\text{Linde}},$$
$$\varrho_i^{z+Z} \lesssim (\varrho_i^{z+Z})_{\text{Linde}}.$$

In this approximation we assume for example that the specific resistivity of a Cd ion at the saddle point in a monovalent matrix (screening charge +2) is of the same order of magnitude as that of a substitutional In ion (screening charge +2) in the same matrix. According to this assumption, the resistivity $\bar\varrho_i$ would be:

$$\bar\varrho_i \lesssim (\varrho_i^z + \varrho_i^{z+Z})_{\text{Linde}}.$$

For a check of this idea, we give in Table 1 a comparison between $\bar\varrho_i$ determined by Doan [10] in Ag and $(\varrho_i^z + \varrho_i^{z+Z})_{\text{Linde}}$ [11].

Table 1. Comparison of $\bar\varrho_i$ and $(\varrho_i^z + \varrho_i^{z+Z})_{\text{Linde}}$ in Silver.

Matrix Ag	z	$\bar\varrho_i$ [10]	$(\varrho_i^z + \varrho_i^{z+Z})$
Cd	1	2.9	2.2
In	2	5.3	6.1
Sn	3	9.1	11.6
Sb	4	14.5	15.

For Sb we have assumed that the resistivity at the saddle point is almost the same as the resistivity at the stable position since a phase-shift analysis [12] shows that the variation of ϱ_i versus z has a maximum for $z \sim 4$.

In spite of the discrepancies between the experimental values of $\bar\varrho_i$ and the estimated values, which may be traced to the very crude approximations made, there is a fairly good agreement between the two values. This type of interpretation would be suitable for transition impurities in normal metals and for impurity diffusion in transition metals.

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[10] N. V. Doan, J. Phys. Chem. Solids, to be published.

[11] J. O. Linde, Ann. Phys. **15**, 219 [1932].

[12] B. Coqblin, J. Delaplace, V. Levy, A. A. Gomes, and J. Hillairet, J. Physique **28**, 75 [1967].