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The temperature and volume fraction dependence of the resistivity of granular Al–Ge near the percolation threshold

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Abstract. Extensive measurements of the temperature and of the Al volume fraction dependence of the resistivity of granular Al–Ge have been made near the percolation threshold ϕ_c. The results at 295 K are analysed using the percolation equations, as modified by Efros and Shklovskii, and by Straley, for systems where the two components have finite conductivity ratios, and by fitting the results to the general effective media (GEM) equation, which also takes into account the finite conductivities of both components. The parameters of these equations are the conductivities (resistivities) of the two components, the critical conductivity exponents s and t, and the critical (percolation) volume fraction ϕ_c. The experimental value of ϕ_c, obtained from resistivity and magnetoresistivity measurements at and below the superconducting transition temperature for Al, agrees remarkably well with the values obtained from the percolation and GEM equations. The observed exponents are found to be high, and the width of the critical region surprisingly large. Attempts to extend this type of analysis to lower temperatures proved unsuccessful, and it is concluded that the resistivity of the more insulating component, namely of the amorphous Al-doped Ge, depends on the total Al content of the sample. It is shown that ϕ_c cannot be identified from the resistivity versus temperature curves between 5 and 295 K, nor from temperature derivatives of these curves. Graphs of the resistivity versus temperature of the amorphous Al-doped Ge for individual samples are extracted using the GEM equation.

1. Introduction

The electrical conductivity of inhomogeneous media such as granular composites has a long and interesting history, which has been thoroughly reviewed by Landauer (1978), who covers two basic theoretical approaches to this problem, namely effective media and percolation theories. Effective media and percolation theories, as well as the more phenomenological mixing rule approaches, are briefly reviewed by McLachlan *et al* (1990), and excellent introductions to percolation theory are given by Zallen (1983) and Stauffer (1985). Wide-ranging reviews on percolation and related phenomena are also given in a recent book by Deutscher *et al* (1983b).

The concentration range where the percolation equations describe the conductivity in a particular system is known as the critical region. This region is not predicted theoretically, but in practice extends for some range of concentration ϕ on either side of the critical concentration ϕ_c. Continuum (lattice) percolation theory is only strictly valid if one component (bond or site) is a perfect conductor or a perfect insulator. Efros and Shklovskii (1976), as well as Straley (1976, 1983), have investigated this limitation theoretically and

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have derived an approximate expression for the conductivity at ϕ_c. They also defined a crossover region, $\Delta\phi$, which is a range in volume concentration ϕ of the good conductor immediately on either side of the percolation threshold ϕ_c, inside which the percolation equations do not hold, due to the finite ratio of the two conductivities. The percolation equations can therefore be expected to only be valid for compositions where ϕ lies outside the crossover region but still within the critical regions.

Granular Al–Ge, in the form of thin films, was selected for these experiments as it has already been extensively studied (see the review by Deutscher *et al* (1983a)) and could be prepared in a set of quasi-continuous compositions. The distinction between random and granular Al–Ge composite films has been previously elaborated by Deutscher *et al* (1983a).

This paper presents the most detailed analysis yet made of the resistivity of the Al–Ge continuum system, near ϕ_c, over a wide range of temperatures, and hence over a wide range of resistivity ratios of the two components. One objective of the paper is to examine the range of concentrations over which the percolation equations apply to this system. Another objective is to see how well the general effective media (GEM) (McLachlan 1987a, McLachlan *et al* 1990) equation can model the results, and to compare the values of ϕ_c and the exponents obtained with those derived from the percolation equations. The GEM equation has already been used to describe the electrical conductivity (resistivity) of a large number of systems (McLachlan 1986a, 1987a, 1988, 1990, Deprez *et al* 1988, McLachlan *et al* 1990), including the Al–Ge system (McLachlan 1987b), over broad ranges of concentration on either side of ϕ_c.

A further objective was to examine the temperature dependence of the resistivity, at and close to ϕ_c, over a wide range of temperatures. Unfortunately, as the experimental ρ versus T curves between 295 K and 5 K showed no abrupt change in their characteristic shape with ϕ near ϕ_c, these results could not be used to directly identify the critical concentration ϕ_c. Therefore resistivity and magnetoresistivity measurements were made close to the superconducting transition temperature of the Al grains to identify ϕ_c directly. The value of ϕ_c obtained in this way was found to agree remarkably well with the values obtained from the analysis of the 295 K resistivity data, using both the percolation and GEM equations.

