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LIQUID AND AMORPHOUS METALS

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Abstract.- A discussion is given of some of the properties of liquid and amorphous metals under conditions when the mean free path has its minimum value. The concept of a 'minimum metallic conductivity' is discussed, with applications to expanded fluid mercury and caesium. Then materials with somewhat higher conductivity are mentioned, particularly liquid transition metals. The conditions under which the author's theory for these materials should be valid are described. A qualitative model for a positive Hall constant in liquid alloys is proposed.

1. METALS WITH SHORT MEAN FREE PATH. In much of our work in the last fifteen years my colleague Professor Davis and I have examined 1 the electrical properties of a degenerate Fermi gas in a disordered environment, where the scattering is so strong that first-order perturbation theory is no longer valid, and the mean free path L is comparable with the interatomic distance <u>a</u> (L \sim a, the Ioffe-Regel condition). We have done this, not by considering multiple scattering, but by the use of the so-called random phase approximation, according to which, in a tight-binding situation, the wave function of an electron near the Fermi energy $\mathbf{E}_{\mathbf{F}}$ is of the form

$$\sum_{n} a_{n} \exp(i\phi_{n})\psi_{n}(r), \qquad (1)$$

where ψ_n are atomic wave functions, and a_n , ϕ_n are random amplitudes and phases at sites denoted by n. This approximation has been used by various authors, notably Hindley² and by Friedman³ in his treatment of the Hall effect, to which I will return later. My aim in this lecture is to see what this concept has to tell us about liquid and amorphous metals.

First of all, however, I must outline what in my view is reasonably certain and what is controversial in the conclusion that can be drawn from the wave-function (1). I start with the expression for the conductivity of a 'metal',

$$\sigma = S_{F}e^{2}L/12\pi^{3}\hbar, \qquad (2)$$

where S_F is the Fermi surface area. If L = a, this becomes

$$\sigma = S_F e^2 a / 12\pi^3 \hbar$$
 (3)

If the number of electrons per unit volume is n/2a (n = 1 for a divalent metal) this reduces to

$$\sigma = \frac{1}{3} n^{2/3} e^2 /\hbar a$$
 (4)

For reasonable values of <u>a</u>, values of σ of the order 3-4000 $\Omega^{-1} \text{cm}^{-1}$ ($\rho \sim 300 \mu \Omega \text{cm}$) are expected. Liquid and amorphous transition metals often have resistivities of more than half this value.

The use of equation (3) when L \sim a can of course be criticised because the wavenumber k is no longer a good quantum number. It can however be derived from the Kubo-Greenwood formula (see ref. 1, p 29), a slightly different value, $\pi/8$ instead of 1/3, being obtained. In deriving this equation, the arbitrary assumption is made that the variation of the a_n is small. It is realised that this is an untested hypothesis, so that the results obtained are qualitative.

It is a fairly common property of narrow band crystalline metals that the resistivity saturates at about 100 μ Ω cm. Thus Wiesmann et al.⁴, Allen et al.⁵ and Chakraborty and Allen⁶ have discussed the d band metals Nb₃Ge and Nb₃Sn in this connection. The present author (see also Fisk and Webb⁷) believes that in these materials the Ioffe-Regel condition is already reached due to the strong phonon scattering at high temperatures. The resistivity is lower than the 300 $\mu \Omega$ cm mentioned above because, in our view, the Fermi surface is likely to be large, on account of several overlapping sub bands. As regards the T-dependence, the authors guoted^{5,6,7} show that

$$\sigma = \sigma_{BG} + const$$
 (5)

gives a good approximation to the experimental results, σ_{BG} denoting the value calculated from the Bloch-Grüneisen formula, taking the electron-phonon interaction from the superconducting properties. The rationale of such a formula, they suggest, is the following. Suppose we make use of (2) with L calculated from the Bloch-Grüneisen treatment for single scattering only. The assumption then is that L >> a. For multiple scattering a calculation in ascending powers of L_0/a (L_0 being the calculated value of the mean free path) should then given an expansion of the form

$$\frac{S_{F}e^{2}L}{12\pi^{3}\hbar}\left[1 + A_{1}\frac{a}{L} + A_{2}\left(\frac{a}{L}\right)^{2} + \ldots\right].$$

The second term will thus be independent of L, and thus of T, so that eqn.(5) is reproduced.

For liquid transition metals it would be interesting to see if the T-dependence of the resistivity could be represented by (5), σ_Z replacing σ_{BG} where σ_Z is calculated from the Ziman formula. The comparison has not been made. We think the model is reasonable for metals such as La, V, Nb, where in the crystal it is not believed that there are separate s and d-like parts of the Fermi surface. The others, such as Pd, are discussed in § 3 of this paper.

