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Structural and electrical properties of granular metal films

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# [ 407 ]

# Structural and electrical properties of granular metal films

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#### ABSTRACT

Granular metal films (50-200,000 Å thick) were prepared by co-sputtering metals (Ni, Pt, Au) and insulators (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>), where the volume fraction of metal, x, was varied from x=1 to x=0.05. The materials were characterized by electron micrography, electron and X-ray diffraction, and measurements of composition, density and electrical resistivity at electric fields & up to 106 V/cm and temperatures T in the range of 1.3 to 291 K. In the metallic regime (isolated insulator particles in a metal continuum) and in the transition regime (metal and insulator labyrinth structure) the conduction is due to percolation with a percolation threshold at  $x \simeq 0.5$ . Tunnelling measurements on superconductor-insulatorgranular metal junctions reveals that the transition from the metallic regime to the dielectric regime (10-50 Å size isolated metal particles in an insulator continuum) is associated with the breaking up of a metal continuum into isolated metal particles. In the dielectric regime the temperature dependence of the low-field resistivity is given by  $\rho_{\rm L} = \rho_0 \exp \left[2\sqrt{(C/kT)}\right]$ , and the field dependence of the high-field, low-temperature resistivity is given by  $\rho_{\rm H} = \rho_{\infty} \exp\left(\frac{\mathscr{E}_0}{\mathscr{E}_0}\right)$ , where  $\rho_0$ ,  $\rho_{\infty}$ , C, and  $\mathcal{E}_0$  are material constants. A simple theory based on the assumption that the ratio s/d (d-metal particle size and s-separation between particles) is a function only of composition yields expressions for  $\rho(\mathscr{E}, T)$  in excellent agreement with experiment. Furthermore, the theory predicts the experimental finding that the resistivity can be expressed in terms of a universal function of the reduced variables kT/C and  $\mathcal{E}/\mathcal{E}_0$ . The inter-relationship between all the important physical properties of granular metals and their structure is also discussed.

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#### § 1. INTRODUCTION

Granular metals are composite materials of metals and insulators. Originally these materials, known as cermets, were used as electrical resistors because of their high resistivities and low temperature coefficients of resistivity (TCR). Granular metals were prepared by a number of different methods such as, for instance, evaporation (Cohen and Abeles 1967) or sputtering (Feinstein and Huttemann 1974) of an oxidizable metal in the presence of some oxygen, co-evaporation (Fuschillo and McMaster 1971) or co-sputtering (Miller et al. 1970, Miller and Shirn 1967) of immiscible metals and insulators, or ion implantation of metals into insulators (Perkins 1972). Another form of granular metals that has been described in the literature as early as 1914 is the metal island film structure which is formed during the initial stage of depositing thin metal films (Neugebauer and Webb 1962). During more recent years there has been an increasing interest in granular metals due to their unique physical properties. In particular, interest has been directed toward granular metals in which the metal particles are of submacroscopic size (10-100 Å). It is the purpose of the present work to study systematically the relationship between the microstructure and the d.c. electrical properties of granular metals.

There are three distinct structural regimes in granular metals (Neugebauer 1970): 1. Metallic regime : when the volume fraction of the metal x is large, the metal grains touch and form a metallic continuum with dielectric inclusions. 2. Dielectric regime : the structure of granular metals in this regime is an inversion of the metallic regime in that the small, isolated metal particles are dispersed in a dielectric continuum. 3. Transition regime : this is the regime in which the structural inversion between the metallic and the dielectric regimes takes place. In the following we present a systematic discussion of how the electric transport properties and other related physical phenomena in granular metals are modified in the three structural regimes.

In the metallic regime, phenomena which depend on transfer of electrons are retained. For instance, granular Ni-SiO<sub>2</sub> exhibits bulk ferromagnetism (Rayl *et al.* 1971, Gittleman *et al.* 1972) for 0.7 < x < 1. However, properties which depend on electronic mean free path are drastically modified due to strong electron scattering from dielectric inclusions and grain boundaries. For instance, the electrical conductivity decreases by orders of magnitude from its crystalline value, and the temperature coefficient of resistivity (TCR), although positive, is very much smaller than in pure metals (Neugebauer 1970). In the case where the constituent metal is a superconductor, the coherence length is very small and the penetration depth is very large, corresponding to a dirty type II superconductor (Cohen and Abeles 1967, Abeles *et al.* 1967). The observed large enhancement in the superconducting transition temperature  $T_c$  (Abeles *et al.* 1966) in this regime has been attributed to softening of the phonon modes (Garland *et al.* 1968, Klein and Leger 1968).

In the transition regime, the dielectric inclusions becomes interconnected to form a maze structure, which, with further decrease in x, progressively breaks up into isolated metal particles dispersed in a dielectric continuum. The electrical conductivity in this regime is due to percolation along the metallic maze and electron tunnelling between isolated metal particles. The TCR changes sign (becomes negative) at the composition and temperature where the contribution to electrical conductivity due to thermally activated tunnelling becomes comparable to the contribution due to percolation. The transition into the dielectric regime occurs at the percolation threshold composition  $x_c$ , below which only the tunnelling process contributes to the conductivity of the granular metal. Bulk superconductivity (Abeles and Hanak 1971, Deutscher 1971) and ferromagnetism (Rayl *et al.* 1971, Gittleman *et al.* 1972) are observed to vanish abruptly at the percolation threshold although individual isolated grains can retain superconductivity (Hauser 1970, Zeller and Giaever 1969) and ferromagnetism (Gittleman *et al.* 1974) if their size is larger than the critical size required for the existence of these phenomena.

In the dielectric regime we are concerned with the physical properties of isolated, small metal particles and with electrical transport due to tunnelling between the isolated particles. In discussing the physics of small, isolated metal particles the two important physical quantities which must be introduced are the finite electronic energy level separation  $\delta$  within a metal particle due to quantization of motion (Kubo 1962, 1969) and the charging energy  $E_{\rm e}$  (Neugebauer and Webb 1962, Hill 1969) required to transfer an electron between two neutral grains. The charging energy is approximately given by  $E_e = 2e^2/Kd$ , where e is the electronic charge, K is an effective dielectric constant of the granular metal, and d is the grain size. Near the Fermi level (Kubo 1962, 1969)  $\delta \simeq E_{\rm F}/N$ , where  $E_{\rm F}$  is the Fermi energy in the metal particle and N is the number of electrons in the particle. Thus, for instance, when d = 50 Å and K = 10,  $\delta \simeq 1$  meV and  $E_c \simeq 60$  meV. As d is reduced,  $\delta$ will eventually become comparable and then larger than  $E_c$ . This happens when d is approximately equal to the lattice constant. In this work the particles are sufficiently large so that the condition  $\delta \ll E_{\alpha}$  is always maintained.

Physical phenomena in the dielectric regime can be naturally classified into intra-grain effects and inter-grain effects. In the case of intra-grain effects, we only consider electronic excitations within a grain. When kT, where k is the Boltzmann constant and T is the absolute temperature, is much less than  $\delta$ , the existence of finite energy level separation affects profoundly thermodynamic equilibrium properties such as specific heat and paramagnetic susceptibility (Denton et al. 1973). The energy level spacing is also expected to affect collective phenomena such as superconductivity (Parmenter 1968, Mühlschlegel et al. 1972) and ferromagnetism inside a grain when  $\delta$  becomes comparable to the superconducting energy gap  $\Delta$  and the ferromagnetic exchange energy  $\epsilon_{ex}$  respectively. Whereas intra-grain electron excitations can be described by the Fermi distribution function, inter-grain excitations involving the transfer of electron between two neutral grains, creating a pair of positively and negatively charged grains, are described by the Boltzmann distribution function with  $E_{e}$  playing the role analogous to that of the Hubbard gap in a Mott-Hubbard insulator (Mott and The transition from the metallic regime, where the Fermi level Davis 1971). is well defined throughout the bulk, to the dielectric regime, can be depicted by the development of a pseudo-gap at the Fermi level with magnitude  $E_{\rm c}$ (Abeles and Sheng 1974).

The field and the temperature dependences of conductivity provide a tool to study effects associated with transfer of electrons between grains. It is found that the low-field electrical conductivity,  $\sigma_{\rm L}$ , of granular metals in the dielectric regime has a characteristic temperature dependence (Sheng et al. 1973, Hauser 1973, Zeller 1972)  $\ln \sigma_{\rm L} \sim 1/\sqrt{T}$  and that at low temperatures, the high-field electrical conductivity,  $\sigma_{\rm H}$ , has an electric field dependence of the form (Sheng et al. 1973, Sheng and Abeles 1972)  $\ln \sigma_{\rm H} \sim -1/\mathcal{E}$ , where  $\mathcal{E}$ is the electric field. This characteristic behaviour of  $\sigma$  as a function of T and  $\mathscr{E}$  is a direct consequence of the fact that there is a distribution of grain sizes d and tunnelling barrier thicknesses s and that there is a strong correlation between s and d. This correlation, which results from the uniformity of composition in the co-sputtered granular metals, can be described by the picture that large grains tend to be farther apart from their neighbours than smaller grain from their neighbours. It was found (Sheng et al. 1973) that the simple assumption s/d = constants for fixed x, which is consistent with the requirement of uniform composition, can explain in detail the temperature and the electric-field dependences of the conductivity in the dielectric regime.

In this paper we present a detailed description of the preparation of granular metals and their characterization using electron microscopy, X-ray, chemical analysis, density determination, tunnelling measurements at 1.3 K, and electrical conductivity measurements over the ranges 1.3 < T < 300 K and  $0 < \mathscr{E} < 10^6$  V/cm. Analysis of the structural and electrical transport data yields detailed information on the granular metal parameters : average metal particle size  $d_0$ , average metal particles separation  $s_0$ , and other structural constants involving the combination of charging energy  $E_c$  and metal particle separation s. In the following, the experimental details are presented in § 2, the experimental and theoretical results for the metallic and the transition regimes are presented in § 3, and those for the dielectric regime in § 4. A summary of the results of this work as well as other relevant results on granular metals are presented in tabular form in § 5. In conclusion, some of the outstanding problems in granular metals are discussed.

# § 2. EXPERIMENTAL

# 2.1. Sample preparation

The granular metals were prepared by sputtering in the system shown schematically in fig. 1. The substrate is mounted on a water-cooled holder using a thin layer of vacuum grease to ensure good thermal contact. The substrate can be rotated into positions for sputtering from a 6 in. diameter target or for evaporation from resistance-heated boron nitride boats. The cylindrical shield surrounding the target protects it from contamination during the evaporation. The substrate plane is  $2\cdot3$  in. above the sputtering target and 10 in. above the evaporation sources. A rotating mask tray permits the selection and accurate alignment of any one of four different masks. Beryllium-copper finger springs were used to press the mask against the substrate. The masks were etched, using photoresist processing, from  $0\cdot010$  in. thick beryllium-copper sheet.

The sputtering was done at frequency of 12.56 MHz using 99.999% pure Ar gas at a pressure of  $4 \times 10^{-3}$  torr. A magnetic field of 50 Oe was used



Sputtering and evaporation system.

to confine the plasma. The r.f. power was 60 W and the sheath voltage was 800 V. The granular metals were sputtered from the composite metalinsulator targets shown schematically in fig. 2. The targets were assembled by placing the insulator, a  $\frac{1}{16}$  in. thick plate cut to the appropriate shape, on top of the metal. The metals and insulators used in this investigation were Ni, Pt, Au, alumina and silica, all of commercial purity. Targets a and b in fig. 2 yielded films with a compositional gradient in the substrate plane. The orientation of the sputtered strip with respect to the sputtering target is indicated in fig. 2 by the dashed lines. In fig. 3 is shown a photograph of a Pt-SiO, film on a glass substrate which was sputtered from a target of The volume fraction x of Pt in the film shown the type shown in fig. 2(b). in fig. 3 varies from x = 0.45 at the opaque end to x = 0.06 at the transparent end of the strip. Targets with the geometry shown in fig. 2 (a) were used when metal-rich films were required. Targets with geometry of fig. 2(c)were employed when films with a large area of uniform composition were required. The co-sputtering method (Hanak et al. 1972, Hanak and Bolker 1973) has the advantage of yielding samples, in one sputtering operation, over a compositional range that can be accurately controlled by the shape of the target components. In addition, the composite targets used in the co-sputtering method have the advantage over targets made by sintering a mixture of insulator and metal particles in that they are easily fabricated, and that they are intrinsically much purer and free from trapped gases.

To sputter granular metals with reproducible properties several rules had to be observed. The base pressure of the system had to be  $< 10^{-7}$  torr.



Metal-insulator composite targets. Shaded areas indicate metal. Dashed lines indicate relative position of the substrate above target. Targets (a) and (b) were used for sputtering films with graded composition, target (c) was used for sputtering uniform composition films.

This was achieved by pumping with a 6 in. diffusion pump for about 10 hours and using a liquid nitrogen-cooled trap inside the system. The pressure of the argon gas used for the sputtering had to be low in order to prevent excessive cross-contamination between the metallic and the insulating parts of the target from back-scattering by the gas molecules. An argon pressure of  $< 4 \times 10^{-3}$  torr and pre-sputtering for several hours to achieve equilibrium sputtering rates from the two components of the target yielded samples whose compositional variation, normal to the plane of the film, was negligible. The electrical resistivities of the granular metals in the dielectric regime were very sensitive to the degree of confinement of the plasma. For instance, extending the height of the shield in fig. 1 to the substrate holder (so that the plasma was nearly completely confined) resulted in films with much higher resistivities in the dielectric regime than those sputtered without the shield

Fig. 3



Photograph of  $Pt-SiO_2$  film sputtered from a target with geometry of fig. 2 (b). The volume fraction of Pt is 0.45 at the left opaque end of the slide and 0.06 at the transparent end of the slide. The gap in the centre of the film is due to a strengthening rib in the mask. The electrical contracts are spaced 0.100 in. apart ; details of one of the contacts is shown in fig. 4.

or with low shield height (see § 4.2). The height of the shield we used, 1.5 in., was just sufficient to prevent target contamination during evaporation. However, its presence did not affect appreciably the electrical resistivities of the sputtered films. The electrical properties in the dielectric regime were also sensitive to the substrate temperature during the deposition. Care had to be taken to avoid a rise in substrate temperature during deposition due to heating by the sputtering. This was accomplished by sputtering at low r.f. power and cooling the substrate well.