2. Theory

The percolation equations for the electrical conductivity and resistivity are, for $\phi \geqslant \phi_c$ and $\sigma(\text{lo}) = 0$

$$\sigma(\text{m}) = \sigma(\text{hi})(1 - f/f_c)^t = \sigma(\text{hi})[(\phi - \phi_c)/(1 - \phi_c)]^t \tag{1a}$$

while for $\phi \leqslant \phi_c$ and $\rho(\text{lo}) = 0$

$$\rho(\text{m}) = \rho(\text{hi})(1 - \phi/\phi_c)^s. \tag{1b}$$

In equation (1*a*), $\sigma(\text{m})$ is the electrical conductivity of the system (medium in the case of a continuum percolation system), $\sigma(\text{hi}) = 1/\rho(\text{lo})$ is the conductivity of the more highly conducting component, $f = 1 - \phi$ is the volume fraction of perfect insulator (fraction of perfectly insulating sites or bonds), $f_c = 1 - \phi_c$, and t is the exponent. In equation (1*b*), $\rho(\text{m})$ is the resistivity of the system or medium, $\rho(\text{hi}) = 1/\sigma(\text{lo})$ is the resistivity of the more resistive (but finite conductivity) component, and ϕ is the volume fraction of the perfectly conducting component (the fraction of perfectly conducting sites or bonds). ϕ_c is

the volume fraction where the perfectly conducting component becomes continuous and s is an exponent.

From these equations, Efros and Shklovskii (1976) and Straley (1976) derive the following expressions:

$$|\Delta\phi| = |\Delta f| = [\sigma(\text{lo})/\sigma(\text{hi})]^{1/(t+s)} = [\rho(\text{lo})/\rho(\text{hi})]^{1/(t+s)} \tag{2}$$

as a definition of the crossover region and

$$\sigma(\phi_c) \simeq \sigma(\text{lo})^{t/(t+s)}\sigma(\text{hi})^{s/(t+s)} \tag{3}$$

as an estimate of the conductivity at the critical volume fraction ϕ_c.

The GEM equation (McLachlan 1987a) written in terms of the electrical conductivity and the volume fraction f of the low-conductivity component $\sigma(\text{lo})$ is

$$f[\sigma(\text{lo})^{1/t} - \sigma(\text{m})^{1/t}]/\{\sigma(\text{lo})^{1/t} + [f_c/(1-f_c)]\sigma(\text{m})^{1/t}\} + (1-f)[\sigma(\text{hi})^{1/t} - \sigma(\text{m})^{1/t}]/\{\sigma(\text{hi})^{1/t} + [f_c/(1-f_c)]\sigma(\text{m})^{1/t}\} = 0 \tag{4}$$

where all the symbols have been previously defined. Equation (4) is an empirical interpolation between Bruggeman's symmetric and asymmetric (conductor surrounding insulator and *vice versa*) media theories and reduces to these in the appropriate limits (McLachlan 1987a, McLachlan *et al* 1990). The GEM equation can also be viewed as a matched asymptotic expression (McLachlan *et al* 1990) between the two percolation equations, as when $\sigma(\text{lo}) = 0$, the GEM equation reduces to equation (1*a*) and when $\sigma(\text{hi}) = \infty$ or equivalently $\rho(\text{lo}) = 0$, it reduces to equation (1*b*), if t in equation (4) is replaced by s. For this reason one may suppose some correspondence between the parameters $\phi_c(f_c)$ and $t(s)$ which appear in equations (1*a*,*b*) and equation (4). However, as equation (4) is phenomenological, this correspondence would have to be determined experimentally.

Percolation on lattices is a strict connectivity problem, with universal values for the exponents. However, in a continuum t and s need not have values which are universal (Halprin *et al* 1985). McLachlan (1987a) has postulated a connection between the shape of the grains of the two components and the exponent t, while Balberg (1987) has postulated that unusually high values of the exponents are to be expected in composites when tunnelling between the grains of the conducting component occurs.

