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Conduction in granular metals—variable-range hopping in a Coulomb gap?

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Abstract. We set out the model for conduction in disordered systems by variable-range tunnelling in a Coulomb gap. Detailed analysis of experimental data for three different types of granular metal shows that the model cannot apply to these systems. We conclude that the problem of the mechanism of conduction in granular metals remains unsolved.

1. Introduction

Granular metals are inhomogeneous mixtures of metal and non-metal. Three-dimensional composites, generally produced by co-evaporation or co-sputtering of a metal and an insulator, are known as *cermets* (Abeles 1976). Two-dimensional *discontinuous metal films* are formed during the early stages of film growth by evaporation or sputtering, the deposited metal first forming isolated islands that only later join up to form a continuous film (Morris and Coutts 1977).

The electrical properties of such systems vary continuously as the composition is changed. When the concentration of metal is small, the metal forms small isolated islands embedded in an insulating matrix and conductivity is activated. This is generally called the *dielectric regime*. As the proportion of metal is increased, the islands become larger, the activation energy falls and eventually, when connected metallic pathways through the sample are established, the system undergoes a metal–insulator transition to a metallic state with positive temperature coefficient of resistance.

Conductivity in the dielectric regime is generally discussed on the basis of the classic model of Neugebauer and Webb (1962), which has two essential features: transfer of electrons between metal islands is by tunnelling, and activation is required to provide the non-negligible electrostatic energy that is associated with placing an electronic charge on an island (creating a 'carrier'). Then, at low temperatures, the conductivity σ should behave as

$$\sigma \propto \exp(-2\alpha s - W/kT) \tag{1}$$

where α is the tunnelling exponent of electron wavefunctions in the insulator, s the separation of islands, W the island charging energy, k the Boltzmann constant and T temperature. Observed activation energies are of the right order, but the predicted

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temperature dependence, simple activation, is not observed. Instead, it is found that

$$\sigma \propto \exp(T_0/T)^x \tag{2}$$

where T_0 and x are constants. For cermets, $x \simeq 0.5$. For discontinuous metal films, various values of x are obtained in the range $0.3 \leqslant x \leqslant 1$, although $x \simeq 0.5$ is probably still typical. The observed 'fractional temperature dependence' has generally been attributed to the distributed nature of s and W in real physical systems. However, detailed analysis of transport in granular systems (by critical-path methods) incorporating realistic distributions of these quantities yields a temperature dependence that is still very close to simple activation (Adkins 1982). The same result is obtained if the presence of large random potentials is included in the analysis (Adkins 1987). (There is experimental evidence for the presence of such random potentials: see Adkins *et al* (1984), Cavicchi and Silsbee (1984).)

The models referred to so far all assume independent carriers. This paper explores whether the observation of fractional temperature dependence with $x \simeq 0.5$ in the dielectric regime of granular metals can satisfactorily be explained on the basis of *electron–electron correlation* and the presence of a *Coulomb gap*.

2. The Coulomb gap and fractional temperature dependence

The best known mechanism for fractional temperature dependence of conductivity is variable-range hopping (Mott 1968). If an electron is tunnelling between localised states that are randomly distributed in energy and space, then, at low temperatures, it will pay the electron to tunnel further in order to find an empty state more proximate in energy. Optimisation of the two terms in equation (1) for a uniform density of states in three dimensions leads to the famous Mott $T^{1/4}$ law (i.e. $x = 0.25$). The argument can be modified to any dimensionality and to non-uniform densities of states. One obtains

$$x = (p + 1)/(d + p + 1) \tag{3}$$

where d is the dimensionality and p is the index for which the density of states $g(\varepsilon)$ is assumed to rise about the Fermi level as

$$g(\varepsilon) = g_p |\varepsilon|^p. \tag{4}$$

We note that we obtain $x = 0.5$ for $p = 2$ in three dimensions and for $p = 1$ in two. These are precisely the forms of $g(E)$ predicted to result from electron–electron interaction in disordered systems of localised electrons by Efros and Shklovskii (1975).