For metallic glasses the temperature - coefficient of resistance is normally small. Mooij 8 and Tangenan 9 point out

the d ρ/dT becomes negative for alloys when $\rho > 170 \ \mu \ \Omega \ cm$. Johnson and Girvin¹⁰ give an explanation of this in terms of the interaction with phonons. In a qualitative way, one might expect that when the condition L \sim a is reached, phonon scatgering cannot increase the resistance; but the smearing out of the scattering potential with increasing T might decrease it. Other possibilities are discussed in ref. 1, p 178 and by Brouers and Brauwers¹¹

2. METAL-INSULATOR TRANSITIONS OF ANDERSON TYPE. Although according to Ioffe and Regel and as is apparent from the wave function (1), values of L less than <u>a</u> cannot exist, eqn.(4) does <u>not</u> give the lowest metallic conductivity possible. If the disorder is great enough to broaden substantially the range of energies of occupied states, then (3) can be written

$$r = S_{\rm p} e^2 a g^2 / 12 \pi^3 h$$
 (6)

where $g = N(E_F)/N(E_F)$ free.

Eqn.(6) can be deduced from the Kubo-Greenwood formula. As g decreases, (6) should remain valid until localization sets in, in the sense of Anderson's¹² paper of 1958. This occurs when $g \sim 1/3$, and the conductivity at this point,

$$\sigma_{\min} \approx 0.025 e^2 / ha \tag{7}$$

has been called by the present $author^{13}$ the 'minimum metallic conductivity' and is in the range 300 - 500 $\Omega^{-1}cm^{-1}$ if <u>a</u> is a few Angstroms; the constant is dependent on coordination and other factors.

The existence of a minimum metallic conductivity is of course controversial. Recent work by Abrahams et al.^{14,15}, using a scaling argument, comes to the conclusion that it does not exist. Wegner¹⁶ and Götze¹⁷ come to a similar conclusion, as did earlier work based on classical percolation theory. They believe that the conductivity is zero if the Fermi energy lies at the mobility edge. According to the Kubo-Greenwood formula, this can be so only if the a_n in eqn.(1) show strong variations over a long range, as shown by the present author in a paper to be published. Theoretical work which does lead to a minimum metallic conductivity is the numerical work of Licciardello and Thouless¹⁸ and the recent analysis of Edwards¹⁹. The experimental evidence comes from many systems in which the Fermi energy can be shifted through a mobility edge by change of composition or in other ways, leading to a metal-nonmetal transition of the type shown in fig. la, rather than that predicted by Abrahams et al. which is probably^{*} as shown in fig. lb.



Fig. 1 ρ -T curves (a) as observed, (b) if σ_{\min} does not exist.

The evidence ^{1,20} necessarily comes from solid systems (impurity bands, $La_{1-x}Sr_{x}VO_{3}$ and similar materials), because it depends on the behaviour of the conductivity at low temperatures; it is reviewed by Mott et al.²⁰ and Mott and Davis¹. As far as I know, the metallic glasses never approach this regime. Within the subject matter of the conference, systems are relevant in which a conduction and a valence band in a non-crystalline system separate with increasing volume. Expanded fluid mercury has been extensively discussed in this connection. What is believed to happen is illustrated in fig. 2. As the two bands separate, localization sets in at the minimum of the so-called 'pseudogap'. When this occurs, two conduction channels are expected in solids, as follows. (a) At high T, by electrons excited to the mobility edge, giving a conductivity



Fig. 2 (a) Density of states with two overlapping bands. (b) the same, showing range of localized states.

$$\sigma = \sigma_{\min} \exp\left(-\varepsilon/kT\right) \tag{8}$$

with $\varepsilon = E_{c} - E_{F}$, E_{c} being the mobility edge as marked in fig. 2.

(b) Variable hopping at low T.

The model which I have discussed up till now is essentially a 'one-electron model'. I want now to look at what happens for 'Hubbard bands' - that is, for systems such as Si:P, metal-ammonia and expanded fluid caesium, in which the material is made up of one-electron centres (D^O). The upper Hubbard band, put forward by Fritzsche for Si:P prior to Hubbard's work and called the D band, represents the movement of an electron from a D centre through an array of D^O centres. The material is an insulator because the upper band is separated from the lower by the 'Hubbard U'. The density of states should be as in fig. 3, the upper Hubbard band being much wider than the lower.



Fig. 3 Suggested density of states in doped silicon: (a) lower Hubbard D^O band, (b) upper Hubbard D⁻ band, (c) conduction band.