The exact value of the conductivity at the critical volume concentration can be calculated from the GEM equation (4) and this value substituted into equations (1*a*) and (1*b*) to obtain the equivalent of the crossover region. In the limit that $\sigma(\text{hi}) \gg \sigma(\text{lo})$ and for ϕ_c not too far from 0.5, one obtains from equation (4) that

$$\sigma(\phi_c) = [\sigma(\text{hi})\sigma(\text{lo})/A^t]^{1/2} \tag{5}$$

where $A = (1-\phi_c)/\phi_c$ or $f_c/(1-f_c)$.

The crossover region can now be defined as the difference in ϕ (or f) between the values of ϕ (or f) obtained in equations (1*a*) and (1*b*) when σ (or ρ) $= \sigma(\phi_c)$ (or $\rho(\phi_c) = 1/\sigma(\phi_c)$). This gives

$$|\Delta\phi| = |\Delta f| = 2[(1-f_c)f_c]^{1/2}[\sigma(\text{lo})/\sigma(\text{hi})]^{1/2t}. \tag{6}$$

When $\phi_c = f_c = \frac{1}{2}$ and $t = s$, these expressions agree with equations (2) and (3).

3. Sample preparation

The 2000 Å films of granular Al–Ge (Deutscher *et al* 1983a) were prepared by evaporating Al and Ge simultaneously from two separate targets using two electron guns. Typical evaporation rates were 10 Å s^{-1} for each material. The substrate set-up consisted of about twenty-one 2.5 mm wide slices, cut from a microscope glass slide, which were lightly glued onto a single glass slide. The typical spacing between slices was 2 mm which allowed easy removal of each slice or 'sample' and provided a change of about 1.5% in the mean Al concentration from slice to slice. The background pressure before evaporation was $3–5\times10^{-6}$ mm Hg.

The substrate set-up was nominally at room temperature in order to obtain the amorphous Ge structure, but since the substrate was not water cooled, it warmed slightly during the evaporation. As ϕ_c is apparently very sensitive to the substrate temperature, this is probably the major cause of the different resistivities observed in the various sample series for the same ϕ values. Note that if the substrates are held at 150 °C or above, the Al–Ge will deposit in the so-called random structure (crystalline Ge) with a ϕ_c of about 0.15 (Deutscher *et al* 1983a).

For $\phi < \phi_c$, the typical grain size is estimated to be 20 Å or less from the electron microscope work on similar Al–Ge series (Lereah *et al* 1991, Lereah 1993). Dark field electron micrographs reveal a featureless sandy structure, and electron diffraction patterns reveal broad diffused diffraction rings both for the amorphous Ge and Al components (Lereah *et al* 1991). For $\phi \simeq \phi_c$, the Al grains are seen to be about 50 Å and rapidly grow in size to 100 to 200 Å above ϕ_c.

Film thicknesses were determined both by an optical interference technique and a depthometer. Both methods gave thicknesses of 2000 Å to within 5%. The relative atomic volume fractions of Al and Ge were determined using the EDAX (energy dispersive analysis of x-rays) facility attached to a scanning electron microscope. The relative Al concentrations from within a series are known to about 1% from EDAX measurements, while the absolute values determined both from EDAX and the relative evaporation rates are known only to ±5%. The specified values of ϕ were obtained as follows. In a series consisting of about twenty-one samples, each third sample was analyzed using EDAX and a smooth curve was drawn through the measured Al concentrations as a function of sample position on the glass slide. The RMS deviation on this line was about 1%. The values obtained from this 'smooth Al calibration curve' have an accuracy of about 0.1%, and are the values specified in the present paper.