The Efros and Shklovskii argument may be summarised as follows. Consider the ground state of a disordered system of localised electrons. States below the Fermi energy will be occupied, those above empty. Let E_i be the site energies *including Coulomb terms* with all other charges. Consider a filled state of energy E_i and an empty state of energy E_j. (These will be the energies associated with removing the electron from state i or with placing one on state j, *all other charges remaining unchanged.*) Now consider the transition of the electron from i to j. The net energy change will be

$$W = \varepsilon_i + \varepsilon_j - e^2/4\pi\varepsilon_r\varepsilon_0 r_{ij} \tag{5}$$

where $\varepsilon_r\varepsilon_0$ is the permittivity of the medium and r_{ij} the separation of the sites. The last term is the Coulomb potential between the negative charge added at j and the positive

(effective) charge added at i. But for stability of the original (ground) state we require $W \geqslant 0$. This limits the density of states at low energies. Efros and Shklovskii argue that the charges will adjust their configuration to form a ground state (a *charge glass*) such that $W = 0$ at all r_{ij}. This condition results in the three- and two-dimensional densities of states†.

$$\text{3D} \qquad g(\varepsilon) = (3^8\pi^2\varepsilon_r^3\varepsilon_0^3/2^5e^6)\varepsilon^2 \equiv g_2\varepsilon^2 \tag{5a}$$

$$\text{2D} \qquad g(\varepsilon) = (2^{11}\pi\varepsilon_r^2\varepsilon_0^2/3^4e^4)|\varepsilon| \equiv g_1|\varepsilon|. \tag{5b}$$

In neither case can the density of states continue to increase, of course, and it is assumed to level off when $g(\varepsilon)$ rises to g_0, the density of states neglecting Coulomb interactions. This defines the Coulomb gap Δ:

$$g(\Delta/2) = g_0. \tag{6}$$

It should be noted that equations (5) contain no material parameters other than the bulk relative permittivity. This remarkable independence from microscopic detail is a result of the densities of states being determined solely by Coulomb's law. Coulomb gaps have been demonstrated in computer simulations (Levin *et al* 1987) and in photo-emission measurements (Davies and Franz 1986).

The possible explanation of $x = 0.5$ in terms of Coulomb interaction therefore involves variable-range hopping in densities of states given by equations (5). Variable-range hopping has normally been rejected as a possibility for granular metals on the basis of the following argument. Typically, in granular metals, the diameter d of metal islands might be 3 nm and their separation s less than 1 nm. In tunnelling beyond a near neighbour, the tunnelling distance must increase by some 4 nm. In a typical insulator, the tunnelling exponent α would be of order $10^{10}\,\mathrm{m}^{-1}$, so the relative probability of tunnelling beyond a near neighbour would be negligible. However, this argument is a little facile for, in the region of an intervening island, the energy deficit of a tunnelling electron will become small so that it is only in the insulator that the wavefunction is significantly attenuated. For tunnelling distances greater than d, a simple geometrical argument (Entin-Wohlman *et al* 1983) then gives

$$\alpha_m \simeq s\alpha_{ins}/(s + d) \tag{7}$$

where α_m is the mean tunnelling exponent and α_{ins} that in the insulator. The reduction of α_{ins} may allow tunnelling beyond near neighbours.

3. Procedure for comparison with experiment

3.1. Extraction of parameters

The essential quantity extracted directly from experiment is T_0 which is obtained by fitting results to equation (2) with $x = 0.5$. From this, one obtains directly W_{opt}, the temperature-dependent optimum hop energy of the variable-range tunnelling process:

$$W_{opt} = 0.5k(T_0T)^{1/2}. \tag{8}$$

This result, correct for both 3D and 2D systems, contains no material parameter. Other quantities depend on the relative permittivity which comes in through involvement of

† The numerical constants are obtained by requiring one empty and one filled state within distance r and with mean energy difference equal to the Coulomb term at the mean separation.

Table 1. Analysis of experimental data. f is the approximate volume (area) fraction of metal. Other quantities are defined in the text. The values of W_{opt} and R_{opt} are given for 80 K (kT = 6.9 meV).

	Cermet	Granular film	Discontinuous film
T_0/K	16000	200	1100
T_r/K	20–300	1.5–200	15–270
d/nm	2.3	3.0	20
s/nm	0.7	0.2	2.0
f	0.24	0.5	0.5
$\varepsilon_{r,ins}$	4	8	4
g_0	$2.3 \times 10^{47}\ J^{-1}\ m^{-3}$	$1 \times 10^{47}\ J^{-1}\ m^{-3}$	$5 \times 10^{38}\ J^{-1}\ m^{-2}$
Δ/eV	$21/\varepsilon_r^{3/2}$	$14/\varepsilon_r^{3/2}$	$660/\varepsilon_r^2$
α_m/m^{-1}	$1.3 \times 10^8\ \varepsilon_r$	$1.7 \times 10^6\ \varepsilon_r$	$7.3 \times 10^6\ \varepsilon_r$
α_{ins}/m^{-1}	$5.8 \times 10^8\ \varepsilon_r$	$2.7 \times 10^7\ \varepsilon_r$	$8.1 \times 10^7\ \varepsilon_r$
W_{opt}/meV	49	5.5	13
R_{opt}/nm	$26/\varepsilon_r$	$230/\varepsilon_r$	$130/\varepsilon_r$

