ELECTRICAL CONDUCTIVITY OF A METAL DISSOLVED IN A MOLTEN SALT*

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A physical assumption concerning the role of the lattice order in electron scattering, together with a method already used for liquid metals,[1,2] has been used to calculate the resistivity ρ of an alkali metal M dissolved in a molten alkali halide MX in the region of small metal concentrations.

We have assumed that (i) the valence electrons of the added metal become the conduction electrons of the system, (ii) the electrons are in plane-wave states and are scattered by the pseudopotentials[3,4] $v_M(\vec{r})$, $v_X(\vec{r})$ of the M^+ and X^- ions, (iii) the scattering of the electrons can be described by first-order time-dependent perturbation theory, and (iv) the resistivity can be obtained by solving the Boltzman equation assuming elastic scattering.[5]

With these assumptions it can be shown[6] that

$$\rho = \frac{m^2}{12\pi^3 e^2 \hbar^3 n_e^2} \int_0^{2k_F} [N_M a_M(\vec{k}) \mid v_M(\vec{k}) \mid^2$$
$$+ N_X a_X(\vec{k}) \mid v_X(\vec{k}) \mid^2 + 2\operatorname{Re}(N_X N_M)^{1/2} a_{MX}(\vec{k})$$
$$\times v_M{}^*(\vec{k}) v_X(\vec{k})] k^3 dk, \qquad (1)$$

where Re means "the real part of." Here m and e are the electronic mass and charge (in emu), n_e, N_M, and N_X are the electron, metal ion, and halide ion number densities, and k_F is the Fermi wave vector. The $v(\vec{k})$ are defined by

$$v(\vec{k}) = \int v(\vec{r}) \exp[i\vec{k}\cdot\vec{r}] d\vec{r},$$

and the $a(\vec{k})$, which are a measure of the ionic order, are

$$a_M(\vec{k}) = (N_M V)^{-1} \mid \sum_i \exp[i\vec{k}\cdot\vec{M}_i] \mid^2$$
$$= 1 + (N_M V)^{-1} \sum_{ij} \exp[i\vec{k}\cdot(\vec{M}_i - \vec{M}_j)],$$

$$a_X(\vec{k}) = (N_X V)^{-1} \mid \sum_i \exp[i\vec{k}\cdot\vec{X}_i] \mid^2$$
$$= 1 + (N_X V)^{-1} \sum_{ij} \exp[i\vec{k}\cdot(\vec{X}_i - \vec{X}_j)],$$

and

$$a_{MX}(\vec{k}) = (N_X N_M V^2)^{-1/2} \sum_{ij} \exp[i\vec{k}\cdot(\vec{X}_i - \vec{M}_j)], \qquad (2)$$

where V is the system volume. $\vec{M}_i$ and $\vec{X}_i$ are

the positions of the metal and halide ions.

Since n_e is small, so is k_F (compared to the pure metal), and we need only the form of $v(\vec{r})$ for regions of $\vec{r}$ outside the ion core. We take

$$v_M(\vec{r}) = -v_X(\vec{r}) = -(ce)^2 r^{-1} \exp[-\lambda r], \qquad (3)$$

where the ions are screened by the electron gas according to the Thomas-Fermi prescriptions, with

$$\lambda^2 = 4\pi^{-1}(ec)^2 \hbar^{-2} k_F.$$

Screening of an ion due to static displacement of other ions is included in the model, as such displacement is contained in the functions $a(\vec{k})$. Polaron effects due to dynamic displacement of the ions by an electron are expected to be small, because the propagation velocities of polarization modes are much less than the electron velocity (at an electron concentration of 1% of that of the pure metal the Fermi velocity is $\approx 20\%$ of that of the pure metal).

If τ and $\Lambda = \hbar k_F m^{-1} \tau$ are the electron relaxation time and mean free path, respectively, then in this model $\hbar\tau^{-1} > E_F$, the Fermi energy (or, equivalently, the mean free path is less than the de Broglie wavelength). Under these conditions there is doubt that the method based on the Boltzman equation and first-order perturbation theory is valid.[7] The following modification of the model is used in recognition of the fact that $\hbar\tau^{-1} > E_F$.

Corresponding to the energy broadening $\Delta E = \hbar\tau^{-1}$ of a state there is a range of k, given by $\Delta k = \Delta E (\partial E/\partial k)_{k_F}^{-1}$, about k_F. If we consider a wave packet constructed from plane waves in this range of Δk, then it is localized over a range $\approx (\Delta k)^{-1} = \hbar^{-1}\tau(\partial E/\partial k)_{k_F} = \Lambda$. Thus during a scattering event the electron exists and travels over a range $\approx \Lambda$. It is physically plausible that the electron "perceives" only the order within a range Λ during the scattering, and hence that only this order determines the scattering. This is described in the model by replacing Eq. (2) by

$$a_M(\vec{k}, \Lambda) = 1 + (N_M V)^{-1} \sum_{ij} W(\mid \vec{M}_i - \vec{M}_j \mid, \Lambda)$$
$$\times \exp[i\vec{k}\cdot(\vec{M}_i - \vec{M}_j)], \qquad (4)$$

where $W(|\vec{M}_i - \vec{M}_j|, \Lambda)$ is a weighting function with the limiting values

$$W(|\vec{M}_i - \vec{M}_j|, \Lambda) = 1, \quad |\vec{M}_i - \vec{M}_j| \ll \Lambda;$$

$$W(|\vec{M}_i - \vec{M}_j|, \Lambda) = 0, \quad |\vec{M}_i - \vec{M}_j| \gg \Lambda.$$