#### 2.2. Electrical measurements

Electrical resistivity and tunnelling measurements were made on samples sputtered on glass substrates with the geometry shown in fig. 3. The electrical contacts in fig. 3 are spaced 0.100 in. apart and have a thickness of 2000 Å. The details of one of the contacts are shown in fig. 4. The Au electrode in fig. 4 (a) is put down by photoresist technique. Steps b, c, and d in fig. 4 were performed sequentially without opening the system to air. The evaporated electrode in step b provided a clean, smooth electrical contact to the granular metal, free of any undissolved photoresist remaining from step a. The electrical resistivity could be measured either in the plane of the film, using the 0.002 in. gap, or normal to the film using the top and bottom evaporated Au electrodes. The contact was made sufficiently narrow (0.020 in.) so that the variation in x along the width of the contacts was

#### Fig. 4



Successive stages in deposition of the film shown in fig. 3. Only one contact is shown.

negligible. Tunnel structures of the form Al–Al<sub>2</sub>O<sub>3</sub>-granular metal–Au were formed by replacing in fig. 4 (b) the evaporated Au by evaporated Al and oxidizing the Al for several minutes in dry O<sub>2</sub> gas to form a thin tunnel barrier with a resistance of about 1 k $\Omega$ . Figure 5 shows schematically the tunnel structure.

The samples were mounted in a sample holder which had berylliumcopper springs that made electrical contacts to the Au tabs. The currentvoltage (I–V) characteristics of the granular metals were measured using a digital voltage source and a PAR model 135 electrometer. The dI/dVcharacteristics of the tunnel structures were measured at 1 kHz using a PAR

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lock-in amplifier and conventional derivative techniques. Conventional Dewar and cryogenic techniques were employed to measure the electrical characteristics in the temperature range  $1\cdot3-291$  K.



Fig. 5

Metal-insulator-granular metal tunnel structure.

#### 2.3. Compositional analysis

The volume fractions of metal and insulator in the granular metals were determined according to the method of Hanak *et al.* (1972, 1973). The basic assumption in this method is the superimposition principle which states that for a multicomponent target the thickness L(P) of the sputtered film, at any point P in the substrate plane, is equal to the sum of the individual film thicknesses  $L_i(P)$  that would be obtained by sputtering from the component i of the target alone. The thickness  $L_i(P)$  is calculated from the relation  $L_i(P) = tR_iG_i(P)$ . The function  $G_i(P)$  is the normalized deposition profile calculated from the shape of the component i of the target on the assumption of Knudsen's law of angular distribution of sputtered material.  $R_i$  is the deposition rate that would be obtained at a point in the substrate plane vertically above the centre of a full disk target of material i, and t is the sputtering time. The volume fraction  $x_i$  is given by

$$x_i(P) = L_i(P)/L(P), \tag{1}$$

where

$$L(P) = \sum_{i} t R_i G_i(P), \qquad (2)$$

and the summation extends over the components of the target. A full description of the method and its accuracy and limitations is given by Hanak *et al.* (1972) and by Hanak and Bolker (1973). We have used three different methods to determine the compositions from eqns. (1) and (2).

By measuring the thickness of the sputtered film at several points, the values of  $R_i$  can be determined by solving the set of linear equations given by eqn. (2) using the computed  $G_i(P)$  for the particular target geometry. This method was used for the Ni-SiO<sub>2</sub> system. In fig. 6 are plotted the measured thicknesses L(P) as a function of P for two Ni-SiO<sub>2</sub> films sputtered for 1 hour using targets with the geometries of figs. 2 (a) and 2 (b). The



Thickness profiles measured on films sputtered from Ni-SiO<sub>2</sub> targets with the geometry of figs. 2 (a) and 2 (b). The abscissa P is the distance in 1/10 in. measured along the length of the sputtered film strip. The points are measured thickness, the full curves are computer fits to the experimental data using eqn. (2).

values P = 2.5 in. corresponds to the point vertically above the centre of the composite target. The computed thickness curve is a least square fit of eqn. (2) to the experimental values of L(P). The deposition rates obtained from the fitting procedure are  $R_{\rm Ni} = 0.64 \,\mu/{\rm h}$  and  $R_{\rm SiO_2} = 0.41 \,\mu/{\rm h}$  for target geometry of fig. 2 (a) and  $R_{\rm Ni} = 0.68 \,\mu/{\rm h}$  and  $R_{\rm SiO_2} = 0.36 \,\mu/{\rm h}$  for target geometry of fig. 2 (b). In fig. 7 are plotted the computed volume fractions x of Ni. As can be seen in fig. 7, the compositional ranges obtained from the two target configurations have a region of overlap, 0.2 < x < 0.5. In order to check the self-consistency of the compositional determination for the two target configurations, we have plotted in fig. 8 the low-field resistivities  $\rho_{\rm L}$ , measured in the plane of the sample at 291 K, as a function of the computed values of x. As can be seen from the figure, there is a discrepancy in the data in the region of overlap. This discrepancy is attributed to the uncertainty in the compositional determination. In determining the composition

of the Ni-SiO<sub>2</sub> system we have not taken into account the possibility that a fraction of the sputtered SiO<sub>2</sub> molecules dissociate, SiO<sub>2</sub> $\rightarrow$ SiO+O or SiO<sub>2</sub> $\rightarrow$ Si+O<sub>2</sub>, and the free oxygen reacts with the nickel to form NiO. The fact that an appreciable fraction of the nickel may be in the form of an insulating oxide could explain why the transition from the metallic regime to the dielectric regime for granular Ni appears to take place at  $x \simeq 0.5$  while for the noble metals, Pt and Au, which do not form oxides readily, the transition takes place at  $x \simeq 0.4$  (see §§ 3.1 and 4.2).



Volume fraction x of Ni in Ni-SiO<sub>2</sub> films as function of position P on substrate, computed from eqns. (1) and (2) using the measured thicknesses of the films. The target geometries for which the curves were computed are indicated in the figure.

In the case of the Pt-SiO<sub>2</sub> films, the deposition rate was determined from the Pt emission rate. The emission rate (defined as the amount of material, in units of thickness, sputtered off the target per unit time) was determined from the weight loss of the Pt target, its area, and Pt density. The relation between the emission rate,  $R_{\rm e, i}$  and the deposition rate  $R_{\rm i}$  is

$$R_{\rm i} = R_{\rm e, i} F_{i} r_{\rm t}^2 / (H^2 + r_{\rm t}^2), \tag{3}$$

where  $F_i$  is the sticking coefficient,  $r_t$  is the radius of the full target and H the height of the substrate above the target. The value of x was computed from eqns. (1) and (2) using the measured values of L(P) and the value

 $R_{\rm Pt} = 0.65 \ \mu/{\rm h}$  determined from eqn. (3) assuming  $\dagger F_{\rm Pt} = 1$ . The value of  $R_{\rm SiO}$ , obtained by this procedure is  $0.33 \ \mu/{\rm h}$ .

In the case of the  $Au-Al_2O_3$  films, we used an atomic absorption analysis (Robinson 1966) to determine the compositions. The films were sputtered from targets with the geometry given in fig. 2 (c). It follows from simple geometric considerations that the composition of films sputtered from this target is given by

$$x = \pi b^2 R_{\rm Au} / 4 R_{\rm Al_2O_3} a^2, \tag{4}$$

where b is the diameter of the metal disks in fig. 2 (c) and a is the spacing between their centres. The composition as a function of P is uniform except



Fig. 8

Low-field resistivity  $\rho_{\rm L}$ , as a function of volume fraction x of Ni, in Ni-SiO<sub>2</sub> films sputtered from targets with the geometry of figs. 2 (a) and 2 (b). The resistivities were measured in the plane of the film at 291 K and 4.2 K. The values of x are the computed ones from fig. 7. The full and dashed curves are smoothed values of the experimental data.

for a small ripple whose amplitude is of the order of a few per cent of the average composition. The films, several microns thick, were sputtered onto a  $1 \times 2$  in. sheet of copper and a  $1\frac{1}{2}$  in. diameter disk of sapphire. The copper was subsequently dissolved away, yielding granular metal samples of 10-50 mg for the atomic absorption analysis. The samples on the sapphire substrates were used for density and resistivity determinations. The atomic absorption

<sup>&</sup>lt;sup>†</sup> We assumed  $F_{\rm Pt}=1$ , since the values of F determined by Hanak and Bolker (1973) under similar sputtering conditions as ours were close to unity.

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analysis yielded weight fractions to an accuracy of  $\pm 2\%$  for Au and  $\pm 5\%$  for Al. The oxygen weight fraction, determined by subtracting from the total weight of the film the weight of the Au and the Al, yielded a ratio of oxygen to aluminium consistent with the formula Al<sub>2</sub>O<sub>3</sub>. The volume fraction of the metal x was computed from the weight fraction of the metal y using the relation

$$x = \frac{y}{y + (1 - y)(S_{Au}/S_{Al_2O_3})},$$
(5)

where  $S_{Au}$  and  $S_{Al_2O_3}$  are the densities of the metal and insulator respectively.

The densities of the  $Au-Al_2O_3$  films were determined from the weight, thickness, and area of the films deposited on the sapphire wafers. The weight was determined by weighing the substrates before and after sputtering. The thickness was determined by measuring with a Bendix Proficorder the height of a step, produced by masking off a small area of the substrate. The



Measured density, S, versus volume fraction x of Au in  $Au-Al_2O_3$ . The films were sputtered on sapphire substrates from targets with geometry of fig. 2 (c). The values of x were determined by the atomic absorption analysis. The solid line represents eqn. (6).

measured densities S of the films versus the volume fraction of Au determined by the atomic absorption method are plotted in fig. 9. The experimental points agree, within the experimental uncertainty, with the linear relationship

$$S(x) = xS_{Au} + (1-x)S_{Al_2O_3},$$
(6)

valid for the case of superposition of the densities of the metal and insulator. The fact that the density of the sputtered  $Al_2O_3$  films (3.0 g cm<sup>-3</sup>) is considerably lower than that of crystalline (Handbook of Chemistry and Physics 1962)  $Al_2O_3$  (3.97 g cm<sup>-3</sup>) and alumina (Handbook of Chemistry and Physics 1962) (3.5–3.9 g cm<sup>-3</sup>) indicates that the  $Al_2O_3$  films contain an appreciable amount of voids. We have also determined that the sputtered  $Al_2O_3$  films have a strong absorption edge at 3000 Å while crystalline  $Al_2O_3$  is transparent at this wavelength.

In fig. 10 are plotted the low-field resistivities  $\rho_{\rm L}$  of the Au-Al<sub>2</sub>O<sub>3</sub> samples measured at 291 K and at 4.2 K in the plane of the films. The points correspond to the resistivities of the films sputtered on sapphire substrates from targets with the geometry of fig. 2 (c), with the values of x determined from the atomic absorption analysis. The full curve in fig. 10 represents the



Fig. 10

Low-field resistivity  $\rho_{\rm L}$ , as a function of volume fraction x of Au, measured at 291 K and at 4.2 K in the plane of the Au-Al<sub>2</sub>O<sub>3</sub> films. The points correspond to resistivities of films sputtered onto sapphire substrates from targets having the geometry of fig. 2 (c) with x determined by the atomic absorption analysis. The full curve corresponds to resistivities of a film sputtered from a target with the geometry of fig. 2 (b), with x determined from eqns. (1) and (2) assuming for the ratio of deposition rates  $R_{\rm Au}/R_{\rm Algo3}=5.7$ .

resistivities of a Au-Al<sub>2</sub>O<sub>3</sub> film sputtered from a target with the geometry of fig. 2 (b). The values of x for this film were computed from eqns. (1) and (2) using the ratio  $R_{\rm Au}/R_{\rm Al_2O_3}$  as an adjustable parameter to obtain best fit to the atomic absorption data point. The best fit value is  $R_{\rm Au}/R_{\rm Al_2O_3} = 5.7$ .

#### 2.4. Determination of microstructure of granular metals

Extensive electron microscopy and X-ray studies were made on the granular metals to determine their microstructure in the three compositional regimes.

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Both the X-ray and the electron diffraction results indicate that the metals and insulators are immiscible. In all cases the lattice constants for the different metals remain constant with increasing amounts of the insulating phase. The invariance of the metal lattice constant with the composition of the granular metal is demonstrated in figs. 11 and 12. In fig. 11 are shown



X-ray diffraction traces of Ni-SiO<sub>2</sub> films. The peaks correspond to the (111) reflection of Ni. The volume fraction x of Ni and the average Ni particle sizes  $d_0$ , determined from line broadening, are indicated in the figure.

the (111) X-ray diffraction peaks of Ni measured on  $2 \mu$  thick Ni–SiO<sub>2</sub> samples sputtered on glass substrates. A highly preferred orientation of the metal particles was found in the metallic and the transition regimes of all the granular metal systems we have examined. The metal particles tend to grow with the (111) planes parallel to the substrate with azimuthal disorder. As the volume fraction of the insulator is increased, the preferred orientation effect decreases, and the diffraction peaks are considerably broadened. However, the lattice constant remains unchanged. For instance, in the Ni-SiO<sub>2</sub> system over the compositional range 1 > x > 0.3 the measured lattice constant is  $3.523 \pm 0.003$  Å, which is the same as the value in bulk Ni. From the line broadening it was possible to determine the average particle size  $d_0$ . The value of  $d_0$  in each case is given in fig. 11. In fig. 12 are compared two electron-diffraction rings measured on two Au-SiO<sub>2</sub> films about 100 Å thick, one with x = 0.3 and the other with x = 0.95. These films, as well as all the other granular metal films used for transmission electron microscopy, were

deposited on carbon films supported by a fine copper mesh. As can be seen from fig. 12, apart from appreciable line broadening for the film with x=0.3, the rings of the two films can be superimposed. For x < 0.3 the accuracy of the lattice constant determination is poor, due to appreciable line broadening; however, within the uncertainty of the line broadening the metal lattice constant remains unchanged. Our finding that the lattice constant of the metal in the granular metal is unchanged differs from that of Hauser (1970), who reported a 3.5% increase in the lattice constant of aluminium in the Al-Al<sub>2</sub>O<sub>3</sub> system, and that of Abrahams *et al.* (1972), who reported an increase of as much as 10% in the lattice constant of small nickel particles in the Ni-SiO<sub>2</sub> system. The discrepancy between these results could be due to differences in the preparation of the samples.

	95 VO	L. % A	u	

Fig. 12

30 VOL. % Au

Electron diffraction patterns obtained on two  $Au-SiO_2$  films. The volume percentages of Au in the films are indicated in the figure.