The resistance between 295 K and 4.5 K were measured using a dipstick-type probe, which was steadily lowered into the He storage dewar over a period of about 3 h. A 0.1 μV resolution digital voltmeter was used to cyclically measure the resistance of a calibrated Cryogenics Consultant RhFe thermometer and the resistance of the samples. The voltage across these samples was always between 1 and 10 mV, and direct and reverse current measurements were taken and averaged. Samples having resistances greater than 10 MΩ were measured using a Keithley 617 electrometer. The voltage across these samples was always between 10 and 100 mV. Due to a background resistance of about 10^{11} Ω in the holder, the maximum resistance that could be reliably measured after a parallel resistance correction is made is 10^{10} Ω. All data were collected by a PC. Every time the temperature changed by 1 K or more, a data point was recorded. In practice about 250 data points per sample were collected. Resistance or resistivity data as a function of Al concentration, at various fixed temperatures (295, 250, 200, 150, 100, 50, 25, 10, and 5 K), were obtained by linear interpolation. The superconducting transition curves as a function of temperature and

in various magnetic fields were measured in a small ^{3}He refrigerator (Eytan *et al* 1993).

The experimental results are fitted to equations (4) or (1*a*) and (1*b*) using a non-linear regression fitting program which minimizes the quantity $\chi^2 = \sum$ (experimental value–calculated value)^2, with ρ(hi) $\equiv \rho$(Ge), ϕ_c, and s or t as variable parameters. The RMS deviation δ is defined as $[\chi^2/(\text{number of data points—number of free parameters})]^{1/2}$. In most cases ρ(lo) $\equiv \rho$(Al) was fixed at the measured value, which was obtained by measuring the resistivity of a 'pure' Al film, produced in the same evaporation system from the same target, as a function of temperature.

Table 1. Granular Al–Ge sample characteristics. The ϕ_c values given in this table are obtained by measurements of the superconducting transition curves for each series—for example, refer to figures 5 and 6 for series 4. The absolute uncertainty in all the resistivity measurements is about 5%, due to the error in the measuring the film thickness. Quoted below are the relative errors.

Series	Volume fraction range (Al) ±0.001	ϕ_c (Al) ±0.007	ρ(high) (295 K) (Ω cm) ±0.2%	ρ(low) (295 K) (Ω cm) ±0.2%	T_{min} (K)	ρ(high) (T_{min}) (Ω cm) ±0.2%	ρ(low) (T_{min}) (Ω cm) ±0.2%
3	0.379–0.579	—	2.81	1.67×10^{-2}	5	4.98×10^{5}	4.75×10^{-2}
4	0.413–0.617	0.559	1.53	3.84×10^{-3}	5	138	5.37×10^{-3}
5	0.359–0.557	> 0.56	9.54	0.197	100	1.65×10^{6}	1.11
8	0.385–0.622	0.568	1.82	2.40×10^{-3}	5	1.55×10^{6}	2.9×10^{-3}
9	0.444–0.633	0.507	0.218	3.11×10^{-4}	5	2.14	2.92×10^{-4}
11	0.205–0.355	—	13.3	4.31	100	3.27×10^{6}	2.89×10^{5}
12	0.497–0.698	0.549	7.69×10^{-2}	4.75×10^{-4}	5	0.568	4.82×10^{-4}
Al	1.0	—	—	7.69×10^{-6}	5	—	4.65×10^{-6}

4. Results and discussion

The concentration and the maximum and minimum resistivity (at 295 K and T_{min} (100 K or 5 K)) for the various sample series are given in table 1. As a prime objective of this paper was to study the crossover region near ϕ_c, the volume fractions of Al were intentionally concentrated in the range from 0.4 to 0.6. Unfortunately, even in this concentration range, the resistivity results showed a considerable spread, and slightly different ϕ_c values were obtained for different series of samples prepared under very similar conditions.

The resistivity plotted against volume fraction for series 4, 11 and 12 at 295 K is shown in figure 1. Also shown at the extremes of concentration are a few points from the original data (series 0) of Deutscher *et al* (1978), to fill in these two concentration regions. The same results for series 4 and 12 at 5 K are shown in figure 2. At all temperatures between 5 K and 295 K and for all series, log ρ varies nearly linearly over a range of ϕ which is somewhat greater than the crossover region (to be discussed below).