Similar expressions are used for $a_X(\vec{k}, \Lambda)$ and $a_{MX}(\vec{k}, \Lambda)$. To be self-consistent, Λ is chosen so that the $a(\vec{k}, \Lambda)$ yield a resistivity and hence a mean free path of Λ (and not $\Lambda' \neq \Lambda$).

We anticipate that at the lowest metal concentrations, $\Lambda \ll b$, the interatomic distance, when the $a(\vec{k}, \Lambda)$ take the form

$$a_M(\vec{k}, \Lambda) = a_X(\vec{k}, \Lambda) = 1, \quad a_{MX}(\vec{k}, \Lambda) = 0, \quad \Lambda \ll b. \quad (5)$$

Combining Eqs. (1), (3), and (5) gives

$$\rho = \frac{4(mec)^2}{3\pi\hbar^3 n_e^2} \int_0^{2k_F} \frac{(N_X + N_M)k^3 dk}{(k^2 + \lambda^2)^2}$$

or

$$\rho n_e^2 = 2(mec)^2(3\pi\hbar^3)^{-1} S(\alpha)(N_X + N_M), \quad (6)$$

where

$$S(\alpha) = \ln(1 + \alpha) + (1 + \alpha)^{-1} - 1$$
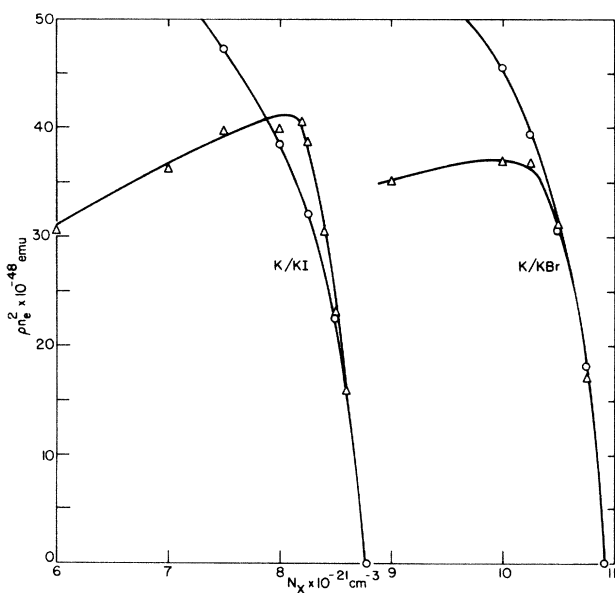
and

$$\alpha = 4k_F^2 \lambda^{-2}.$$

In Fig. 1 is plotted ρn_e^2 as a function of N_X determined by Eq. (6), for the systems K/KI and K/KBr, together with the experimental variation[8,9] of ρn_e^2 for these systems. In processing the data, it has been assumed (i) that the electronic conductance is the actual conductance minus the ionic conductance of the pure salt, and (ii) in the absence of density data, that the molar volumes of M and MX are additive.

In Fig. 2 are plotted the theoretical and experimental values of Λ. The choice of $a(\vec{k}, \Lambda)$ of Eq. (5) is consistent in that at low metal concentrations the predicted Λ are such that $\Lambda \ll b$. In view of the fact that this is an a priori calculation, the agreement of theory and experiment is considered excellent.

When Λ increases to a value comparable to b, the $a(\vec{k}, \Lambda)$ begin sampling the order of the nearest neighbors, in which case

$$a_M(\vec{k}, \Lambda) < 1, \quad a_X(\vec{k}, \Lambda) < 1, \quad a_{MX}(\vec{k}, \Lambda) > 0, \quad 0 < k < 2k_F.$$

Noting that in Eq. (1) the sign of $v_M^*(\vec{k})v_X(\vec{k})$ is essentially negative, the effect of all these changes of the $a(\vec{k}, \Lambda)$ is to decrease the value of ρn_e^2 below that predicted by Eq. (6). In Fig. 1 it is evident that there is a departure of the experimental value of ρn_e^2 below that of Eq. (6) when Λ in-
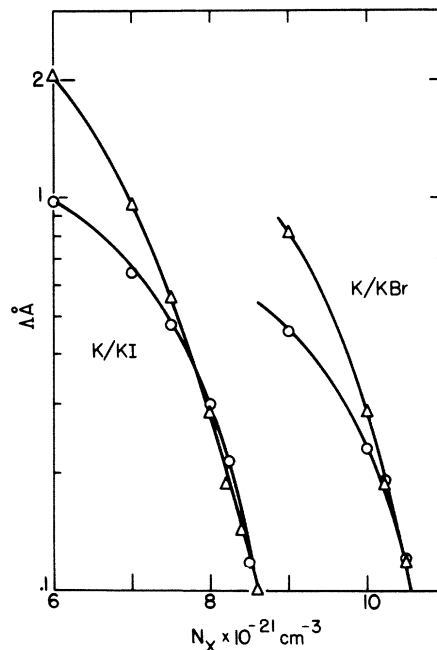

Fig. 1. ρn_e^2 as a function of N_X for K/KBr at 760°C and K/KI at 700°C. Circles represent theoretical points; triangles represent experimental points.