As was first pointed out by Cyrot²¹,

The analysis is mine; the authors quoted do not make clear what behaviour they expect.

the M-NM transition in such systems occurs when the bands begin to overlap and this model leads to the formula

$$n^{1/3} a_{tr} \simeq 0.26$$
 (9)

with the constant depending little on the refinements introduced into the model. The present author believes, however, that the transition is none the less of Anderson type, as in fig. 2, occurring when $E_{\rm F}$ and E_C coincide. Disorder, however, introduces a difference. In a crystalline system, at a metal-insulator transition, a first order transition as in fig. 4, is expected. If one varies the parameter x (volume or composition) which leads to the transition, there should be a discontinuous change in n, the number of free electrons. If, however, the disorder is great enough, I believe that this discontinuity is wiped out, and have discussed the conditions for this²². I assume that this is the case in Si:P. For the liquids NaNH3 and expanded fluid caesium, it seems that this is not so and, as fig. 4 illustrates, the transition of necessity leads to a



Fig. 4 Free energy as a function of volume or composition at a metalinsulator transition.

critical point. At this critical point, then, the concentration should be given by (9) and the conductivity - at any rate approximately - by (7). For expanded fluid caesium, it is satisfactory that the work of Freyland 23,24 shows that both predictions are satisfied.

I might add that, for reasons I have given elsewhere, for band crossing

transitions such as that in expanded fluid mercury the critical point will not be of this type, but of the normal fluid-vapour form. For mercury the conductivity at the critical point is much smaller, by about five orders of magnitude.

3. LIQUID AND AMORPHOUS TRANSITION METALS AND ALLOYS. In this section I discuss transition metals, such as Ni or Pd₂ in which an s-like and a p-like part of the Fermi surface are thought to exist. In 1936 I put forward a theory²⁵ of the electrical resistance of such metals. In this, conduction is due to parts of the Fermi surface which are s-like, but the main scattering processes are to parts that are d-like, where the density of states is high. Assuming the Fermi surface areas to be S_s and S_d respectively, the conductivity should be

$$e^{2}/12\pi^{3}\hbar)\left[S_{c}L_{c}+S_{d}L_{d}\right]$$
(10)

where L_s and L_d are the respective mean free paths. The mean free paths are due both to phonons and in alloys and liquids to disorder. For L_s I write

$$\frac{1}{L_s} = \frac{1}{L_{ss}} + \frac{1}{L_{sd}} , \qquad (11)$$

the two terms on the right referring to scattering to another s-like point on the Fermi surface and to a d-like part; 1/Lsd >> 1/L_{ss}. The success of this model for crystalline metals was last reviewed by the present author²⁶ in 1964. It should be strongly emphasised that it depends on the assumption of a narrow d-band hybridised with an s-band, and that this is probably only a good model if the transition metal is Ni or Pd or the elements next to it in the periodic table. Thus $\texttt{Pettifor}^{27} \texttt{ calculates } \texttt{m}_d \texttt{ about twice as}$ great for Pd or Rb as for Zr and Nb. For the latter the considerations of § 2 should be valid.

For isolated transition metal atoms, as first proposed by Friedel²⁸, resonance can lead to a large d phase shift n_2 and so to a large residual resistance. When many

body theory is applied, interaction between the conduction electron and the electron on the impurity can lead to Kondo behaviour.

For liquid transition metals Dreirach et al.²⁹ put forward some years ago a model in which there is a single Fermi surface, S_s , and a large phase shift, n_2 , giving a large value of 1/L. The present author³⁰ proposed an alternative theory, in which the resistivity is explained by a model similar to that for solids. The two models were discussed further by Evans et al.³¹ and I do not think the controversy about them is resolved. They make rather different predictions. In the author's model, and if $s \rightarrow d$ scattering is the predominant mechanism, the theory gives little T-dependence of the resistivity. That of Evans et al., being an adaptation of Ziman's theory of conduction in liquid metal, gives a positive TCM if n is of the order unity, a negative one if n \sim 2. believe a distinction between the two models can be made only if L_s > a; if not, in my view, a distinction between the s and d bands cannot be made; there is no Fermi surface and there is no obvious reason why the Ziman theory should be applicable or its dependence of dp/dT on n should be valid.

In my paper³⁰ of 1972 I do not attempt to calculate L_d , but suppose that it has reached its minimum value ($L_d \sim a$). In that case the s \rightarrow d transition probability will not depend on T, and can be estimated. So for $L_s > a$, a roughly T-independent behaviour of the reactivity is predicted. Moreover in some of the liquid transition metals the situation $L_d \sim a$ is reached below the melting point, so the change of resistivity there is small.