As series 4 and 12 overlap so well at both 295 K and 5 K and at all intermediate temperatures, they are considered to be a single series. Note in figure 1 that series 0, 4, 11, and 12 form a reasonably continuous sigmoid-shaped curve at 295 K and are analysed as a single series. The full curve through the experimental results in figure 1 is calculated from the GEM equation using the fitting parameters obtained by minimizing χ^2 and shown in column 1 of table 2. These values are very close to those previously obtained (McLachlan 1987b) from the (far more scattered data in the crossover region) results of

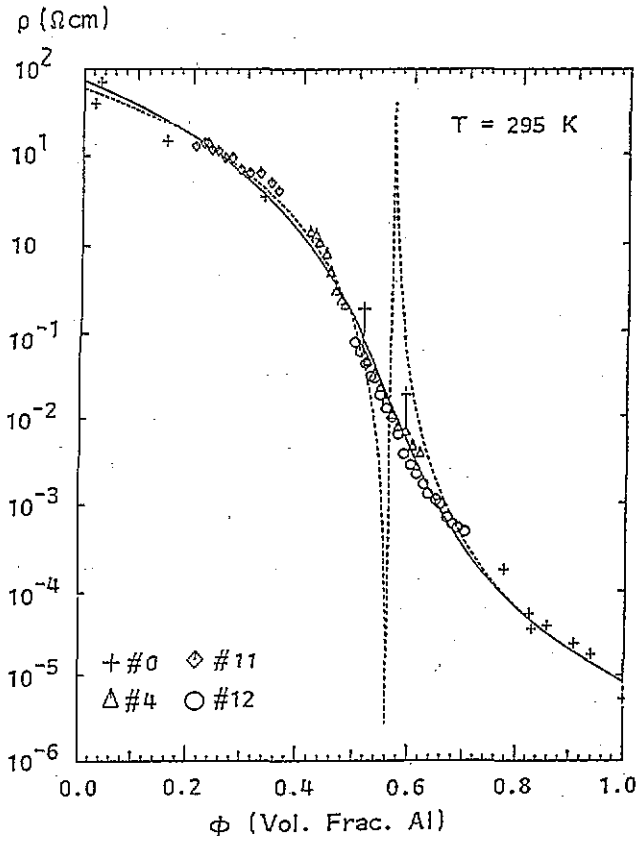

Figure 1. A plot of experimental and theoretical resistivities versus Al volume fraction ϕ at 295 K. The experimental points are series 0, 4, 11 and 12. The full curve is a plot of the GEM equation (4) and the broken curves are plots of the percolation equations (1*a*) and (1*b*). The parameters used in these plots are given in column 1 and column 4 of table 2. The daggers indicate the experimental points closest to ϕ_c incorporated in the fit. The broken curve between these two points is an extrapolation.

Deutscher *et al* (1978), which are shown in column 2. The broken curves are obtained when fitting the results on the metallic side to equation 1(*a*) and those on the insulator side to equation 1(*b*) using a common $\phi_c(f_c)$. The parameters describing the broken curves plotted in figure 1 are given in column 4 of table 2. Data points within the crossover region $|\Delta\phi| = [\sigma(\text{Ge}/\sigma(\text{Al})]^{1/(t+s)}$ were rejected from χ^2 (and δ) when making this fit, hence the experimental points lying between the daggers in figure 1 were not incorporated in the fits shown by the two broken curves. It is believed that this is the first time this type of analysis, using equations 1(*a*), 1(*b*) and (2) has been made. When a similar fit was made using the parameters obtained from the GEM equation that are listed in column 1 of table 2, δ increases by a small amount to 2.73 as indicated in column 5 of table 2. The values of $\Delta\phi$ and $\rho(\phi_c)$ calculated from equations (1) and (2) (columns 4 and 5) and (5) and (6) (column 1, 2, and 3) are also given in table 2. These fits yielded the following mean values: $\phi_c = 0.557$, $\rho(\phi_c) = 0.028\ \Omega$ cm and $\Delta\phi = 0.094$. The mean experimental value for $\rho(\phi_c)$, obtained by interpolation, is 0.0125 Ω cm, which is certainly within the expected experimental error in this region. Considering that the different formulas used for $\Delta\phi$ and $\rho(\phi_c)$ are similar for $A \simeq 1$ and the parameters used are not very different, the agreement between the different calculated $\Delta\phi$ and $\rho(\phi_c)$ values is not too surprising. Series 3, 5, 8, and 9 do not lie close to the full GEM curve shown in figure 1, but all lie on similarly shaped sigmoid curves.