Fig. 2. Λ as a function of N_X for K/KBr and K/KI. Circles represent theoretical points; triangles represent experimental points.

433

creases to a value of $\Lambda \approx b/10$, when the function $W(|\vec{M}_i - \vec{M}_j|, \Lambda)$ begins to include nearest neighbors in the $a(\vec{k}, \Lambda)$. This is regarded as further confirmation of the assumptions concerning the ionic order.

It remains to point out that the theoretical reasons why the assumptions of first-order perturbation theory and the Boltzman equation should be so successful in a region where $\hbar\tau^{-1} > E_F$ are obscure.

A full description of this work, and its successful application to the high metal concentration region, will appear later. It is a pleasure to thank Professor S. A. Rice, who drew my attention to metal-molten salt systems, for help and encouragement.

[1]J. M. Ziman, Phil. Mag. 6, 1013 (1961).
[2]C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, Phil. Mag. 7, 865 (1962).
[3]J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1958).
[4]M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).
[5]See, for example, J. M. Ziman, Electrons and Phonons (Clarendon Press, Oxford, England, 1960), Chap. VII.
[6]The method is a simple extension of the one used in reference 1.
[7]See, for example, R. E. Peierls, Quantum Theory of Solids (Clarendon Press, Oxford, England, 1955), Chap. VI, or, H. W. Lewis, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. VII.
[8]H. R. Bronstein and M. A. Bredig, J. Am. Chem. Soc. 80, 2077 (1958).
[9]H. R. Bronstein and M. A. Bredig, J. Phys. Chem. 65, 1220 (1961).

MAGNETORESISTANCE AND FERMI SURFACE TOPOLOGY OF THALLIUM*

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Alekseevski and Gaidukov[1] have recently published the results of a detailed study of the transverse magnetoresistance in thallium at low temperatures. We have independently studied the magnetoresistance in a number of pure thallium crystals, including three oriented along the principal symmetry directions, and our results agree with those of Alekseevski and Gaidukov. It is the purpose of this paper to show that these results can be explained in terms of the nearly-free electron Fermi surface of thallium provided that magnetic breakdown occurs over almost the whole of the hexagonal face of the third Brillouin zone.

Figure 1(a) shows the directions of magnetic field for which open orbits can exist in thallium as inferred by Alekseevski and Gaidukov from these experiments. The shaded area represents a two-dimensional region of open directions while the lines are one-dimensional regions. In Fig. 1(b) our measurements of the transverse magnetoresistance of a specimen in which the current is along the [0001] direction are plotted as a function of the magnetic field direction in the basal plane. The one-dimensional regions are revealed as sharp minima in this curve, as in the results of Alekseevski and Gaidukov.

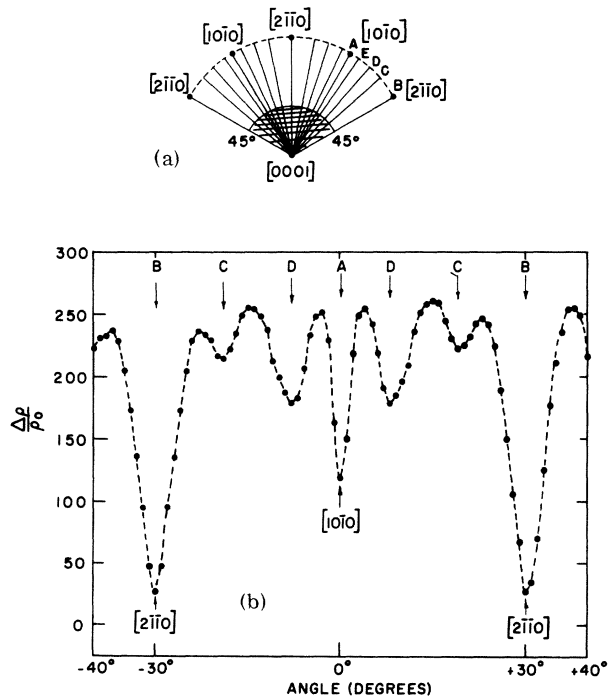The third and fourth bands of Harrison's[2] nearly-

FIG. 1. (a) Open-orbit directions in thallium. The shaded area is a two-dimensional region and the lines are one-dimensional regions. (b) Transverse magnetoresistance in an [0001] crystal of thallium at 1°K and 20 kG as a function of field direction in the basal plane.