

is conserved on entering the new grain, then, since the momenta differ, scattering occurs.

Let us consider the influence of temperature. Suppose that the reflection probability is proportional to the fraction of states which are filled for an electron traveling in the 2 direction with an energy such that momentum is conserved [i.e.,  $E_2 = (m_1/m_2)E_1$ , where  $m_1$  and  $m_2$  are the effective masses associated with the 1 and 2 directions, respectively, and  $m_2 > m_1$ ]. If we suppose that the Fermi surface is cylindrically symmetrical around the 1 direction, then the total probability of the electrons being scattered from 1 to any other state is

$$2 \int_0^{\pi/2} \frac{2\pi \sin\theta d\theta}{\exp\left\{\left(\frac{m_1}{m_2}-1\right)\frac{E_1}{kT}\right\} + 1} \quad (1)$$

where  $\theta$  is the angle through which the crystallographic axes in grain 2 are rotated relative to those in grain 1. The assumption has been made that all values of  $\theta$  are equally likely. The ratio  $m_1/m_2$  of course depends upon  $\theta$ , i.e., upon the detailed shape of the surfaces of equal energy in  $k$  space. Suppose that

$$(m_1/m_2)E_1 = (1-\alpha \sin\theta)E_1. \quad (2)$$

In this case the equi-energy surfaces resemble an oblate spheroid. Upon substitution and integration of Eq. (1) one obtains

$$2 \frac{kT}{\alpha E_1} \log(1 + e^{-\alpha E_1/kT}) + 1 - \frac{kT}{\alpha E_1} \log 2 \cong 1 - \frac{kT}{\alpha E_1} \log 2. \quad (3)$$

We shall assume that the resistance introduced is proportional to the total probability of scattering of the electron most likely to be scattered. Thus the grain boundary resistance for the special case considered is given by Eq. (3) and decreases as the temperature increases. The particular dependence is in qualitative agreement with the observations of Yntema<sup>2</sup> for copper. It should be noted that the exact shape of the resistance versus temperature curve will depend not only on the shape of the Fermi surface, but also on the distribution of orientation changes at grain boundaries.

If the resistivity at absolute zero is determined by a mean free path which is of the order of the grain size, then

$$\rho = 2mv/ne^2l, \quad (4)$$

where  $l$  is the mean free path,  $n$  is the number of electrons per unit volume, and  $v$  is the velocity of the electrons at the top of the Fermi distribution. Blewitt states that his grain size is of the order of a millimeter after recrystallization. Inserting values appropriate for copper into (4), one obtains  $\rho = 1.4 \times 10^{-10}$  ohm cm which compares reasonably well with results obtained by extrapolating Blewitt's data linearly to absolute zero (i.e.,  $\rho_{\text{obs}} = 4.0 \times 10^{-10}$ ,  $2.7 \times 10^{-10}$ , and  $2.3 \times 10^{-10}$  ohm cm).

The author would like to thank T. H. Blewitt for stimulating discussions which led to the idea during a visit to Oak Ridge.

<sup>1</sup> Blewitt, Coltman, and Redman, Phys. Rev. 93, 891 (1954).

<sup>2</sup> G. B. Yntema, Phys. Rev. 91, 1388 (1953).

## Soft X-Ray Emission Bands in Metals

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EXPERIMENTAL observations of the soft x-ray emission from light metals<sup>1</sup> shows that, in general, the width of an emission band corresponds closely to the maximum energy of the

TABLE I. Excess band width due to exchange, for metallic sodium as a function of  $\beta$ , and the ratio of the electronic specific heat  $C_v$  to the Sommerfeld value  $C_v^{(0)}$ .