$g(\varepsilon)$. The formulae for the tunnelling exponent are

3D $$\alpha_m = kT_0(\pi g_2)^{1/3}/10.5 \tag{9a}$$

2D $$\alpha_m = kT_0(\pi g_1)^{1/2}/2^{7/2}. \tag{9b}$$

In both cases, for given T_0, α_m is linearly proportional to ε_r.

The temperature-dependent optimum hop distance R_{opt} is given in both two and three dimensions by

$$R_{opt} = 0.25\alpha_m^{-1}(T_0/T)^{1/2}. \tag{10}$$

R_{opt} is inversely proportional to ε_r.

The meaning of ε_r in all these results needs explaining. The relative permittivity comes in through the Coulomb energy of two charges localised on metal islands. The appropriate value will not be exactly the same as that which would be measured by applying a macroscopic electric field to a sample of the material, because the field configuration is different. In particular, field lines originate on islands that are totally surrounded by dielectric. Only if charged islands are relatively far apart will ε_r tend to the bulk value. The second point about ε_r is that it diverges as the metal–insulator transition is approached from the insulating side (Abrahams *et al* 1979). (Among other consequences is the collapse of the Coulomb gap.) In principle, the bulk ε_r could be estimated using effective medium theory (Landauer 1978) and, in some cases, it has been measured. Nevertheless, in view of the uncertainty over the appropriate value to take, we give values of model parameters in table 1 in terms of ε_r.

Also listed in table 1 are values of Δ, which depend on knowing g_0. For g_0 we take the metallic density of states diluted in proportion to the volume (or area) concentration of metal in the system. An alternative, but one we think less soundly based, would be to take the density of *charge* states of the metal islands calculated from their estimated capacitance. This generally gives a value of g_0 about one order of magnitude smaller, and hence gives a corresponding reduction in the estimate of Δ.

3.2. Limits on parameters for validity of model

The conditions under which various transport mechanisms may operate in granular metals have been discussed by Entin-Wohlman *et al* (1983). For the model we are considering to be valid, the model parameters are limited as follows.

(i) T_0 *and* W_{opt}. All treatments of activated hopping conduction assume the Boltzmann limit for the phonon statistics. The model set out here can therefore only be valid if deduced values of W_{opt} satisfy

$$W_{opt} \geqslant kT. \tag{11}$$

From equation (8) we see that this corresponds to

$$T_0 \geqslant T. \tag{12}$$

There is also an upper limit on acceptable values of W_{opt}, for if activation energies become too large processes involving the constant density of states outside the Coulomb gap will become dominant (and one would go over to variable-range hopping in a constant density of states with $x = 0.25$ and $x = 1/3$ in three and two dimensions). Calculated values of W_{opt} must also therefore satisfy

$$W_{opt} < \Delta. \tag{13}$$

Correspondingly, with (11),

$$\Delta \gg kT. \tag{14}$$

(ii) R_{opt}. For variable-range tunnelling to be occurring, calculated optimum hop distances must be considerably larger than the distances between neighbouring islands:

$$R_{opt} \gg d. \tag{15}$$

As $R_{opt} \rightarrow d$ (a possible high-temperature limit) the hopping process would go over near-neighbour tunnelling which would give simple activation (Adkins 1987).

4. Analysis of experimental data

We analyse results for three different kinds of granular metal: two three-dimensional systems, a conventional cermet and a fine grained granular metal film; and one two-dimensional system, a discontinuous metal film.

4.1. Cermet

The data quoted are for a Ni–SiO_2 film produced by conventional co-sputtering of metal and insulator (Abeles *et al* 1975). We note a high T_0 and that $T^{1/2}$-behaviour is shown over a good range of temperature (T_r). At 80 K the optimum hop energy is considerably greater than kT. In the absence of measurement, we may estimate the bulk relative permittivity using effective medium theory (Landauer 1978). With the quoted volume fraction of metal, the enhancement factor is 3.6, giving a bulk relative permittivity of about 14. The Coulomb gap Δ remains adequately large, of order 0.5 eV, α_{ins} becomes very reasonable at $8 \times 10^9\ m^{-1}$, which, for a free electron mass, would correspond to a

barrier height of 2.5 eV. There are problems, however, with R_{opt}, which becomes 1.8 nm, significantly smaller than the particle size of 2.3 nm.