Typical electron micrographs of granular metals are shown in figs. 13-16. The dark areas are metal, the light areas insulator. The characteristic features of the micrographs are<sup>†</sup>: in the metal-rich films the metal forms a continuum, containing a dispersion of amorphous insulator particles (figs. 13 a, 13 b, 15 a). At a certain composition, the granular metal forms a labyrinth structure (figs. 13 c, 14 a, 15 b, 16). With further decrease in x a complete matrix inversion takes place so that the insulator now forms a continuum and the metal particles are dispersed (figs. 13 d, 14 c, 14 d, 15 c, 15 d). In fig. 17 are plotted the average metal particle size  $d_0$  as a function of x and fig. 18 shows

 $<sup>\</sup>dagger$  Electron micrographs of Au-SiO<sub>2</sub> and Ag-SiO<sub>2</sub> exhibited the same general behaviour (Cohen *et al.* 1973).



Electron micrographs of Ni–SiO<sub>2</sub> films. The vol.% of Ni in the films and the length scale are indicated in the figure. The thicknesses of the films are about 100 Å.



Electron micrograph of Pt-SiO<sub>2</sub> films. The vol.% of Pt in the films and the length scale are indicated in the figure. The thickness of the films are (a) 150 Å, (b) 180 Å, (c) 200 Å, (d) 200 Å.

Fig. 14





#### (c) 35 Vol % Au

100Å (d) 18 Vol % Au

Electron micrographs of Au-Al<sub>2</sub>O<sub>3</sub> films. The vol.% of Au in films and the length scale are indicated in the figure. The thicknesses of the films are (a) 110 Å, (b) 140 Å, (c) 110 Å, (d) 70 Å.



Fig. 16

55 VOL % Au

Electron micrograph of Au–SiO<sub>2</sub> film containing 55 vol.% Au. The length scale is indicated in the figure. The thickness of the film is 100 Å

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a typical metal particle size distribution function. We note that  $d_0$  is insensitive to the type of metal or insulator in granular metals. However, the composition at which the matrix inversion occurs appears to depend on the particular metal insulator combination. Thus, in the case of Au-Al<sub>2</sub>O<sub>3</sub> and Pt-SiO<sub>2</sub>, the matrix inversion takes place at  $x \simeq 0.4$  while for the case of Ni-SiO<sub>2</sub> the inversion is at  $x \simeq 0.6$ .



Fig. 17

Average particle size  $d_0$  as a function of the volume fraction of the metal x for different granular metal systems.

Fig. 18



Histogram of particle sizes d in a Pt-SiO<sub>2</sub> film with volume fraction x=0.21 of Pt.

Figure 17 shows that the average particle size  $d_0$  in the dielectric regime decreases rapidly with decreasing x. In the case of Pt-SiO<sub>2</sub> and Ni-SiO<sub>2</sub> the metal particles are separated from each other by an insulating film about 10 Å thick. In the case of Au-Al<sub>2</sub>O<sub>3</sub> close examination of the micrographs corresponding to the dielectric regime indicates that the phase surrounding the metal particles appears to contain an extremely fine dispersion of much smaller (~5 Å) metal particles. Stereo electron microscopy studies of the granular metals, done by the defocus method, show that there is no dominant elongation or contraction of the particles in a preferred direction. We have also made X-ray (H. Pinch, private communication) and electron diffraction studies of sputtered Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> films and found them to be amorphous.

#### § 3. The metallic and the transition regimes

The behaviour of the resistivity of granular metals is closely related to the microstructure of the materials. In the metallic regime, in which the structure is that of insulator dispersed in the form of isolated particles in a metal continuum (figs. 13 a, 13 b, 15 a), the electrical resistivity increases gradually with decreasing volume fraction of metal x (figs. 8 and 10) and the temperature coefficient of resistivity (TCR) is positive. At some critical composition  $(x \sim 0.5)$ , the exact value of which depends on the particular combination of metal and dielectric, the insulator particles become interconnected, and a labyrinth structure results (figs. 13 c, 14 a, 15 b, and 16). In this compositional range, the transition regime, the resistivity increases rapidly with decreasing x(figs. 8 and 10) and the TCR changes sign. An interesting observation is that the value of conductivity at the composition where TCR vanishes is in the range of  $10^2-10^3 \Omega^{-1} \text{ cm}^{-1}$ . This value of 'minimum metallic conductivity' in granular metals agrees with Mott's prediction of the limiting conductivity of As x is further reduced, we have the structure of the dielectric a metal. regime (figs. 13 d, 14 c, 14 d, 15 c, 15 d), in which the electrical conduction is due to tunnelling of electrons between isolated metal particles. In this section we use two complementary approaches, electrical conductivity and tunnelling into granular metals, to study the metallic and the transition regimes. Whereas electrical conductivity provides information on percolation path density and threshold, the tunnelling provides information on the details of how the metallic continuum breaks up into isolated metal particles.

### 3.1. Percolation conductivity

The gradual increase of the resistivity in the metallic regime is believed to be primarily a geometric effect resulting from the increase of conduction path length due to the intervening insulating particles. This increase in conduction path length is clearly seen in fig. 16. The scattering of electrons by impurities dissolved in the metal is believed to be independent of composition in the metallic regime, as is borne out by measurements of thermoelectric power.<sup>+</sup> As x is reduced, the density of percolation channels diminishes

<sup>†</sup> Apart from an abrupt change near x=1 the Seebeck coefficient in Au-Al<sub>2</sub>O<sub>3</sub> is small and independent of x down to x=0.4. For x<0.4 the measurement becomes inaccurate because of high sample resistance (B. Abeles & J. I. Gittleman, unpublished).

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and thermally activated tunnelling of electrons between isolated metal particles becomes a significant parallel conduction process. This accounts for the decrease and the eventual change of sign of TCR. As x is further reduced the classical percolation threshold<sup>†</sup> is reached after which only the tunnelling process remains. To compare the percolation behaviour of granular metals with theory, we have plotted normalized conductivity,  $\sigma(x)/\sigma(1)$ , in fig. 19 for the Ni–SiO<sub>2</sub> and the Au–Al<sub>2</sub>O<sub>3</sub> films of figs. 8 and 10. Also included in the figure are data for sputtered granular W–Al<sub>2</sub>O<sub>3</sub> films (Abeles *et al.* 1975) as prepared and after annealing at 1200°C in H<sub>2</sub>. The straight line in fig. 19 is the prediction of Landauer's (1952) effective medium theory,

$$\sigma(x)/\sigma(1) = (x - x_{\rm e})/(1 - x_{\rm e}), \tag{7}$$



Fig. 19

Normalized electrical conductivity  $\sigma(x)/\sigma(1)$  as a function of volume fraction of metal x for Ni–SiO<sub>2</sub> (from fig. 8), Au–Al<sub>2</sub>O<sub>3</sub> (from fig. 10) and annealed and unannealed W–Al<sub>2</sub>O<sub>3</sub> (Abeles *et al.* 1975), measured at 291 K in the plane of the films. The solid line is computed from eqn. (7) with  $x_c = 1/3$ .

where  $x_c$  is the percolation threshold composition. The observed value of  $x_c \sim 0.5$  for annealed W-AO<sub>2</sub>O<sub>3</sub> is appreciably larger than Landauer's theoretical value of 0.33. We note that the deviation of the unannealed W-Al<sub>2</sub>O<sub>3</sub>, Au-Al<sub>2</sub>O<sub>3</sub> and Ni-SiO<sub>2</sub> films from eqn. (7) is larger than that of the annealed films. This is attributed to the fact that in the unannealed granular metals the dielectric tends to coat the metal particles and therefore is more effective in lengthening the conduction path and decreasing the conductivity than when the dielectric particles are spherical in shape. We believe that the annealing rounds the particles, which in turn results in a better agreement with the assumed particle shape of the effective medium theory. Another source of the deviation of Ni-SiO<sub>2</sub> data from the theoretical behaviour may be due to the appreciable uncertainty in the composition of the Ni-SiO<sub>2</sub> system (see § 2.3).

<sup>&</sup>lt;sup>†</sup> For a general review of percolation conductivity see Kirkpatrick (1973).

### 3.2. Tunnelling

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We have studied the tunnelling characteristics of superconductor-insulatorgranular metal tunnel junctions in which the superconductor was aluminium<sup>†</sup> and the granular metal was Ni-SiO<sub>2</sub>. A schematic of the tunnel structure is shown in fig. 5. In fig. 20 are shown the dI/dV versus V characteristics obtained for several Ni-SiO<sub>2</sub> granular metal compositions at 1.3 K. In all cases the voltage drop across the granular metal was negligible so that the measured dI/dV reflects the true tunnelling characteristics of the junction.



dI/dV characteristics versus voltage V measured at 1.3 K on Al-Al<sub>2</sub>O<sub>3</sub>-granular Ni-SiO<sub>2</sub> tunnel junctions. The volume fractions x of the Ni in the granular metal films are indicated in the figure. For clarity the curves are displaced vertically with respect to one another with the corresponding base line of each curve indicated by the dashed horizontal line.

We find that for  $x \ge 0.7$  the measured dI/dV are in good agreement with the theoretical BCS behaviour for a superconductor-normal metal tunnel junction (Giaever *et al.* 1962). This confirms that the granular metal in the metallic regime has a well-defined Fermi energy. As x decreases from 0.70 to 0.60, the structure due to the superconducting density of states disappears

<sup>&</sup>lt;sup>†</sup> The aluminium superconducting transition temperature was enhanced to 2.3 K by using the technique described by Cohen and Abeles (1967) and Abeles *et al.* (1966, 1967).

rapidly and a broad minimum in dI/dV near V=0 developes. This rapid change in the tunnelling characteristics is attributed to the breaking up of metal continuum into isolated particles and the appearance of the granular metal charging energy. In the following, a simple theory of tunnelling into isolated metal particles in the granular metal is presented which leads in a natural manner to an effective tunnelling density of states with a gap at the Fermi energy. Using the tunnelling density of states extracted from the experimental data, quantitative information is obtained on the size distribution of isolated clusters of metal particles in the transition regime.

In order to calculate the tunnelling density of states of the granular metal, consider the following model. The tunnelling current consists of two distinct parts : electrons which tunnel into the metallic continuum and those which tunnel into isolated particles (or clusters of touching metal grains). Such an assumption is consistent with the observed microstructure of the granular metals in the transition regime such as shown in fig. 13 (c). We assume that the particle size has a distribution function D(d). In order to place an electron on an isolated particle of size d, it is necessary to provide the energy of the electrostatic field associated with the extra electron. In the bulk granular metal this charging energy is of the order  $E_{c} \sim e^{2}/(Kd)$  (e the electronic charge and K the effective dielectric constant of the granular metal (see  $\S$  4)). At the insulator-granular metal interface this charging energy can be calculated in the following manner. In order for an electron to tunnel from one electrode to the other electrode of a junction it is necessary to provide a charging energy  $E_{\rm i} = e^2/2C_{\rm e}$ , where e is the electronic charge and  $C_{\rm e}$  is an effective junction capacity. In the case where the electrodes consist of ordinary metals this charging energy is negligible because the effective capacity  $C_{e}$ , given by the junction capacity  $C_i = \epsilon A/(4\pi L_i)$  ( $\epsilon$  dielectric constant of insulator,  $L_i$  thickness of insulator, A area of junction), is very large. In the case of an electron tunnelling into an isolated grain of a granular metal the effective junction area for the tunnelling electron is  $\pi d^2/4$  so that, when  $L_i \ll d$ , the effective capacity becomes  $C_e = C_i \pi d^2/4A$ , and  $E_i$  need no longer be negligible (Abeles and Sheng 1974). Because of the finite charging energy  $E_{i}$ , the electrons which tunnel into the isolated particles must have energies at least  $E_i$  above the Fermi level of the metal continuum and for a reverse voltage under which holes are injected (electrons extracted) from isolated particles the holes must have energies at least  $E_{i}$  below the Fermi level. Thus, the effective tunnelling density of states for localized states has a gap about the Fermi energy. The total tunnel current density between a superconducting film and a GM film is written in the form

$$I(V) = \frac{C_{\rm NN}}{e} \left\{ p \int_{0}^{\infty} d\xi \ D(\xi) \xi^{2} \int_{-\infty}^{\infty} dE \ \theta[E_{\rm j}(\xi) - |E + V|] \rho_{\rm s}(E)[f(E) - f(E + V)] + (1 - p) \int_{-\infty}^{\infty} dE \rho_{\rm s}(E)[f(E) - f(E + V)] \right\}$$
(8)

$$\equiv \frac{C_{\rm NN}}{e} \int_{-\infty}^{\infty} \rho_{\rm GM}(E+V) \rho_{\rm s}(E) [f(E) - f(E+V)] dE, \qquad (9)$$

where D(d), divided by unit area, is the distribution function for d, with the normalization requirement  $\int_{0}^{\infty} d\xi \ D(\xi)\xi^{2} = 1$ ,

$$\rho_{\rm GM}(E) = p \int_{0}^{\infty} d\xi \ D(\xi) \xi^2 \theta[E_{j}(\xi) - |E|] + (1-p)$$
(10)

is defined as the normalized tunnelling density of states,  $E_{j}(d) = 2e^{2}A/(\pi d^{2}C_{j})$ ,  $\rho_{s}(E) = |E|/\sqrt{(E^{2} - \Delta^{2})}$  for  $|E| > \Delta$  and  $\rho_{s}(E) = 0$  for  $|E| < \Delta$  is the BCS density of states,  $\Delta$  is the superconducting energy gap,  $C_{NN}$  is the conductance of the normal junction,  $f(E) = [1 + \exp(E/kT)]^{-1}$  is the Fermi distribution function, and the function  $\theta(u)$  is defined so that  $\theta(u) = 1$  for  $u \leq 0$  and  $\theta(u) = 0$  for u > 0.

I(V) is written as the sum of two terms. The first term represents the current density into isolated particles and the second term represents the current density into the metallic continuum, the dimensionless parameter p expresses the relative weight of the two contributions. In the limit of p=0, eqn. (8) assumes the usual form for the tunnelling current between a superconductor and normal metal. In the limit of p=1 all the current is due to tunnelling into isolated particles. The appearance of the function  $\theta$  takes



The tunnelling density of states  $\rho_{\rm GM}$  as a function of electron energy E, for Ni-SiO<sub>2</sub> films, computed from eqn. (9) using the experimental data in fig. 20. E=0 coincides with the Fermi energy. The volume fraction x of Ni is indicated in the figure.

into account the finite charging energy  $E_j(d)$  necessary to transfer an electron (or hole) between the electrodes. The factor  $\xi^2$ , appearing in eqn. (8), takes into account the fact that the rate of tunnelling is proportional to the area available for tunnelling into isolated particle.