As the temperature is lowered, the inadequacy of the data and possible limitations of equations (1)–(6) when applied to these samples become apparent. The resistivity of series 11 rises rapidly above series 4–12, and the combined series 4, 12 and 11 data are no

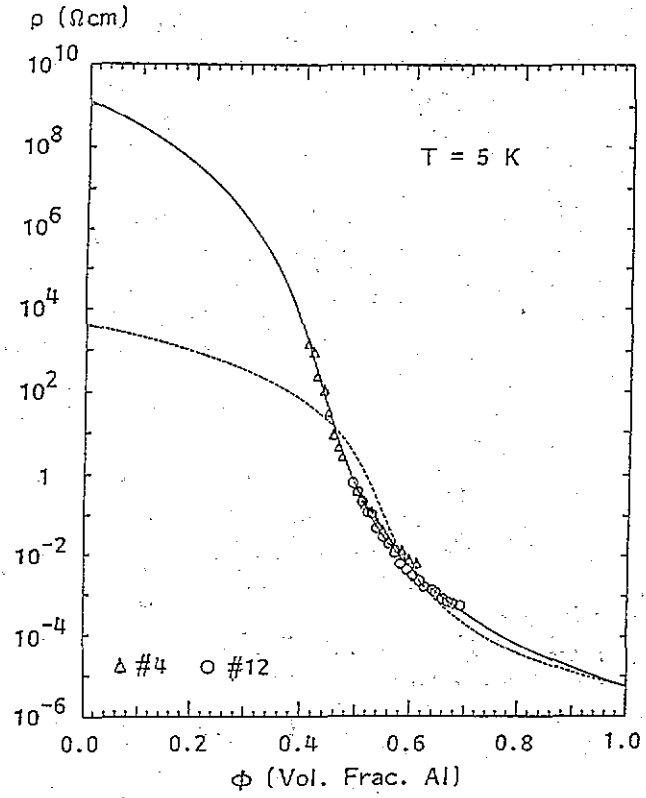

Figure 2. A plot of experimental and theoretical resistivities versus Al volume fraction ϕ at 5 K. The experimental points are series 4 and 12. The full and broken curves are plots of the GEM equation (4). The parameters used in these plots are given in the text.

Table 2. Fitting parameters for the room temperature resistivity data. This table shows parameters determined from the percolation and GEM equations and the $\Delta\phi$ and $\rho(\phi_c)$ values derived from these parameters. In columns 1 to 3, equations (4), (5) and (6) are used; while in columns 4 and 5, equations (1*a*), (1*b*), (2) and (3) are used. Underlined quantities are fixed during the fitting procedure. The results of column 2 were obtained using the experimental data of Deutscher *et al* (1978) only. The errors given below were determined by the fitting program.

	1 GEM	2 GEM	3 GEM	4 Percolation	5 Percolation
ϕ_c	0.559 ± 0.01	0.54 ± 0.01	0.554	0.560 ± 0.02	0.559
t	3.46 ± 0.3	3.70 ± 0.3	3.49 ± 0.4	3.35 ± 0.4	3.46
s	—	—	—	2.92 ± 0.5	3.46
ρ(Ge)(Ω cm)	75.6 ± 20	68.0 ± 24	79.2 ± 20	61.3 ± 22	75.6
ρ(Al)($\mu\Omega$ cm)	7.69	7.3 ± 0.1	7.69	7.51 ± 0.1	7.69
δ	2.13	2.82	2.14	2.35	2.73
$\Delta\phi$	0.098	—	0.098	0.080	0.098
$\rho(\phi_c)$(Ω cm)	0.024	—	0.024	0.037	0.024

longer even quasi-continuous and can no longer be fitted as a single series using the GEM equation. In figure 2, the full theoretical curve for series 4–12 at 5 K is calculated from the GEM equation using $\rho(\text{Ge}) = 1.47 \times 10^9$ Ω cm, $\rho(\text{Al}) = 4.65$ $\mu\Omega$ cm (measured value), $\phi_c = 0.434$, $t = 5.84$ and $\delta = 0.67$; these values for ρ(Ge), ϕ_c and t being those that gave the optimum GEM fit to the 5 K data. One disturbing feature of the best (not very good) fits in the range 295–5 K is that if all three parameters [ρ(Ge), ϕ_c, t] are allowed to assume different values at each temperature in the GEM fitting routine, ϕ_c decreases from 0.559 at

295 K to 0.434 at 5 K for series 4–12; t also increases and ρ(Ge) increases dramatically as the temperature is lowered. It is obvious that only if the value of ρ(Ge) or ϕ_c is known or specified can more realistic fits using the GEM equation be identified.