If then one looks at eqn.(10) and (11), one expects these conditions to be valid only if $1/L_{sd} >> 1/L_{ss}$ and this should be so only if there is a narrow d band with high density of states. Enderby and Dupree³², by giving evidence that, if the thermopower is

$$S = \frac{\pi^2}{3} \frac{kT}{e} \frac{1}{E_F} \frac{d \ln Nd}{dE} , \qquad (12)$$

observations for liquid Ni, Co and Fe agree with calculations by Keller and coworkers for these liquids, come to the support of the model. For trivalent rare earth metals Delley et al.³³ show that, although for the metal Lu the change of resistance across the melting point is small, the TCR corresponds with that obtained from the extended Ziman theory, as due to a change in n throughout the series. Perhaps the quantity $1/L_{SS}$ in eqn.(10) is the predominant term, L_{SS} being due to the d phase shift.

Basak et al.³⁴ have investigated both the resistivity ρ and the thermoelectric power of a non-magnetic Be-Ti-Zn glass. Here photoemission experiments on a similar glass³⁵ show that a d band is less than half full so the s \rightarrow d model would indicate n-type thermopower, contrary to the p-type form observed. Here we must suppose no narrow and partially separated d band exists. These authors suggest that in magnetic glasses there are some sites where a moment exists in zero magnetic field, and that these give rise to a Kondo effect and resistance minimum. This is an interesting suggestion. It may well be that in most amorphous just metallic systems, such as one finds in impurity bands and inversion layers, at special sites electron-electron interaction gives rise to local moments which give Kondo spin flips with the surrounding sea. Some of the evidence is given by Tunstall³⁶ and Mott^{37,38}.

Asano and Yonezawa³⁹ have evaluated the density of states and the resistivity ρ from the Kubo-Greenwood formula. They assert that their results do not agree with the prediction that ρ is proportional to $\{N(E_F)\}^{-2}$, but this prediction was never made for the liquid transition metals considered here. It was proposed that $\rho \ll N_d(E_F)$ for a certain class of transition metal, liquid or solid, and I do not think that these calculations present any evidence against this.

4. HALL EFFECT IN LIQUID TRANSITION METALS. I turn now to the positive Hall effect found a decade ago by Busch et al. 40,41 for liquid Ge-Co alloys with resistivity about 140 $\mu \Omega \text{ cm}$ (σ = 7000 $\Omega^{-1} cm^{-1}$). These can perhaps be considered as in the range L \sim a, or near it (cf.§ 1), and were discussed by the present $author^{30}$ on this basis. We attempt a new explanation here, along somewhat different lines. We remark also that recently Guntherodt and co-workers (private communication) have found positive Hall coefficients in a large number of liquids and metallic glasses, having resistivities of this order, and that there is some evidence that this is related to a high magnetic susceptibility.

We remark first that, even if L \circ a in a liquid or metallic glass, a Hall coefficient of normal sign and value $R_{\rm H} =$ $1/{\rm nec}$ is normally predicted. Ballentine⁴² considered the possibility of deviations due to skew scattering from spin-orbit interaction and Roth⁴³ considered the sign of $R_{\rm H}$, but came up with a negative value even when the thermopower is p-type.



Fig. 5 Three- and four-site models for the Hall effect.

To consider a positive sign, we start from the analysis of Friedman³. This derives from the theory of the Hall effect for polaron motion due to Holstein and Friedman⁴⁴. In this theory the Hall effect arises from the interference between the two paths shown in fig. 5a. The Hall coefficient is negative for electrons <u>or</u> holes, unless a four-site model is assumed (fig. 5b) which is unlikely for liquids or glasses. Friedman³ extended this analysis to unactivated conduction in the case L \sim a, that is, for unactivated motion between atomic sites. The conclusion was the same with, for the Hall mobility $\mu_{\rm H}$,

$$\mu_{\rm H} \simeq 0.1 \, {\rm ea^2}/\hbar$$
 (13)

This statement, as regards the magnitude of $\mu_{\rm H}$, is in satisfactory agreement with experiment for a large number of semiconductors; also for metals eqn.(13) is often satisfactory. But as regards the sign,(13) is very often at fault. Thus in amorphous hydrogenated silicon R_H is positive for holes, negative for electrons. Emin^{45,45} first pointed out that a sign reversal could be explained if, instead of s-orbitals, the polarons were formed round bond orbitals of antibonding type; this, however, seems to us unlikely for the conduction band of a-Si. The present author 4/ suggested that the sign reversal might occur if wave function at E_F were constructed from anti-bonding orbitals without polaron formation. Although the theory remains anything but precise, the observations suggest that it may be on the right lines.

We now suggest that the same consideration might be applied to a <u>degenerate</u> electron gas. Thus a positive Hall coefficient could be expected if:

(a) L ∿ a.

(b) The wave function at the Fermi edge are now the type (1), the ψ_n being antibonding orbitals. This is, perhaps, likely to be the case where the orbitals are mainly of d-type and a d-band is nearly full. Our model is, of course, speculative and entirely qualitative at present.

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