Equation (9) permits the determination of the density of states  $\rho_{\rm GM}$  from I(V). Using the experimental data in fig. 20 and the measured value 0.32 meV for  $\Delta$ , numerical integration of eqn. (9) yields the effective tunnelling densities of states shown in fig. 21. Near x = 0.7 a dip develops in  $\rho_{\rm GM}$  at the Fermi energy which rapidly broadens and deepens into a smeared gap with decreasing x. Using the measured tunnel junction parameters  $C_{i}$  =  $9 \times 10^{-9}$  F and  $A = 3.3 \times 10^{-3}$  cm<sup>2</sup> we find that  $\rho_{GM}$  in fig. 21 is well approximated by using in eqn. (10) the function  $D(d) \propto d^{\lambda} \exp \{-(d/d_0)^{\lambda}\}$ , where  $d_0$ is the most probable value of d and with the value of the exponent  $\lambda = 0.75$ . For x = 0.66 the value of  $d_0$  is 100 Å and p = 0.25, which indicates that only a fraction of the tunnelling current is into isolated particles. As x decreases to 0.6,  $d_0$  falls to 30 Å, in reasonable agreement with the mean particle size determined from electron microscopy (see fig. 17), and p increases to 0.97, indicating that most of the tunnelling current is now into isolated particles. The limiting case of tunnelling into isolated grains in the granular metal is equivalent to the experiments of Zeller and Giaever (1969) on tunnelling into isolated tin particles.

The analysis of the tunnelling data shows that in the transition regime the metallic continuum phase and the isolated metal particle phase co-exist. The fraction of the latter phase increases at the expense of the former as x is reduced. Furthermore, tunnelling yields the mean size of isolated particles in the transition regime.

# § 4. The dielectric regime

### 4.1. Theory

Electrical conduction in the dielectric regime of granular metals results from transport of electrons and holes by tunnelling from one isolated metallic grain to the next. In order to generate a charge carrier, an electron has to be removed from one neutral metal grain and placed on another neutral metal grain, thereby creating a pair of positively and negatively charged grains (Neugebauer and Webb 1962, Hill 1969). Due to the fact that every metal grain has a small capacitance, such a process of carrier generation requires a non-negligible charging energy  $E_c \sim e^2/c$ , where *e* is the electronic charge and *c* is the capacitance of a grain. In a granular metal, the charging energy has the form

$$E_{\rm c} = (e^2/d)F(s/d),$$
 (11)

where d is the size of a grain, s is the separation between grains, and F is a function whose form depends on shape and arrangement of the grains and on the interaction between the pair of charges. We distinguish two limiting values of the charging energy  $E_c$ : the energy  $E_c^0$  required to generate a pair of fully dissociated positively and negatively charged grains and the energy  $E_c^1$  required to generate a pair of neighbouring positively and negatively charged grains. Approximate forms of  $E_c^0$  and  $E_c^1$  are derived in Appendix A, and it is shown that  $E_c^1 \simeq E_c^0/2$ .

The existence of a finite  $E_{\rm c}$  has far-reaching consequences on the electrical transport properties of granular metals. The effects of  $E_{\rm c}$  are manifest both in the temperature and the electric field dependences of the conductivity. In the case of a weak electric field, that is, when the voltage drop,  $\Delta V$ , between neighbouring metal grains is much smaller than kT/e, charge carriers are thermally activated. The number density of the charge carriers, whose generation requires a charging energy  $E_{c}^{0}$ , is proportional to the Boltzmann factor exp  $[-E_c^{0}/2kT]$ . When the temperature is lowered, the number density of charge carriers rapidly decreases until near T = 0 K almost all the metal grains are electrically neutral. At such low temperatures an electric current can be obtained only by the application of a large electric field, in which case the charge carriers are generated by the electric field whenever the potential difference between two neighbouring metal grains is larger than  $E_{c}^{1}/e$ . This field generation process is illustrated in fig. 22. In order to translate the above qualitative arguments into quantitative calculations, we are confronted with the problem that there is a broad distribution in



(b) FINAL STATE

Schematic illustration of effect of an electric field on the electronic energy levels in the granular metal. The voltage drop between adjacent grains is  $\Delta V$ . The relative potential levels indicated are as seen by a negative test charge. For the sake of illustration the structure is taken as uniform. (a) Each grain is neutral before the tunnelling takes place. (b) After tunnelling has occurred, a hole is left on one grain and an electron is added to the other grain. The hole and the electron will then drift to the electrodes.

<sup>&</sup>lt;sup>†</sup> The fact that the equilibrium density of charge carriers is proportional to  $\exp\left[-E_{c}^{0}/2kT\right]$ , not  $\exp\left[-E_{c}^{0}/kT\right]$ , is a direct consequence of the law of mass action. An analogous situation prevails in intrinsic semiconductors where the band gap plays the same role as  $E_{c}^{0}$  does in granular metals. We note that in prior literature the charge carrier density in granular metals has been taken to be proportional to  $\exp\left[-E_{c}^{0}/kT\right]$ , which is incorrect.

the values of  $E_c$  due to the variation of metal grain size in granular metals, and as a result  $E_c$  is not a useful quantity for characterizing the material. However, a closer look at the structural origin of  $E_c$  suggests that although d, s, and  $E_c$  are not constant in a granular metal, their variations are correlated so that the quantity  $sE_c^{0}$  is a constant whose magnitude depends only on the volume fraction of metal x in the sample and the dielectric constant of the insulator. In the following, a simple plausibility argument for the relationship  $sE_c^{0} = \text{constant}$  is presented.

Due to the fact that the metal grains are formed by surface diffusion of sputtered metal atoms and insulator molecules, we can expect the relative volume fraction of metal and dielectric to be uniform when averaged over a volume larger than a few surface diffusion lengths ( $\sim 100$  Å). That is, if we take any 100 Å sized region and analyse its relative volume fractions of metal and insulator we would expect that number to be a constant and equal to that of the bulk sample. This condition of uniform composition on the scale of surface diffusion length implies a close relationship between the average grain size and the average distance of separation between the grains within small regions (100 Å, say) of the sample. Roughly speaking, we can expect the large grains to be further separated than small grains. If it is further assumed that the grains are roughly uniform in size inside small regions of the sample (but can vary from one region to the next), then the grain size d in each region should be directly proportional to the grain separation s in that region and the ratio, s/d, is a constant whose magnitude depends only on x. This simple fact is illustrated for the one-dimensional case in fig. 23. From eqn. (11) and the condition s/d = constant it follows directly that  $sE_{0}^{0} = \text{constant}$  for a given granular metal composition.

$$\begin{array}{c} & & & & & & & & & \\ \hline & & & & & & & & \\ X = .5 & & & & & & \\ & & & & & & & \\ X = .5 & & & & & & \\ & & & & & & & \\ X = .5 & & & & & & \\ \end{array}$$

One-dimensional illustration of the idea that the ratio of metal particle separation s to metal particle size d is only a function of x. Particles are shaded. The average particle size in (b) is about twice that in (a).

We now derive, on the basis of the rule  $sE_0^0 = \text{constant}$ , the low-field and the high-field behaviours of the conductivity in granular metals. In order to carry out the calculation, a distribution function D(s) of s is required. This D(s) is to be distinguished from that used in eqn. (8). An estimate of D(s) can be obtained from electron micrographs. D(s) must have the general feature of vanishing in the limits of  $s \rightarrow 0$  and  $s \rightarrow \infty$ , and  $\int_0^{\infty} ds D(s) = 1$ . In the following we will express D(s) in the form  $D(s) \equiv g(s)D_0(s)$ , where  $D_0(s) = (s/s_0^2) \exp((-s/s_0))$ , and  $s_0$  is the most probable value of s.

### (i) Low-field regime

In this regime the voltage difference between neighbouring metal grains,  $\Delta V$ , is much smaller than kT/e. Thermal activation is therefore the main mechanism responsible for charge-carrier generation. We assume that the generated positive-negative pairs of charged grains are roughly of the same size so that each contributes about half of the charging energy  $E_{c}^{0}$ . Let us consider all those charge carriers with charging energy  $E_{c}^{0'}$ . Their number density is proportional to the Boltzmann factor  $\exp[-\check{E_{o}}^{0'}/2kT]$ . When a weak electric field  $(e\Delta V \ll kT)$  is applied, the charge will drift along a path of largest mobility towards the electrodes. The charge is inhibited from tunnelling to a much smaller grain with  $E_{c}^{0} \gg E_{c}^{0'}$  because the charge has insufficient energy. The charge will, therefore, tunnel to grains with  $E_{c}^{0} \leq E_{c}^{0'}$ . However, since smaller  $E_{c}^{0}$  is associated with a larger tunnelling barrier by the rule  $sE_{c}^{0} = \text{constant}$ , the optimal path, which we will refer to as the percolation path, follows the regions with the least deviations of  $E_{c}^{0}$  from  $E_{c}^{0}$ . The corresponding mobility is proportional to the tunnelling probability (Schiff 1968) exp  $[-2\chi s']$ , where  $s' = \text{const.}/E_c^{0'}$  and  $\chi = [2m\phi/\hbar^2]^{1/2}$  with *m* denoting the electron mass,  $\phi$  the effective barrier height, and  $\hbar$  Planck's constant. The total low-field conductivity,  $\sigma_{\rm L}$ , is the sum of products of mobility, charge, and number density of charge carriers over all possible percolation paths, and can be written as

$$\sigma_{\rm L} \propto \int_{0}^{\infty} \beta(s) \exp\left[-2\chi s - (E_{\rm c}^{0}/2kT)\right] ds = \int_{0}^{\infty} \beta(s) \\ \times \exp\left[-2\chi s - (C/2\chi skT)\right] ds, \qquad (12)$$

where

$$C \equiv \chi s E_{\rm e}^{0} \tag{13}$$

is a constant and  $\beta(s)$  is the density of percolation paths<sup>†</sup> associated with the value s. The integral in eqn. (12) contains two factors,  $\beta(s)$  and exp [f(s)], with  $f(s) = -2\chi s - (C/2\chi skT)$ . It should be noted that f(s) is a peaked function of s. The maximum value of f(s) occurs at  $s_{\rm m} = \sqrt{(C/kT)/2\chi}$ . Expanding f(s) around  $s_{\rm m}$ , we have

$$f(s) = f(s_{\rm m}) + \frac{1}{2} f''(s_{\rm m})(s - s_{\rm m})^2 + \dots$$
  
=  $-2 \sqrt{\left(\frac{C}{kT}\right)} - \sqrt{\left(\frac{kT}{C}\right)} (2\chi s - 2\chi s_{\rm m})^2 + \dots$  (14)

 $\exp[f(s)]$  can now be expressed as

$$\exp\left[f(s)\right] \simeq \exp\left[-2\sqrt{\left(\frac{C}{kT}\right)}\right] \exp\left[-4\chi^2\sqrt{\left(\frac{kT}{C}\right)} \times \left[s - \frac{1}{2\chi}\sqrt{\left(\frac{C}{kT}\right)}\right]^2\right], \quad (15)$$

<sup>&</sup>lt;sup>†</sup> The density of percolation path  $\beta(s)$  was not included explicitly in the original work (Sheng *et al.* 1973); however, the final result is unchanged.

where the first exponential is independent of s and the second exponential is a Gaussian with a width  $\Delta s = [1/\sqrt{8}]\chi(C/kT)^{1/4}$ . Thus, the position of the maximum of  $\exp[f(s)]$ ,  $s_m = \sqrt{(C/kT)/2\chi}$ , is a function of temperature and the height of the peak increases as  $\exp[-2\sqrt{(C/kT)}]$  with temperature. Let us now examine the behaviour of the product  $\beta(s) \exp[f(s)]$ . If  $\beta(s)$  is a broad function of s,  $\sigma_L$  can be approximated by

$$\sigma_{\rm L} \propto \beta(s_{\rm m}) \exp\left[-2\sqrt{\left(\frac{C}{kT}\right)}\right] \int_{0}^{\infty} \exp\left[-\sqrt{\left(\frac{kT}{C}\right)} \times \left[2\chi s - \sqrt{\left(\frac{C}{kT}\right)}\right]^{2}\right] ds \simeq \frac{\sqrt{\pi}}{2\chi} \left(\frac{C}{kT}\right)^{1/4} \beta\left[\sqrt{\left(\frac{C}{kT}\right)}\frac{1}{2\chi}\right] \times \exp\left[-2\sqrt{\left(\frac{C}{kT}\right)}\right], \quad (16)$$

where  $\beta(s)$  was replaced by its value at  $s = s_{\rm m}$  and the assumption was made that  $C/kT \ge 1$  so that the Gaussian integrals can be performed. This assumption is well satisfied in the temperature range where data were obtained.

From eqn. (16) it is clear that in order for  $\exp\left[-2\sqrt{(C/kT)}\right]$  to be the dominant temperature dependence of  $\sigma_{\rm L}$ ,  $\beta(s_{\rm m}) \ (\equiv \beta(\sqrt{(C/kT)/2\chi})$  must have a slower temperature variation than  $\exp\left[-4\chi s_{\rm m}\right] \ (\equiv \exp\left[-2\sqrt{(C/kT)}\right])$ . In order to be more quantitative, let us suppose that by increasing the temperature,  $s_{\rm m}$  is decreased by 1 Å. If we take (Sheng and Abeles 1972)  $\chi \simeq 1$  Å<sup>-1</sup>, the factor  $\exp\left[-4\chi s_{\rm m}\right]$  is increased by  $\exp\left[4\right] \simeq 50$  times. As long as the variation of  $\beta(s)$  is much smaller than a factor of 50 in the interval s and s+1 Å, the temperature dependence introduced by  $\beta(\sqrt{(C/kT)/2\chi})$  is negligible. In the following we will proceed with the assumption that  $\beta(s)$  is sufficiently slowly varying so that the above condition is satisfied.

In order to evaluate the temperature dependence of the pre-exponential factor, a detailed knowledge of  $\beta(s)$  is required. Such a calculation is beyond the scope of this work. The uncertainty in the exact temperature dependence of the pre-exponential factor introduces some error in the experimental determination of C. For the purpose of comparing the theory with experiment, we will neglect the temperature dependence of the pre-exponential factor completely and write

$$\sigma_{\rm L} = \sigma_0 \exp\left[-2\sqrt{(C/kT)}\right],\tag{17}$$

where  $\sigma_0$  is a constant independent of temperature.

#### (ii) High-field regime

In the low-field regime the number density of charge carriers is given by the thermal equilibrium value. As the magnitude of electric field is increased, an additional mechanism, field-induced tunnelling, becomes important and the concentration of charge carriers gradually deviates from its thermal equilibrium value. The relative importance of the two generation processes, thermal activation and field-induced tunnelling, is gauged by the ratio  $kT/e\Delta V$ , where  $\Delta V$  is the voltage drop between neighbouring grains. The transition between the high-field and the low-field regimes is observed as a rapid increase in conductivity when  $e\Delta V$  becomes comparable to or greater than kT (see § 4.2). When the strength of electric field is further increased, electrical conductivity becomes highly non-ohmic, which, as we will show below, is a direct manifestation that field-induced tunnelling has replaced thermal activation as the dominant process of charge- carrier generation.