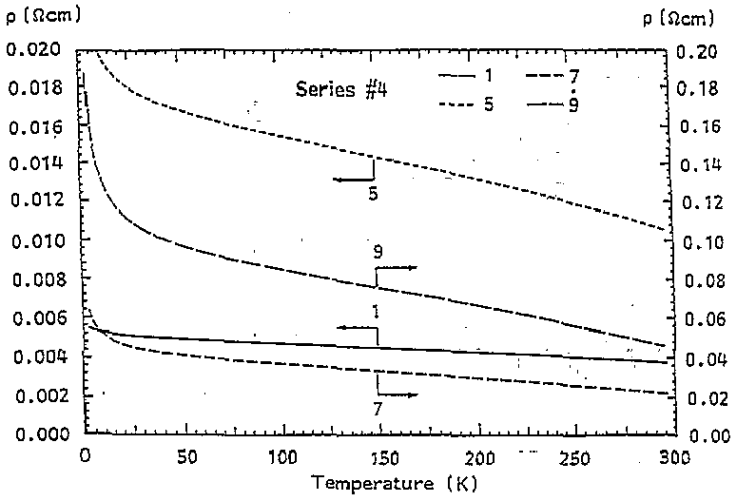

Figure 3. The figure shows plots of the resistivity against the temperature for samples 1, 5, 7, and 9 from series 4, with $\phi = 0.617$, 0.565, 0.543, and 0.520 respectively.

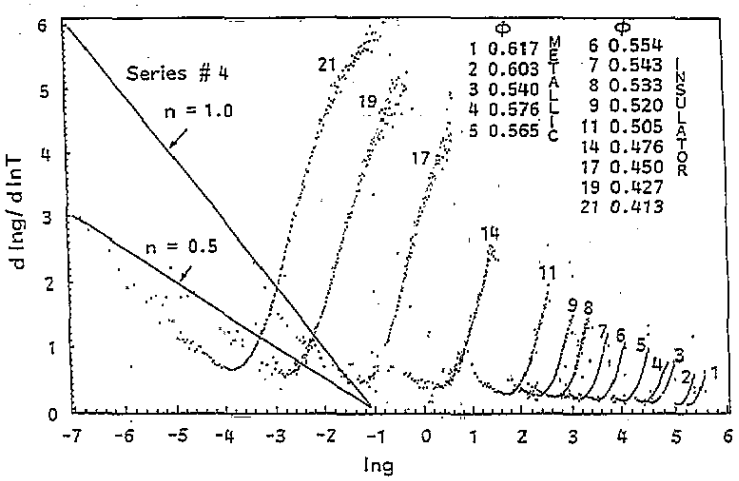

Figure 4. A plot of $d \ln g / d \ln T$ against $\ln g$ for the series 4 films. The full lines indicate the expected behaviour for data that show $\rho \propto \exp[T_0/T]^n$ for $n = \frac{1}{2}$ and 1.

One obvious approach is to try to identify ϕ_c from the ρ–T behaviour. Shown in figure 3 are ρ–T plots of samples 1, 5, 7, and 9, from series 4 between 295 K and 5 K. The ϕ values of these samples are (1) 0.617, (5) 0.565, (7) 0.543, and (9) 0.520. Table 2 shows