4.2. Granular film

These data are for a fine-grained granular aluminium film produced by evaporation of aluminium in an oxygen ambient (Chui *et al* 1981). Although the $T^{1/2}$-law appears to be reasonably well obeyed over a large temperature range, we note that T_0 is low, at the upper end of the temperature range for which the $T^{1/2}$-law appears to be followed. There is a consequent problem with W_{opt}, which is less than kT at 80 K. This time, using effective medium theory to estimate the enhancement of the permittivity, we obtain a factor of 10 and a bulk relative permittivity of order 80. This would imply a rather small Δ (of order 20 meV) but α_{ins} is reasonable at $2.2 \times 10^9\ m^{-1}$ corresponding to a barrier height of 180 meV. This would appear small for alumina but it should be pointed out that the tunnelling barriers are believed to be very thin in this system, only a few tenths of a nanometre, so that there would be considerable lowering of the barrier by image forces (Simmons 1969). R_{opt} again presents problems, however, with a calculated value just under 3 nm, again of the order of the particle size.

4.3. Discontinuous metal film

These data are from our own measurements with a typical discontinuous film of gold on glass. The mean thickness of the film was of order 5 nm and this figure was used to calculate g_0 (here in units of $J^{-1}\ m^{-2}$). The $T^{1/2}$-law is obeyed over a good temperature range, T_0 is adequately high and W_{opt} is sufficiently greater than kT at 80 K.

In this system there is only a small enhancement of the permittivity by the presence of the metal because, while the film may be approximated to a 2D structure, the electric fields are 3D. For an isolated island, the effective permittivity would be the average of those of glass and vacuum and that is the figure quoted, 4. Since there will be some concentration of fields towards the plane of the film, there will be some enhancement and we may reasonably estimate an effective relative permittivity of order 6.

With this value, Δ remains large but there are problems with $\alpha_{ins} \approx 5 \times 10^8\ m^{-1}$, corresponding to an effective barrier height of only 9 meV. This is unreasonably small, and is comparable with kT, so transport would not be by tunnelling but by activation over the barrier. (As regards this small value of α_{ins}, it should be remarked that attempts to account for the magnitudes of observed conductivities of discontinuous metal films in terms of their known structures also require small values of α (Simmons 1963, Benjamin 1981). No explanation for this has been found.) More serious than the small value of α_{ins}, however, is the small size of R_{opt}, which again comes out to be of the order of the island size.

5. Discussion

In all the cases analysed, the crucial result is the small size of the calculated optimum hop distances. In all three systems it comes out of order of the diameter of the metal islands. For variable-range hopping to be occurring, the hop range must be sufficient to allow the tunnelling electrons to sample a reasonable number of islands. This would require tunnelling beyond near neighbours and $R_{opt} > 2d$. It is possible that effective

medium theory overestimates the enhancement of the effective permittivity. To see the effect of using a reduced value we consider the figures in the extreme case of no enhancement.

For the cermet film we would have $R_{opt} \simeq 3d$ which would be satisfactory; but α_{ins} would be about $2.3 \times 10^9\ m^{-1}$, corresponding to a barrier height of only 200 meV which would be on the small side even allowing for barrier lowering in the relatively thin tunnel barriers. Clearly the range of ε_r that would yield acceptable values for R_{opt} and α_{ins} is small. Although one might convince oneself that the model is viable in this particular case, it seems extremely unlikely that it could account for all cermets. Yet for cermets, the $T^{1/2}$-behaviour is ubiquitous.

For the granular film, with no enhancement of the permittivity, we would obtain $R_{opt} \approx 10d$, which would be satisfactory, but α_{ins} would become unreasonably small, corresponding to a barrier height of about 1 meV ($\ll kT$). For $R_{opt} \simeq 3d$, we would require a permittivity that would give $\alpha_{ins} = 6.9 \times 10^8\ m^{-1}$ corresponding to a barrier height of only 18 meV, again unreasonably small. In any case, W_{opt} and T_0 remain unacceptable and one concludes that there is no latitude at all that could allow the possibility of the model being valid in this case.

For the discontinuous film there is little room for adjustment of the numbers and again one concludes that the model cannot apply.

The overwhelming weight of evidence indicates, therefore, that the conductivity of granular metals cannot be accounted for in terms of electron correlation and variable-range hopping. The problem of the mechanism of transport in these systems therefore remains unsolved.

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