When an electric field is applied to a granular metal it is reasonable to assume that the equipotential surfaces are roughly perpendicular to the direction of the macroscopic field, and every metal grain is on one of the equipotential surfaces. The equipotential surfaces naturally divide up the sample into layers, as schematically illustrated in fig. 24, so that the grains



Schematic illustration of equipotential surfaces in a granular metal when a macroscopic field  $\mathscr{E}$  is applied. Significant voltage difference occurs only between pairs of particles that are situated on different layers.

within each layer are approximately at the same potential, and significant voltage difference between neighbouring grains occurs only when the two grains are on different layers. We will make the simplifying assumption that the applied electric field  $\mathscr{E}$  gives rise to equal voltage drops  $\Delta V = \mathscr{E} w$  between layers of neighbouring grains.<sup>†</sup> The layers are separated on the average by  $w \simeq s_0 + d_0$ , and are roughly perpendicular to the direction of the macroscopic field. The quantity w can be regarded as the 'lattice constant' of granular metals.

We first calculate the current density at T = 0 K in order to emphasize the physics of the field-induced tunnelling conduction. Generalization to the case of finite temperatures will be straightforward. At T = 0, the tunnelling

<sup>†</sup> It should be noted that in our original treatment of field-induced tunnelling (Sheng and Abeles 1972) we assumed a constant charging energy  $E_{\rm o}$ , a distribution in barrier thicknesses s and a constant electric field in the insulator. Although such an assumption leads to the observed field dependence of the conductivity, it predicts a wrong temperature dependence,  $\log \sigma_{\rm L} \sim -1/T$ , for the low-field conductivity.

rate, r, of electrons from a grain on one layer to a neighbouring grain on the next layer is given by<sup>†</sup>

$$r(s) = \gamma G \int_{-\infty}^{\infty} \theta(E) [1 - \theta(E + e\Delta V - E_{c}^{-1})] \nu \exp\left[-2\chi s\right] \rho(E) dE.$$
(18)

Here G is the grain volume, E is the electronic energy (E=0 is the Fermi level),  $\rho(E)$  is the density of states,  $\chi = [2m(\phi - E)/\hbar^2]^{1/2}$ ,  $\phi$  is the effective barrier height, and  $\nu$  is the frequency at which the electron strikes the barrier. The function  $\theta(\mu)$ , defined such that  $\theta(\mu) = 1$  for  $\mu \leq 0$  and  $\theta(\mu) = 0$  for  $\mu > 0$ , ensures that the energy of the tunnelling electron is conserved and that the initial state has an electron and the final state is empty.  $\gamma$  is a geometric factor which takes into account the fact that tunnelling occurs across nonplanar barriers. For a planar barrier of uniform thickness,  $\gamma = 1$ . For the case of tunnelling between two irregularly shaped grains the value of  $\gamma$  can be considerably smaller than unity because the 'effective' area of tunnelling is smaller. The value of  $\gamma$  for two spheres is estimated in Appendix B. In eqn. (18) the energy dependence of  $\chi$  can be neglected since in our system the barrier height  $\phi$  is significantly larger than  $e\Delta V$ . Therefore,  $\chi$  can be regarded as a constant  $\simeq (2m\phi/\hbar^2)^{1/2}$ . Furthermore, we have neglected in eqn. (18) the effect of the field on barrier shape and assumed the barrier to be rectangular-shaped. The value of the frequency  $\nu$  can be obtained by arguments similar to that of Blatt and Weisskopf (1952),‡ and can be expressed as  $\nu = 1/(G \cdot \rho(E) \cdot h)$ , where  $h = 2\pi\hbar$ . Equation (18) is now rewritten as

$$r(s) = \frac{\gamma}{h} \exp\left(-2\chi s\right) \int_{-\infty}^{\infty} \theta(E) \left[1 - \theta(E + e\Delta V - E_{c}^{-1})\right] dE$$
$$= \frac{\gamma}{h} \exp\left(-2\chi s\right) x \begin{cases} 0 \qquad E_{c}^{-1} \ge e\Delta V \\ (e\Delta V - E_{c}) \qquad E_{c}^{-1} < e\Delta V \end{cases}$$
(19)

or, in terms of the quantity  $C = \chi s E_{e^0}$ ,

$$r(s) = \frac{\gamma}{h} \exp((-2\chi s)x) \begin{cases} 0 & \frac{C}{e\Delta V} \ge 2\chi s \\ \left(e\Delta V - \frac{C}{2\chi s}\right) & \frac{C}{e\Delta V} < 2\chi s \end{cases}$$

where we have used the relation  $\chi s E_c^0 = C$  and the fact that  $E_c^1 \simeq E_c^0/2$  (see Appendix A).

<sup>&</sup>lt;sup>†</sup> In eqn. (18) we use the total kinetic energy of the electron in the expression for  $\chi$ , which is appropriate for irregularity shaped particles in the WKB approximation. This is to contrasted with the case of planar tunnelling junction where only the kinetic energy of the electron normal to the barrier appears in  $\chi$ , and the transverse momentum is conserved in the tunnelling process.

<sup>&</sup>lt;sup>‡</sup> The frequency of oscillation for an electron in a particle is analogous to nucleons oscillating in a nucleus. The period of such oscillation is given by  $2\pi\hbar/\delta$ , where  $\delta$  is the energy level separation.

Equation (19) expresses the essential physics of field-induced tunnelling conduction. The tunnelling of electrons between adjacent neutral grains represents the charge carrier generation process. For a certain barrier thickness s there is a voltage threshold due to the existence of a charging energy  $E_c^{-1} = C/2\chi s$  below which there is no tunnelling. An equivalent restatement of the threshold condition is that at a given voltage, electrons will only tunnel through barriers with thickness  $\geq C/2\chi e\Delta V$ . Since the tunnelling rate depends exponentially on the barrier thickness, the dominant contribution to the conductivity is due to electron tunnelling across barrier with thickness  $s \simeq C/2\chi e\Delta V$ . Therefore, the dominant field dependence of the high-field conductivity is given by

$$\exp\left[-2\chi C/2\chi e\Delta V\right] \equiv \exp\left[-C/e\Delta V\right] \equiv \exp\left[-C/ew\mathscr{E}\right].$$

We now calculate the high-field current density  $j_{\rm H}$ . Consider inside the sample an imaginary plane of unit area perpendicular to the direction of the macroscopic field. The current density  $j_{\rm H}$  is equal to the sum of negative charges which cross the plane along the field direction and positive charges which cross the plane in the opposite direction during unit time. If electrons and holes have a recombination length l, then only those charges generated within a distance l of the plane need to be considered. Assuming all generated negative charge carriers would be swept by the field from left to right and all the positive charge carriers the opposite direction, the high-field current density  $j_{\rm H}$  is equal to twice the rate of generation of charge carriers in a volume of unit area and thickness l to the left (or right) of the plane.

Therefore,

$$j_{\mathbf{H}} = 2e_{\frac{1}{2}} \mathcal{N}l \int_{0}^{\infty} r(s) D(s) \, ds, \qquad (20)$$

where  $\frac{1}{2}\mathcal{N}$  is the number of pairs of metal grains per unit volume. Substituting eqn. (19) in eqn. (20), we have

$$j_{\rm H} = \frac{e \mathcal{N} l \gamma}{h} \int_{\frac{1}{2\chi} \frac{C}{e \delta w}}^{\infty} \exp\left[-2\chi s\right] \left(e \delta w - \frac{C}{2\chi s}\right) g(s) D_0(s) \, ds. \tag{21}$$

Making the change of variable

$$Z = \left(2\chi + \frac{1}{s_0}\right)s - \frac{C\left(1 + \frac{1}{2\chi s_0}\right)}{e\mathscr{E}w}$$
(22)

yields

$$j_{\rm H} = \frac{e^2 \mathcal{N} l_{\gamma} w}{h(2\chi s_0 + 1)^2} \,\mathscr{E} \, \exp\left(-\frac{C_0}{e\mathscr{E} w}\right) \,\int_0^\infty \, Z \, \exp\left(-Z\right) g \left[\frac{Z + \frac{C_0}{e\mathscr{E} w}}{\left(2\chi + \frac{1}{s_0}\right)}\right] dZ, \quad (23)$$

where

$$C_{0} = C \left( 1 + \frac{1}{2\chi s_{0}} \right) \equiv \chi s E_{c}^{0} \left( 1 + \frac{1}{2\chi s_{0}} \right).$$
(24)

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Since usually  $1/2\chi s_0 \ll 1$ , it follows that  $C_0 \simeq C$ . In the case when g(s) is a slowly varying function of s, the dominant behaviour of  $j_{\rm H}$  is obtained by setting g(s) = 1. Then

$$\sigma_{\rm H} \equiv j_{\rm H}/\mathscr{E} = \sigma_{\infty} \exp\left[-\mathscr{E}_0/\mathscr{E}\right],\tag{25}$$

with

$$\sigma_{\infty} = e^2 l \gamma / [(s_0 + d_0)^2 (2\chi s_0 + 1)^2 h]$$
<sup>(26)</sup>

 $\sim$ 

and

$$\mathscr{E}_0 = C_0 / ew, \tag{27}$$

where we have expressed  $\mathcal{N} = 1/(s_0 + d_0)^3$  and  $w = s_0 + d_0$  in eqn. (26).

Generalization to the case of finite temperatures can proceed in two steps. First, we replace  $\theta(E)$  in eqn. (18) by the Fermi function

$$f(E) = 1/[1 + \exp(E/kT)].$$

Then eqn. (19) is replaced by

$$r(s) = \frac{\gamma}{h} \exp\left(-2\chi s\right) \frac{e\mathscr{E}w - \frac{C}{2\chi s}}{1 - \exp\left[\left(\frac{C}{2\chi s} - e\mathscr{E}w\right)/kT\right]},$$
(28)

where the term due to electrons tunnelling counter to the applied electric field, which is negligible for the case  $e\mathscr{E}w \gg kT$  and vanishes for T=0, has been dropped. Calculation of current density then yields

$$j_{\rm H} = \frac{e\mathcal{N}l\gamma}{\hbar} \int_{0}^{\infty} \exp\left[-2\chi s\right] g(s) D_0(s) \frac{\left(e\mathscr{E}w - \frac{C}{2\chi s}\right)}{1 - \exp\left[\left(\frac{C}{2\chi s} - e\mathscr{E}w\right)/kT\right]} ds.$$
(29)

Making the same change of variable as eqn. (22), we get

$$\sigma_{\rm H} \equiv j_{\rm H} / \mathscr{E} = \sigma_{\infty} \exp\left[-\mathscr{E}_0 / \mathscr{E}\right] \int_{-\mathscr{E}_0 / \mathscr{E}}^{\infty} dZ \, Z \exp\left[-Z\right] \\ \times \frac{g[s(Z)]}{1 - \exp\left[-\frac{Z}{Z + (\mathscr{E}_0 / \mathscr{E})} \frac{\mathscr{E}C_0}{\mathscr{E}_0 k T}\right]}$$
(30)

or

$$\sigma^* = \exp\left[-1/\mathscr{E}^*\right] \int_{-1/\mathscr{E}^*}^{\infty} dZ \, Z \exp\left[-Z\right] \, \frac{g[s(Z)]}{1 - \exp\left[-\frac{Z}{Z + (1/\mathscr{E}^*)} \frac{\mathscr{E}^*}{T^*}\right]}, \quad (31)$$

where  $\sigma^* \equiv \sigma_{\rm H}/\sigma_{\infty}$ ,  $\mathscr{E}^* = \mathscr{E}/\mathscr{E}_0$ , and  $T^* = kT/C_0$  are the reduced dimensionless conductivity, field, and temperature, respectively. Equation (31) predicts a scaling behaviour for the temperature and the field dependences of the high field conductivity. In other words, eqn. (31) states that when the highfield conductivity data for granular metals with different compositions are

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plotted on scales of reduced temperatures and reduced field, they obey a universal behaviour which is characteristic of field-induced tunnelling. The constants  $C_0$  and  $\mathscr{E}_0$ , whose values depend on the composition and dielectric constant of the granular metal, determine the field and the temperature scales over which this universal behaviour is observed. This remarkable result, a direct consequence of the rule  $sE_c^0 = \text{constant}$ , can be easily verified experimentally, and offers an additional test of the theory. In order to evaluate the integral in eqns. (23) and (31) it is necessary to assume explicit forms for the function g. Computer calculations have shown that eqns. (23) and (31) are insensitive to the form of g(s) as long as g(s) does not vary by more than a factor of 10 when s is varied by 1 Å. Therefore, in comparing the theory with experiment, we will for simplicity set g(s) = 1.

The second step in the generalization of the zero temperature result is to note that due to quantization of electronic motion within every metal particle, phonon-assisted tunnelling must be taken into account. Energy levels are separated on the average by (Kubo 1962, 1969)

$$\delta = \frac{1}{\rho(E_{\rm F})G} = \frac{4}{3} \frac{E_{\rm F}}{(\pi/6)d^3 \cdot n},\tag{32}$$

where  $E_{\rm F}$  is the Fermi energy and n is the number of conduction electrons per unit volume. Due to this discrete separation between electronic energy levels, sometimes the closest empty state which the electron can tunnel to is at an energy  $\Delta E$  away, where  $0 < \Delta E < \delta$ . When this happens, there can be no direct tunnelling between the grains, even when the condition  $e\Delta V \ge E_c^{-1}$ is satisfied, and the electron must emit or absorb a phonon during the tunnelling process in order to reach the final state. The probability of such a tunnelling process (with phonon emission or absorption) is expected to increase with temperature and to approach a high temperature limit when kT is of the order of  $\delta$  or larger. A similar temperature dependence is found in the analogous case of phonon-assisted tunnelling between localized states in amorphous semiconductors (Mott and Davis 1971, pp. 39, 157). Since the increase in tunnelling probability due to phonon absorption or emission is independent of the field, the resulting increase in conductivity will manifest itself in a temperature-dependent  $\sigma_{\infty}(T)$ . We will thus treat  $\sigma_{\infty}$  in eqn. (30) as a temperature-dependent adjustable parameter.