$\beta$	0.5	0.6	0.7	0.8	0.9	1.0
Excess width in ev	1.83	1.30	0.74	0.17	-0.43	-1.04
$C_v/C_v^{(0)}$	0.77	0.83	0.90	0.95	1.0	1.05

Fermi distribution of the conduction electrons as calculated by the Sommerfeld free electron formula. According to Koopman's theorem, however, the width of an emission band should be given by the difference between the eigenvalues of the Fock equation for the lowest and the highest occupied states of the conduction band. These eigenvalues contain a term arising from exchange effects and are given by

$$\epsilon_k = \frac{\hbar^2 k_0^2}{2m} \alpha^2 - \frac{e^2 k_0^2}{\pi} y(\alpha),$$

where

$$y(\alpha) = 1 + \frac{1}{4} \left( \frac{1}{\alpha} - \alpha \right) \log \left( \frac{1+\alpha}{1-\alpha} \right)^2,$$

$\alpha = k/k_0$  and  $\hbar k_0$  is the radius of the occupied sphere in momentum space. Hence the width of an emission band is equal to  $\zeta_0 + e^2 k_0/\pi$ , when  $\zeta_0$  is the Fermi width for free electrons. The additional term due to exchange amounts to 5.1, 4.1, and 8.0 electron volts for Li, Na, and Al, respectively, and thus completely destroys the good general agreement with the value of  $\zeta_0$ . This effect shows very directly the need for some modification of the Hartree-Fock theory as applied to the conduction electrons of metals. According to the theory of Bohm and Pines<sup>2</sup> the exchange effects should be calculated, not with the Coulomb, but with a screened potential. When this is done the additional term in the band width due to exchange is  $(e^2 k_0/\pi)(1-\beta-\beta^2/4)$ , where  $\beta = (\alpha n'/n)^{1/2}$ ;  $n$  is the number of electrons per unit volume and  $n'$  is the number of plasma waves per unit volume.

Table I shows the excess band width, due to exchange, for metallic sodium as a function of  $\beta$ . The last line shows the ratio of the electronic specific heat  $C_v$  to the Sommerfeld value  $C_v^{(0)}$  which neglects exchange altogether. An expression for this ratio is given by Pines<sup>3</sup> [Eq. (38)]. The observed band width for Na is rather less than the free electron  $\zeta_0$ , and the observed electronic specific heat is greater than  $C_v^{(0)}$ . However it is perhaps open to doubt whether the theory of Bohm and Pines is strictly applicable when  $\beta$  is as large as 0.9 or 1.0.

It may be of some significance that the observed band width for metallic Al is nearly equal to the free electron  $\zeta_0$ , thus implying that here also a screened potential is operative for the whole conduction band of three electrons per atom, and hence that plasma oscillations occur even in a conduction band where the electrons move in a strong periodic potential.

Finally it may be noticed that if one uses a purely empirical screened potential of the form  $e^{-\lambda r}/r$ , the excess band width is given by

$$\frac{e^2 k_0}{\pi} \left\{ 1 - \frac{\gamma^2}{4} \log \left( 1 + \frac{4}{\gamma^2} \right) + \gamma \tan^{-1} \frac{2}{\gamma(\gamma^2+3)} \right\},$$

where  $\gamma = \lambda/k_0$ . In this case the excess band width decreases monotonically to zero as  $\gamma$  increases and could not, therefore, lead to a band width less than  $\zeta_0$ .

<sup>1</sup> H. W. B. Skinner, Trans. Roy. Soc. (London) 239, 95 (1940).

<sup>2</sup> D. Bohm and D. Pines, Phys. Rev. 92, 609 (1953).

<sup>3</sup> D. Pines, Phys. Rev. 92, 626 (1953).

## Interpretation of Ionic Mobilities in Nitrogen

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JOHNSON<sup>1</sup> has interpreted the measured<sup>2</sup> ionic mobilities in nitrogen as being primarily determined by the quadrupole interaction between ion and gas molecule. The purpose of this note is to point out that the agreement between Johnson's roughly calculated mobility and the experimental value is fortuitous, the main defects in Johnson's calculation being the neglect of the polarization interaction and the overestimate of the quadrupole interaction. The interaction between the ion and induced dipole of the molecule (polarization interaction) is  $V_p = -\frac{1}{2} e^2 \alpha r^{-4}$ ,