It is instructive to point out the similarities and the differences between Mott's model (Mott 1969, Ambegaokar *et al.* 1971) of variable range-hopping in amorphous semiconductors and our model. In Mott's model the density of charge carriers is assumed to be temperature independent, and the percolation paths for the charge carriers are determined by optimizing the mobility. In our model the charge carriers are thermally activated in the low-field regime and field-generated in the high-field regime ; tunnelling occurs between nearest neighbours only ; and the optimization, when it is used in deriving the temperature dependence of  $\sigma_{\rm L}$ , is applied to the product of mobility and number density of charge carriers. The differences between charging energies in our model are analogous to the relative displacements of the energy levels for the localized states in Mott's model. However, in our case not only the differences but also the magnitudes of  $E_c$  play an important role. This is

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especially obvious in the high-field regime where the governing factor for field generation of charge carriers is the value of  $E_{\rm c}$  rather than the differences in  $E_{\rm c}$ .

#### 4.2. Comparison of theory with experimental results

We now present our experimental results for the electrical resistivity in the dielectric regime of granular Ni-SiO<sub>2</sub>, Pt-SiO<sub>2</sub>, and Au-Al<sub>2</sub>O<sub>3</sub> films. The temperature dependence of the low-field ohmic resistivity  $\rho_{\rm L} (\equiv 1/\sigma_{\rm L})$  is shown in figs. 25, 26, and 27. As seen from these graphs, the characteristic low-field



Electrical resistivity in the low field ohmic regime  $\rho_{\rm L}$ , as a function of  $1/\sqrt{T}$ , for several Ni–SiO<sub>2</sub> films. The resistivity was measured normal to the plane of the films. The volume fractions x of Ni are indicated in the figure. The points are the experimental data, the straight lines represent the relation  $\ln \rho_{\rm L} \sim 1/\sqrt{T}$ .

behaviour is of the form  $\ln \rho_{\rm L} \sim 1/\sqrt{T}$  (except for the Au-Al<sub>2</sub>O<sub>3</sub> film with x = 0.41, which is in the transition regime) as predicted by eqn. (17). From the slopes and the intercepts of the  $\ln \rho_{\rm L}$  versus  $1/\sqrt{T}$  plots we obtain the values of C and  $\sigma_0$  tabulated in tables 1, 2, and 3. It should be remarked that due to the fact that our experimental data cover a large range of temperature and resistivity values, the characteristic  $\ln \rho_{\rm L} \sim 1/\sqrt{T}$  behaviour is readily distinguishable from the Mott  $\ln \rho_{\rm L} \sim 1/T^{1/4}$  or the  $\ln \rho_{\rm L} \sim 1/T$  behaviour.

The field dependence of the high-field, non-ohmic resistivity  $\rho_{\rm H} (\equiv 1/\sigma_{\rm H})$  at 1.4 K is shown in fig. 28 for several Ni–SiO<sub>2</sub> films of different compositions and thicknesses. For each composition, with the exception of x = 0.41, we show resistivities, measured with  $\mathscr{E}$  normal to the sample plane, for two films

#### Fig. 25



Electrical resistivity in the low-field ohmic regime  $\rho_{\rm L}$ , as a function of  $1/\sqrt{T}$ , for several Pt-SiO<sub>2</sub> films. The volume fractions x of the Pt are indicated in the figure. The resistivity was measured normal to the plane of the films. The points are the experimental data, the straight lines represent the relation  $\ln \rho_{\rm L} \sim 1/\sqrt{T}$ .



Electrical resistivity in the low field ohmic regime  $\rho_{\rm L}$ , as a function of  $1/\sqrt{T}$ , for several Au-Al<sub>2</sub>O<sub>3</sub> films. The volume fractions x of the Au is indicated in the figure. The resistivity was measured in the plane of the films. The points are the experimental data, the straight lines represent the relation  $\ln \rho_{\rm L} \sim 1/\sqrt{T}$ .

(Å) el. micro.	50 49 25 20
w calc.	60 44 38 38 38
$(\Omega^{-1}  \mathrm{cm}^{-1})$	$\begin{array}{c} 3 \times 10 \\ 3 \\ 4 \times 10^{-1} \\ 7 \times 10^{-2} \\ 2 \cdot 5 \times 10^{-2} \end{array}$
$\sigma^{\sigma_{\infty}(0)}_{(\Omega^{-1}\mathrm{cm}^{-1})}$	$\begin{array}{c} 1\times 10^{-2}\\ 3\times 10^{-3}\\ 2\times 10^{-4}\\ 2\times 10^{-5}\\ 1\times 10^{-6}\end{array}$
С (еV)	0-13 0-22 0-35 0-68 1-1
$C_{0} \\ (eV)$	$\begin{array}{c} 0.085 \\ 0.30 \\ 0.90 \end{array}$
$(10^6 \mathrm{V/cm})$	0-22 0-48 1-0 3-4
$T \ (\mu)$	$\begin{array}{c} 0.55\\ 0.55\\ 0.11\\ 0.50\\ 0.10\\ 0.10\end{array}$
x vol. fraction Ni	$\begin{array}{c} 0.44 \\ 0.34 \\ 0.24 \\ 0.14 \\ 0.08 \end{array}$
P sample pos.	10 19 34 34 42

$t-SiO_2$	
ameters of <b>P</b>	
$\mathbf{Par}$	
Table 2.	

γ (Å) el. micro.	15 115 115 115 115 115 115 115 115 115
u calc.	$23 \\ 29 \\ 29 \\ 29 \\ 29 \\ 29 \\ 29 \\ 29 \\ $
$(\Omega^{-1}  \mathrm{cm}^{-1})$	$\begin{array}{c} 3\cdot 2\times 10^{-1}\\ 3\cdot 6\times 10^{-2}\\ 1\cdot 0\times 10^{-2}\\ 7\cdot 7\times 10^{-4}\\ 1\cdot 7\times 10^{-4}\\ 2\cdot 0\times 10^{-4}\end{array}$
$(\Omega^{\sigma_\infty}_{-1}^{(0)})$	$\begin{array}{c} 7\cdot\mathbf{i}\times10^{-4}\\ 4\cdot6\times10^{-5}\\ 3\cdot1\times10^{-6}\\ 2\cdot3\times10^{-7}\\ 4\cdot3\times10^{-8}\\ 1\cdot0\times10^{-8}\end{array}$
(c C)	$\begin{array}{c} 0.20\\ 0.35\\ 0.41\\ 0.56\\ 0.77\\ 1.1\end{array}$
C <sub>0</sub> (eV)	$\begin{array}{c} 0.17\\ 0.31\\ 0.35\\ 0.46\\ 0.65\\ 0.90\end{array}$
$(10^6 V/\mathrm{cm})$	$\begin{array}{c} 0.39\\ 0.84\\ 1.1\\ 1.7\\ 2.7\\ 2.9\end{array}$
$(\eta)$	$\begin{array}{c} 0.25\\ 0.24\\ 0.23\\ 0.23\\ 0.20\\ 0.18\\ 0.18\end{array}$
x vol. fraction Pt	0-18 0-14 0-07 0-05 0-05
P sample pos.	24 33 44 48 48

1

Table 1. Parameters of Ni–SiO<sub>2</sub>

1

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i

1

I

L

P sample pos.	x vol. fraction Au	C (eV)	$(\Omega^{-1}  { m cm^{-1}})$
27	0.38	0.004	$6.0 \times 10^{-2}$
32	0.28	0.051	$1 \cdot 1 \times 10^{-3}$
34	0.23	0.11	$6\cdot1 imes10^{-4}$
37	0.18	0.12	$2.7 imes10^{-5}$

Table 3. Parameters of Au-Al<sub>2</sub>O<sub>3</sub>

whose thickness ratios are 5:1. The films were obtained by two sputtering runs, one five times the duration of the other. The resistivity of the sample with x=0.41 was measured with  $\mathscr{E}$  in the plane of the sample. The fact that, within the experimental uncertainty in the thickness determination and the possible variation of compositions, the resistivities for the thick and thin samples are functions of field only (the discrepancy between the resistivities of the thick and the thin samples can be accounted for by the uncertainty of thickness determination) is proof that the observed non-linear behaviour is a bulk rather than a surface effect. In all cases,  $\ln \rho_{\rm H} \sim 1/\mathscr{E}$ , which is the characteristic field dependence of  $\rho_{\rm H}$  at low temperatures (see eqn. (25)).



The high-field electrical resistivity  $\rho_{\rm H}$  measured at 1.4 K as a function of 1/ $\mathscr{E}$  for several Ni–SiO<sub>2</sub> films. The thicknesses of the films and the volume fraction x of Ni are indicated in the figure. The resistivity of the sample with x=0.41 was measured with the electric field  $\mathscr{E}$  in the plane of the film, the remaining films were measured with  $\mathscr{E}$  normal to the plane of the film. The points are the experimental data, the solid lines represent the relation  $\ln \rho_{\rm H} \sim 1/\mathscr{E}$ .

From the slopes and the intercepts of the ln  $\rho_{\rm H}$  versus 1/ $\mathscr{E}$  plots we determine the values of the parameters  $\mathscr{E}_0$  and  $\sigma_{\infty}$ . The values of these parameters for Ni–SiO<sub>2</sub> and Pt–SiO<sub>2</sub> are tabled in tables 1 and 2. Again, due to the wide range of resistivity and field values of our data, the ln  $\rho_{\rm H} = \mathscr{E}_0/\mathscr{E} + {\rm const.}$ behaviour is readily distinguished from the Poole–Frenkel effect ln  $\rho_{\rm H} \sim -\sqrt{\mathscr{E}}$ . We can also exclude the Fowler–Nordheim effect, which has a similar field dependence (Good and Muller 1956, Snow 1967) ln  $\rho_{\rm H} = \mathscr{E}^{\rm FN}/\mathscr{E} - \ln \mathscr{E} + {\rm const.}$ , because the constant  $\mathscr{E}^{\rm FN}$  is about 40–400 times larger than the values of  $\mathscr{E}_0$ in tables 1 and 2. Moreover, we find that  $\mathscr{E}_0$  varies appreciable with x while in the case of the Fowler–Nordheim effect the variation of  $\mathscr{E}^{\rm FN}$  with x is expected to be small<sup>†</sup>.

The field dependences of  $\rho_{\rm H}$  for two Ni–SiO<sub>2</sub> films at several temperatures are shown in figs. 29 and 30. As seen from the figures, with increasing field, ln  $\rho_{\rm H}$  at elevated temperatures asymptotically approaches the low temperature behaviour ln  $\rho_{\rm H} \sim 1/\mathscr{E}$ , the values of  $\mathscr{E}_0$  are independent of temperature, but as the temperature is increased, the intercepts ln  $\rho_{\infty}$  are shifted to lower values. As the field is decreased, ln  $\rho_{\rm H}$  deviates from the 1/ $\mathscr{E}$  behaviour and becomes less field-dependent. The solid curves are the theoretical fits



The high-field electrical resistivity  $\rho_{\rm H}$ , as a function of  $1/\mathscr{E}$ , for a Ni–SiO<sub>2</sub> sample measured at several temperatures with the electric field  $\mathscr{E}$  normal to the plane of the film. The volume fraction x of Ni, the thickness L and the temperatures T of the film are indicated in the figure. The points are experimental, the solid curves were computed from eqn. (30) with  $C_0$  and  $\sigma_{\infty}$  as adjustable parameters, g(s)=1, and the values of  $\mathscr{E}_0$  from table 1.

<sup>&</sup>lt;sup>†</sup> The variation of  $\mathscr{E}^{\text{FN}}$  with x is expected to result from the fact that for a given macroscopic field the value of the microscopic field in the insulator depends on the volume fraction of metal x. Therefore, if we use the value of the macroscopic field  $\mathscr{E}$  in the expression  $\log \rho \sim \mathscr{E}^{\text{FN}} |\mathscr{E}$ , then  $\mathscr{E}^{\text{FN}}$  is a function of x.



The high-field electrical resistivity  $\rho_{\rm H}$ , as a function of  $1/\mathscr{E}$ , for a Ni–SiO<sub>2</sub> sample measured at several temperatures with the electric field  $\mathscr{E}$  normal to the plane of the film. The volume fraction x of Ni, the thickness L, and the temperatures T of the film are indicated in the figure. The points are experimental, the solid curves were computed from eqn. (30) with  $C_0$  and  $\sigma_{\infty}$  as adjustable parameters, g(s)=1, and using the value of  $\mathscr{E}_0$  from table 1.

of eqn. (30) (with the function g set equal to 1) to the experimental data. The values of  $\mathscr{E}_0$  used in eqn. (30) were determined from the high-field, lowtemperature data (see fig. 28 and column 4 of tables 1 and 2),  $C_0$  and  $\sigma_{\infty}$  (0), used as adjustable parameters in eqn. (30), are tabulated in tables 1 and 2. The temperature dependence of  $\sigma_{\infty}(T)$  obtained from the fit will be used later to estimate the value of  $\delta$ , the average separation of electronic energy levels in a grain. The theoretical prediction that the values of  $C_0$  and C should agree, apart from a factor  $[(1 + (1/2\chi s_0)]$  which is close to unity, is borne out experimentally as is seen from tables 1 and 2.

The theory further predicts that the reduced resistivity  $\rho^* \equiv \rho_{\rm H}$  ( $\mathscr{E}, T$ )/  $\rho_{\infty}(T)$ , plotted as a function of reduced field  $\mathscr{E}^* \equiv \mathscr{E}/\mathscr{E}_0$ , and reduced temperature,  $T^* \equiv kT/C_0$  (or  $T^* = kT/C$ , since  $C_0 \simeq C$ ), is a universal function independent of the composition of the granular metals. To demonstrate the validity of this scaling behaviour we have measured the field dependences of granular metals with widely different compositions but at approximately the same reduced temperature and found that they indeed follow a single curve. This is seen in figs. 31 and 32. We note that the resistivities for films with similar  $T^*$  follow the same curve even though their compositions and measuring temperatures are widely different. The values of  $T^*$  obtained by fitting eqn. (31) to the experimental data is somewhat larger than the values of  $T^*$  obtained from low-field measurements.

The quantities  $C_0$  and  $\mathscr{E}_0$  are related through the simple relationship given by eqn. (27), and the parameter w, as stated earlier, is of the order  $w \simeq s_0 + d_0$ . The fact that the values of w computed from  $w = C_0/\mathscr{e}_0$  (column 9 in tables 1 and 2) are in order of magnitude agreement with those determined from



Reduced resistivity  $\rho_{\rm H}/\rho_{\infty}(T)$ , as a function of reduced field  $\mathscr{E}^* = \mathscr{E}/\mathscr{E}_0$  and reduced temperature  $T^*$ , for several Ni–SiO<sub>2</sub> and Pt–SiO<sub>2</sub> samples, measured with the electric field  $\mathscr{E}$  normal to the plane of the films. The volume fraction of the metal x, the temperature T and reduced temperature  $T^* = kT/C$  of the samples are indicated in the legend. The points are experimental, the solid curves were computed from eqn. (31) for the values of  $T^* = kT/C_0$  indicated next to each curve.

electron micrographs (column 10 in tables 1 and 2) is a further verification of the model. The parameter w can also be deduced from the value of the field at which the conductivity goes from the ohmic (low-field) to the non-ohmic (high-field) behaviour. This is expected to occur when  $e\Delta V \equiv e\mathscr{E}w = kT$  (see § 4.1). In fig. 33 is plotted the resistivity  $\rho(\mathscr{E}, T)$  at constant temperature, normalized by the zero-field resistivity  $\rho(0, T)$ , as a function of the field  $\mathscr{E}$ , normalized in the form  $e\mathscr{E}w/kT (\equiv \mathscr{E}^*/T^*)$ . It can be seen that over a wide range of compositions and reduced temperatures the transition from the lowfield, ohmic behaviour to the non-ohmic, high-field behaviour occurs at a field for which  $e\mathscr{E}w/kT = 1$ , at which point  $\rho(\mathscr{E}, T)/\rho(0, T) \simeq \frac{1}{2}$ . Thus, the microscopic granular metal structural constant w can be deduced from macroscopic measurements of temperature and field dependence of the electrical conductivity.

The structural constant C defined by eqn. (13) depends only on the composition x and the insulator dielectric constant  $\epsilon$  of granular metals. Thus, in a granular metal for a definite value of x the constant C is expected to be independent of grain size, and the constituent metal and insulator will affect the value of C only insofar as the tunnelling barrier height is affected. This invariance of C with respect to grain size has been demonstrated experimentally in the W-Al<sub>2</sub>O<sub>3</sub> system. In those experiments it was found that on annealing with W-Al<sub>2</sub>O<sub>3</sub> samples at 1100 K for 150 hours the values of  $d_0$ 



Reduced resistivity  $\rho_{\rm H}/\rho_{\infty}(T)$ , as a function of reduced field  $\mathscr{E}^* = \mathscr{E}/\mathscr{E}_0$  are reduced temperature  $T^*$  for several Ni–SiO<sub>2</sub> and Pt–SiO<sub>2</sub> samples, measured with the electric field  $\mathscr{E}$  normal to the plane of the films. The volume fraction of the metal x, the temperature T and reduced temperatures  $T^* = kT/C$  of the samples are indicated in the legend. Solid curves were computed from eqn. (31) for the values of  $T^* = kT/C_0$  indicated next to each curve.



Fig. 33

Normalized  $\rho(\mathscr{E}, T)/\rho(0, T)$ , as a function of electric field  $\mathscr{E}$  (normalized by kT/ew), for several Pt-SiO<sub>2</sub> samples, measured with  $\mathscr{E}$  normal to the plane of the film. The volume fraction x of Pt, the temperature and the reduced temperatures  $T^* = kT/C$  of the samples are indicated in the figure.

increased by a factor 2 to 5 depending on the composition x. At the same time, the resistivities in the dielectric regime were found to increase by several orders of magnitude, yet the values of C remained unchanged. Large variations in the resistivities of granular metals in the dielectric regime with small or no variation in C has also been observed to occur due to differences in sputtering conditions (see § 2.1). Thus, C is a useful materials characterization parameter because, unlike the resistivity, it is insensitive to the grain size and the method of preparation. In fig. 34 we have plotted C as a function of x for several granular metal systems. With the exception of the Ni-SiO<sub>2</sub>, we note that C(x) is insensitive to the constituent metals and insulators. In the case of Ni-SiO<sub>2</sub> the displacement of the C(x) curve to higher values of x may be due to the presence of NiO in the films (see § 2.3).



Fig. 34

The parameter C, as a function of volume fraction of the metal x, for Ni-SiO<sub>2</sub>, Pt-SiO<sub>2</sub>, Au-Al<sub>2</sub>O<sub>3</sub> (tables 1-3) and W-Al<sub>2</sub>O<sub>3</sub> (Abeles *et al.* 1975). The points are experimental, the solid curve was computed from eqns. (33) and (34) for  $\eta = 1 \text{ eV}$ .

The theoretical expression for C(x) was calculated assuming a model in which the granular metal is replaced by a simple cubic lattice of metal spheres of constant diameter d with a lattice constant s+d. The expression for C, the derivation of which is given in Appendix A, is

$$C = \eta \, \frac{(s/d)^2}{(\frac{1}{2} + (s/d))},\tag{33}$$

where

$$s/d = (\pi/6x)^{1/3} - 1,$$
 (34)

$$\eta = 2\chi e^2/\epsilon, \tag{35}$$

and  $\epsilon$  is the dielectric constant of the insulator. The solid curve in fig. 34 represents the best fit of eqns. (33) and (34) with a value of  $\eta = 1 \text{ eV}$ . We can calculate a theoretical value of  $\eta$  from eqn. (35). For instance, using for  $\chi$  and  $\epsilon$  the values corresponding to bulk SiO<sub>2</sub> (Sheng and Abeles 1972, Goodman 1966)  $\uparrow \chi = 1$  Å<sup>-1</sup> and  $\epsilon = 3.8$ , we obtain  $\eta \simeq 7.5$  eV, which is an order of magnitude larger than the experimental value. The reason for this discrepancy may lie in the fact that in the granular metal the insulator may have a smaller value of  $\chi$  and a larger dielectric constant  $\epsilon$ . Furthermore, the representation of irregularly shaped metal particles by metal spheres is a gross over-simplification. Since tunnelling naturally selects the minimum separation between two grains, the effective tunnelling barrier thickness could be appreciably smaller than the average separation between the grains if the metal particles have sharp protrusions. We take such an effect into account by defining an effective tunnelling barrier thickness  $s_t = \alpha s$  with  $\alpha < 1$ , so that  $C = \chi s_t E_c^0$ . In the expression for  $E_c^0$ , eqn. (A 2), we continue to use for s the average separation between the grains, since the sharp protrusions do not significantly affect the total electrostatic field energy in the insulator. Therefore, the expression for C is given by eqn. (33), with  $\eta =$  $2\alpha\chi e^2/\epsilon$ . The experimental value of  $\eta = 1 \text{ eV}$  can be achieved by setting for instance,  $\alpha = 0.5$ ,  $\chi = 0.5$  Å<sup>-1</sup>, and  $\epsilon = 7$ . Such values are not unreasonable.

Fig. 35



Temperature dependence of  $\sigma_{\infty}$  plotted as a function of T.

<sup>†</sup> We are using the low-frequency value of  $\epsilon = 3.8$  (Handbook of Chemistry and Physics (Cleveland : The Chemical Rubber Co.), p. E-67).

However, further experimental work is required for a more direct determination of  $\chi$  and  $\epsilon$ .

From the measured temperature dependence of  $\rho_{\infty}(T)$  information can be obtained on the finite energy level separation  $\delta$  within a grain due to quantization of electronic motion. In fig. 35 is plotted  $\sigma_{\infty}(T)/\sigma_{\infty}(0)$  versus T for a Ni–SiO<sub>2</sub> film. We note that  $\sigma_{\infty}(T)/\sigma_{\infty}(0)$  saturates at high temperatures. If we take 40 K as the point at which  $kT \simeq \delta$  (see § 4.1), we obtain the value  $\delta \simeq 4$  meV. Using the values (Campbell 1970)  $E_{\rm F} \simeq 7$  eV, n = $8 \cdot 8 \times 10^{22}$  cm<sup>-3</sup> corresponding to Ni, and the values of  $\delta$  given above, we get from eqn. (32)  $d_0 \simeq 40$  Å in reasonable agreement with the value of  $d_0 = 25$  Å in fig. 17 for x = 0.24.

#### § 5. SUMMARY AND DISCUSSION

In order to facilitate the summary of our present work, we present in table 4 all the main theoretical and experimental results of this paper. To emphasize the inter-relationship between the different physical effects and the structure of granular metals, we have included in table 4 also some of the other physical phenomena in granular metals (Abeles 1976).

We would now like to make a few specific remarks regarding the experimental observations by other workers on the electrical properties of granular metals. In comparing the results of various research groups on the temperature dependence of the resistivity of granular metals, care must be taken to distinguish the regimes in which the data were taken. In the transition regime the temperature dependence deviates from the dielectric regime behaviour  $\ln \rho_{\rm L} \sim 1/\sqrt{T}$ , because in addition to the thermally activated tunnelling, classical percolation conduction also contributes to the electrical current. Examples of the temperature dependences of  $\rho_L$  in the transition regime are Au-Al<sub>2</sub>O<sub>3</sub> with x = 0.41 in fig. 27, Gittleman et al. (1972) and Abeles and Sheng (1974) for Ni-SiO<sub>2</sub> films, Devenyi et al. (1972) for Nb-Al<sub>2</sub>O<sub>3</sub> films, and Hauser (1973) for Al-Al<sub>2</sub>O<sub>3</sub>, Sn-SnO<sub>2</sub>, and Ni-NiO films. In the dielectric regime, the results presented in this paper, as well as those published by other workers (Hauser 1973, Zeller 1972), show that granular metals are well characterized by the temperature dependence of  $\ln \rho_{\rm L} \sim 1/\sqrt{T}$ . Some previous workers have plotted  $\ln \rho_{\rm L}$  versus 1/T in order to extract a single activation energy  $E_c$ . However, closer inspection shows that either a better fit to the data (Miller et al. 1970, Miller and Shirn 1967, Shashital and Parker 1971, Pollard et al. 1969) can be obtained with  $\ln \rho_{\rm L} \sim 1/\sqrt{T}$  or the temperature range of measurement was too small to distinguish from the  $1/\sqrt{T}$  behaviour (Fuschillo and McMaster 1971). Although the  $\ln \rho_{\rm L} \sim 1/\sqrt{T}$  behaviour is expected to be valid for most granular metals in the dielectric regime, it does not follow that the low-temperature field dependence of  $\rho_{\rm H}$  cannot deviate from the  $\ln \rho_{\rm H} \sim 1/\mathscr{E}$  behaviour observed in this work. Such a deviation can occur when thermally activated emission over the barrier (Poole-Frenkel effect) is more probable than tunnelling through the barrier (field-induced generation of charge carriers). In our materials the barrier height is sufficiently high so that the tunnelling always dominates.

There are a number of questions regarding the electrical transport properties of granular metals that require further investigation. In the dielectric regime

the electron-hole pairs have a finite lifetime and recombination length l. Such a finite recombination length l should manifest itself in the measurement of field-dependent conductivity when the thickness of the sample is made comparable or less than l. In the present work the experimental results indicate that in all our samples the condition l < L pertained. Another phenomenon is that of trapping of charge carriers, which we believe is responsible for interesting polarization effects; observed at high fields and low temperatures. The observed effect is a slowly decaying small residual electric field of opposite polarity to the applied field after the external field Such an effect could be due to the trapping of charge carriers is removed. on large particles surrounded by smaller particles. Another interesting effect is field breakdown. At sufficiently high fields, when the voltage drop  $\Delta V$ between particles becomes comparable to  $\phi/e$ , where  $\phi$  is the height of the tunnelling barrier, the Fowler-Nordheim effect is expected to become dominant. In that case the electrons tunnel through a triangular barrier directly into the conduction band of the insulator. The field dependence of  $\rho_{\rm H}$  in this new regime is still expected to be of the form  $\ln \rho_{\rm H} \sim 1/\mathscr{E}$ ; however, the proportionality constant given by the Fowler-Nordheim theory is expected to be one or two orders of magnitude larger than the  $\mathscr{E}_0$  (see § 4.2) due to fieldinduced tunnelling between grains. We have made preliminary observation of switching phenomenon at high fields which we believe can be ascribed to the onset of Fowler-Nordheim tunnelling. The a.c. conductivity is another area where more experimental and theoretical studies are required. Our preliminary results indicate that in the dielectric regime, a.c. conductivity (at 100 MHz)  $\sigma_{a,c} \sim \omega^2$  (where  $\omega$  is the frequency) and that the dielectric constant is an increasing function of x, becoming very large (~100) near the percolation threshold. Granular metals represent an interesting physical system for studying percolation conductivity (Abeles et al. 1975). So far. most of the work in this field was restricted to computer experiments (Kirkpatrick 1973) and to simplified systems such as conducting papers peppered with holes (Last and Thouless 1971), grid of carbon resistors (Adler et al. 1973), and two-dimensional mesh screens with sites removed (Watson and Leath 1974). Further work on granular metal should provide valuable information on the conductivity threshold behaviour in three-dimensional systems. Granular metals also provide an interesting system for studying noise phenomena. Noise is expected to arise from a contribution due to the fluctuation of charge carrier density and a contribution due to the tunnelling From the temperature dependence of the noise one should be able process. to distinguish the two types of noise. Finally, a problem of considerable theoretical interest is the transition of a granular metal characterized by a finite metal particle size to an amorphous material consisting of a random dispersion of insulator molecules and metal atoms. Such an 'amorphous metal', which one might be able to produce by cryogenic deposition, is expected to have drastically different properties from the granular metal. Whereas the transition from the metallic to the dielectric regimes in granular metals is due to the breaking up of the metal continuum into isolated metal particles, the corresponding transition in the amorphous metal is likely to be

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Table 4.

Structural	Me	tallic
Phenomena	Observation	Mechanism, theory
Structure	Isolated insulator particles in metal continuum $0.5 \lesssim x < 1$	
Electrical transport, d.c.	$ ho \lesssim 10^{-2} \ \Omega \ { m cm}$	Increased conduction path length; effective medium theory
	TCR > 0	Thermally activated tunnelling negligible
A.C. conductivity 1 kHz–100 MHz	Increased skin depth	Decreased effective mean free path
Seebeck coefficient	Metallic, independent of $x$	See beck coefficient not affected by the dielectric particles $\ensuremath{^{2}}$
Superconductivity	Enhanced $T_{\rm c}$ (I)	Lattice softening ? (Garland et al. 1968, Klein and Lever 1968)
	Large penetration depth (Cohen and Abeles	
	Short coherence distance (Cohen and Abeles 1967) $\sim 1/\sqrt{\rho}$ High critical magnetic field (Cohen and Abeles	Dirty type II superconductor (Cohen and Abeles 1967)
	I967) Broadening of resistive transition (II)	Thermodynamic fluctuation (III)
	Gap parameter $\Delta$ finite at $T_{ m e}\left({ m IV} ight)$	Fluctuation effect (IV)
Ferromagnetism	Gradual decrease of $T_{\rm o}$ with decreasing $x$ (Rayl <i>et al.</i> 1971, Gittleman <i>et al.</i> 1972)	
Specific heat	Decrease of Debye temperature (V)	Lattice softening $?$
Sound velocity	No change (VI)	Absence of lattice softening ?
Optical	Increase in optical transmission in the infra-red (Cohen <i>et al.</i> 1973) Plasma frequency unchanged (Cohen <i>et al.</i> 1973)	Maxwell-Garnett theory (Cohen <i>et al.</i> 1973)

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Table 4 (Continued)

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nsition	Mechanism, theory		Percolation threshold, effect medium theory	Transition from classical percolation to thermally activated tunnelling	Percolation threshold	Percolation threshold
Tra	Observation	Maze. $0.4 \lesssim x \lesssim 0.5$	Resistivity edge	TCR changes sign	Disappearance of bulk superconductivity (Abeles $et al.$ 1971, Hauser 1970)	Disappearance of bulk ferromagnetism (Rayl et al. 1971, Gittleman et al. 1972)
Structural	Phenomena	Structure	Electrical transport, d.c.		Superconductivity	Ferromagnetism

# Properties of granular metal films

Continued-
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Table

Structural	Diel	lectric
	Observation	Mechanism, theory
	Isolated metal particles in insulator continuum $x \lesssim 0.4$	
.c.	TCR < 0	Thermally activated tunnelling with charging
	$\ln \left[\rho(0, T)/\rho_0\right] = 2\sqrt{(C/kT)}$	$\sum_{X^3} E_o^{\text{energy}} = C(x)$
	<i>C</i> independent of grain size and constituent metals and insulators $\ln \left[\rho(\mathscr{E}, 0)   \rho_{\infty}\right] = \mathscr{E}_0   \mathscr{E}$	Composition uniformity on the scale of surface diffusion length. $s/d$ ratio only a function of $x$ Field-induced charge carrier general $(e\Delta V \ge E_c)$
	Transition of $\rho$ from ohmic to non-ohmic behaviour occurs at $\mathscr{C} = kT   ew$ where	with the control $\chi^{s} \mathcal{D}_{0} = \mathcal{O}_{0}   e \mathcal{E}_{0}$
	$w \approx s_0 + a_0$ Scaling ; $\rho^*(\mathscr{E}^*, T^*)$ a universal function	$\int \chi_S E_{\rm e}^0 = C$
	$\left.\begin{array}{l} \text{with}\\ \mathscr{C}^* = \mathscr{C}   \mathscr{C}_0\\ T^* = kT   C\\ \rho^* = \rho(\mathscr{C}, T)   \rho_{\infty}\end{array}\right\}$	$\left\{\rho^{*} = \exp\left[\frac{-1}{\delta^{*}}\right] \int_{-1/\delta^{*}}^{\infty} \frac{Z \exp\left(-Z\right) dZ}{1 - \exp\left(-\frac{Z}{Z + (Z/\delta^{*})} \frac{\delta^{*}}{T^{*}}\right)}\right]$
	$C \simeq C_0$	$C_0 = C\left(1 + \frac{1}{2\chi s_0}\right)$
	$C = C(x)$ with $\eta = 1 eV$	$\begin{cases} C(x) = \eta \frac{[(\pi/6x)^{1/3} - 1]^2}{[(\pi/6x)^{1/3} - \frac{1}{2}]} \\ \eta = 2\chi \alpha e^2/\epsilon \end{cases}$
	$ ho_{\infty} =  ho_{\infty}(T)$	Quantization of electronic energy levels inside each metal particle, phonon-assisted tunnelling
	Dielectric constant $\simeq 10$	
	$\rho(\omega) \sim \omega^{-2}$ at 100 MHz $\int$	ELLECTIVE IDECTURE TREATED THE WED-GARTIEL THEORY :
	Critical particle size for the existence of superconductivity (Zeller and Giaever 1969)	Thermodynamic fluctuations (Parmenter 1968, Mühlschlegel <i>et al.</i> 1972)

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Ferromagnetism	$T_{\rm o}$ for the paramagnetic-superparamagnetic transition as seen by $1/\chi$ versus $T$ plots is broadened (Gittleman et al. 1974)	Fluctuations due to finite sized particles (VIII)
	For $T_{\rm c} > T >$ blocking temperature $T_{\rm B}$ the $1/\chi$ versus $T$ plots have finite slopes of the order ~ 1000 times small than the high-temperature marameter $1/\chi$ versus $T$	Superparamagnetism (Gittleman <i>et al.</i> 1974)
	slope (Gittleman <i>et al.</i> 1974) $\chi$ decreases with temperature for $T < T_{\rm B}$ (Gittleman <i>et al.</i> 1974)	Blocking due to anisotropy energy barrier $(Gittleman \ et \ al. \ 1974)$
Specific heat	Increase of low temperature lattice specific heat (VII)	Existence of surface phonons (V)
	Decrease of lattice specific heat at very low temperatures (VII)	Granular size effects
		Theory of Kubo (1962, 1969), Denton <i>et al.</i> 1973). For $kT < electronic energy levelseparation \delta, specific heat \sim T^n wheren=1, 2, 3$ , or 5
Pauli paramagnetism		Theory of Kubo (1962, 1969, Denton <i>et al.</i> 1973). For $kT < \text{electronic energy level}$ separation $\delta$ , $1/\chi \sim T^n$ where $n = -1$ , 0, 1, or 4
Optical	Absorption peak appears at the optical and higher frequencies (Cohen <i>et al.</i> 1973) Plasma frequency shifted down $(IX)$	Dielectric anomaly, Maxwell-Gamett theory Maxwell-Gamett theory (IX)
(I) Enhancement of 1 (II) Strongin, M., Kan Cohon, P. W. 200	$T_e$ only in some superconductors, see Cohen and Abel nmerer, O. F., Crow, J., Thompson, R. S., and Fine, H T. 1, 1, 100, DL, 1, 1, 0, 0, 70	es (1967). H. L., 1968, <i>Phys. Rev. Lett.</i> , <b>20,</b> 922. Gittleman, J. I.,

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a microscopic electronic transition. Further research in this area is expected to play an important role in the understanding of metal-non-metal transition.

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# APPENDIX A

In this Appendix we derive approximate expressions for the charging energy  $E_c$  (Miller *et al.* 1970, Miller and Shirn 1967, Neugebauer and Webb 1962, Neugebauer 1970, Hill 1969) and an expression for C(x). Consider a cluster of neutral metal particles, schematically shown in fig. 36 (a). In order to remove an electron from the central grain to infinity, a certain amount of energy is required. That energy is equivalent to the total energy





For the purpose of calculating the charging energy  $E_c$ , the geometry in (a) is approximated by that of (b).

stored in the electrostatic field of a positively charged metal grain. In order to calculate this electrostatic field energy  $E_{\rm es}$ , we assume that most of the energy is stored in the space between the central metal particle and its nearest neighbours. For simplicity we replace the geometry of fig. 36 (a) by that of fig. 36 (b). Then by elementary electrostatic theory

$$E_{\rm es} = \frac{1}{8\pi} \epsilon \int_{d/2}^{d+2s/2} \left(\frac{e^2}{\epsilon^2 r^4}\right) 4\pi r^2 dr$$
$$= \frac{e^{2s}}{\epsilon d \left(\frac{d}{2} + s\right)},$$
(A 1)

where  $\epsilon$  is the dielectric constant of the insulator. In the case of charge carrier generation, a pair of negatively and positively charged metal particles

are created. If we neglect the interaction energy between the pair, the charging energy is given by

$$E_{\rm c}^{\ 0} = 2E_{\rm es} = \frac{e^2}{d} \left[ \frac{2(s/d)}{\epsilon \left(\frac{1}{2} + \frac{s}{d}\right)} \right].$$
 (A 2)

From eqn. (13) it follows that

$$C = \chi e E_{c}^{0} = \frac{4\chi e^{2}}{\epsilon} \frac{(s/d)^{2}}{\left(\frac{1}{2} + \frac{s}{d}\right)}.$$
 (A 3)

If we write  $E_c^0 = 2e^2/Kd$ , where K is defined as effect dielectric constant of the granular metal, then from eqn. (A 2) it follows that  $K = \epsilon [1 + (d/2s)]$ .

In order to relate the ratio s/d to the composition x, we will approximate the granular metal in the dielectric regime by a simple cubic lattice of metal spheres with lattice constant s+d and metal sphere diameter d. The volume fraction of metal x is then given by

$$x = \frac{\frac{\pi}{6}}{\left(1 + \frac{s}{d}\right)^3}.$$
 (A 4)

In other words,

$$\frac{s}{d} = \left(\frac{\pi}{6x}\right)^{1/3} - 1. \tag{A 5}$$

Therefore, substitution of eqn. (A 5) in eqn. (A 3) yields

$$C(x) = \frac{2\chi e^2}{\epsilon} \frac{[(\pi/6x)^{1/3} - 1]^2}{[(\pi/6x)^{1/3} - \frac{1}{2}]}.$$
 (A 6)

In order to estimate the energy  $E_c^1$  required to generate a pair of neighbouring, positively and negatively charged grains, we consider the model of two equal metal spheres of diameter d in an effective medium with dielectric constant  $K = \epsilon [1 + (d/2s)]$ . If the separation between the centres of the two spheres is d+s, elementary electrostatics theory gives

$$E_{\rm c}^{1} = \frac{2e^2}{Kd} \left( \sinh \alpha \sum_{n=1}^{\infty} \operatorname{csch} n\alpha \right)^{-1} \tag{A 7}$$

with

$$\alpha = \cosh^{-1}\left(\frac{d+s}{d}\right). \tag{A 8}$$

When we substitute eqn. (A 5) for s/d in eqns. (A 7) and (A 8), we get an equation for  $E_c^1$  as a function of x. This is shown in fig. 37. It is obvious from the graph that over a wide range of composition,  $E_c^1 \simeq E_c^0/2$ .



Variation of  $E_{\rm e}{}^1/E_{\rm c}{}^0$  with composition.

# APPENDIX B

In this Appendix we estimate the magnitude of the geometric factor  $\gamma$ . As defined in § 4.1, the geometric factor takes into account the effect of the non-planar tunnelling barrier. An approximation to the value of  $\gamma$  can be obtained by calculating, in the transfer Hamiltonian formalism, the ratio of the tunnelling matrix elements squared for the two cases shown in fig. 38.

The matrix element in the Bardeen formalism can be written as (Bardeen 1961, Duke 1969)  $-(\hbar^2/2m)\int (\psi_{\rm L}\nabla\psi_{\rm R}-\psi_{\rm R}\nabla\psi_{\rm L}) \cdot d\mathbf{S}$ , where  $\psi_{\rm L}(\psi_{\rm R})$  is the wavefunction of the electron when it is at left (right) side of an imaginary surface  $\mathscr{S}$ , between the two grains, shown as dashed line in fig. 38, and  $d\mathbf{S}$  is the surface element of the surface  $\mathscr{S}$  with unit vector perpendicular to the surface.

Fig. 38



Geometries used in estimating the geometric factor  $\gamma$ .

For case (a), we take the wavefunction of a spherically symmetric state

$$\psi(r) = \frac{1}{\sqrt{(4\pi)}} \frac{1}{q} \frac{1}{r} \begin{cases} \sin (kr)/\sin (kd/2), & r < d/2 \\ \\ \exp (-\chi)(r-d/2), & r > d/2 \end{cases}$$
(B 1)

where r is the distance from the centre of one spherical grain,

and

$$q = \left[\frac{1}{2\chi} \left(\frac{\chi d}{2} \frac{\phi}{E} + \frac{\phi - E}{E} + 1\right)\right]^{1/2}$$

 $k = (2mE/\hbar^2)^{1/2}$ .

is the normalization constant. The matrix element is therefore

$$|M_1| \simeq \frac{\hbar^2 \chi^2}{2m} \exp((-\chi s)) \frac{2}{\left(\chi \frac{d}{2} \frac{\phi}{E} + \frac{\phi - E}{E} + 1\right)} \frac{1}{\chi(d+s)},$$
 (B 2)

where we have assumed  $\chi(d+s) \gg 1$ , which is true in our case.

For case (b), we note that the wavefunction can be written in the form  $\psi(x)\psi(y)\psi(z)$ , and the matrix element becomes

$$|M_{2}| \simeq -\frac{\hbar^{2}}{2m} \left[ \psi_{\mathrm{L}}(x) \frac{\partial}{\partial x} \psi_{\mathrm{R}}(x) - \psi_{\mathrm{R}}(x) \frac{\partial}{\partial x} \psi_{\mathrm{L}}(x) \right] \int \int dy \, dz |\psi(y)|^{2} |\psi(z)|^{2} = -\frac{\hbar^{2}}{2m} \left[ \psi_{\mathrm{L}}(x) \frac{\partial}{\partial x} \psi_{\mathrm{R}}(x) - \psi_{\mathrm{R}}(x) \frac{\partial}{\partial x} \psi_{\mathrm{L}}(x) \right], \tag{B 3}$$

where x is the direction along the line joining the centres of the two grains.

For  $\psi(x)$  we choose

$$\psi(x) = \frac{\sqrt{2}}{q} \begin{cases} \cos(kx)/\cos[k(d/2)] & |x| < d/2 \\ \\ \exp\{-\chi[x - (d/2)]\} & |x| > d/2 \end{cases}$$
(B 4)

where x=0 is the centre of the grain and q and k are defined as before. The matrix element in this case is

$$|M_{2}| = \frac{\hbar^{2} \chi^{2}}{2m} \exp((-\chi s) \frac{2}{\left(\chi \frac{d}{2} \frac{\phi}{E} + \frac{\phi - E}{E} + 1\right)}.$$
 (B 5)

By assuming  $\phi$  and E in cases (a) and (b) to be the same, we get estimates of the geometric factor:  $\gamma \simeq |M_1|^2 / |M_2|^2 = 1/[\chi(d+s)]^2$ . From this form of  $\gamma$  we can get a theoretical estimate of the recombination length l using eqn. (26):

$$l = \frac{hw^2(2\chi s_0 + 1)^2 \sigma_{\infty}}{e^2 \gamma}$$
  
=  $\frac{h\chi^2 w^4(2\chi s_0 + 1)^2 \sigma_{\infty}}{e^2}$ . (B 6)

Using the values of  $\sigma_{\infty} = 7 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ ,  $\chi = 1 \text{ Å}^{-1}$ ,  $s_0 = 10 \text{ Å}$ , and w = 30 Å (sample 24, table 2), we get  $l \simeq 200 \text{ Å}$ .

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