that ϕ_c for series 4 must be close to 0.557. Shown in figure 4 are plots of $d\ln g/d\ln T$ against $\ln g$, where g is the conductance in units of Ω^{-1}, for selected samples of series 4. In this curve g is not normalized by $e^2/\pi h$ as is sometimes done. One might expect that this type of plot (White and McLachlan 1986), or $d\ln g/d\ln T$ versus $\ln T$, would emphasize any change in the temperature dependence of the samples. Note that a negative slope in figure 4 indicates a $\rho = \rho_0 \exp(T_0/T)^n$ type behaviour, while the temperature dependences characterizing weak localization and electron–electron interaction give positive values of the slope. None of the ρ–T and $d\ln g/d\ln T$ against $\ln g$ or $\ln T$ plots of series 3, 4, 8, 9, and 12 ever show any abrupt or anomalous change in the ρ–T characteristics, which could indicate a change from a continuously linked Al network to one disrupted by thin Ge tunnelling barriers between the Al clusters. Similar results are observed series 3 and 8, while most of series 5 and all of series 11 show linear negative slopes. It is interesting to note that very similar $d\ln g/d\ln T$ versus $\ln g$ plots are observed (Albers and McLachlan 1993) in the amorphous Fe–Ge system, near the metal–insulator transition.

In figure 3 the upturn in the resistivity below 50 K, observed for samples 1 and 5 with $\phi > \phi_c$, must be attributed to localization and electron–electron interaction effects in the fine Al networks, while the resistivity curves for samples 7 and 9 with $\phi < \phi_c$ must surely be dominated first by tunnelling and then by the hopping conductivity in the Al doped amorphous Ge component. The authors can offer no explanation as to why the temperature dependence shown in figure 3 and emphasized in figure 4 should be so continuous across ϕ_c. It should also be noted that the effects of localization and electron–electron interactions should be insignificant at 295 K and so should not affect ρ(Ge) given in table 2 near the percolation threshold.

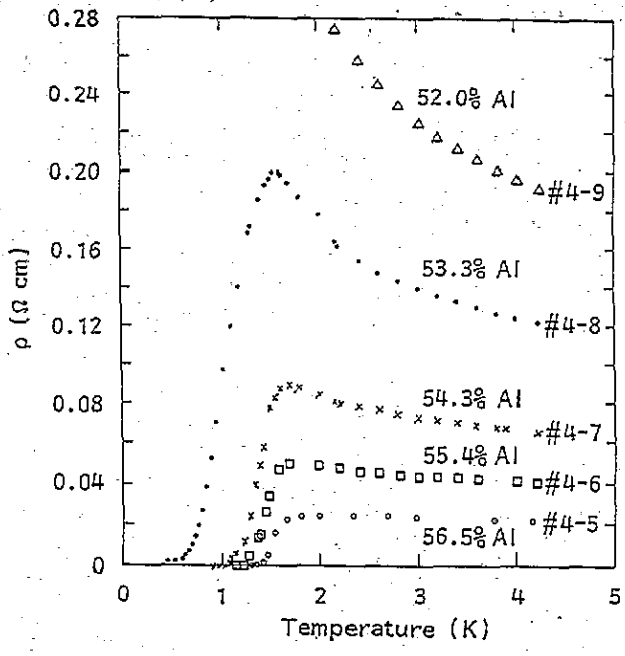

Figure 5. This figure shows a plot of the resistivity versus temperature for samples in series 4, in zero magnetic field. Note that all the points shown in this figure have small finite resistances with the exception of the points below 1.4 K of the films 4–5 (56.5% Al sample), which is superconducting below 1.4 K.

A novel method that identifies ϕ_c through resistivity and magnetoresistivity measurements below the superconducting critical temperature for Al is now described. Figure 5 shows zero-field resistivity results for 56.5–52.0% Al samples of the series 4. It should

be noted that all the samples with 55.4% Al and less still have finite resistivities at 0.5 K. The resistivity of the 56.5% Al sample is at the noise level of the system below 1.4 K. Figure 6 contrasts the magnetoresistance of the 54.3 and 55.4% Al samples with that of the 56.5% Al sample. A finite-resistivity tail extending well below the superconducting transition temperature (1.5–1.7 K) in the Al grains, which increases with the application of a moderately small magnetic field (< 1 T), is taken to indicate Josephson junction coupling (Eytan *et al* 1993). Samples which show Josephson junction coupling are interpreted as having some disconnected clusters and/or filaments, and are therefore considered to be insulating in character. In the 56.5% Al sample and more metallic samples just above ϕ_c, a large magnetic field of 1.3 T starts to drive the tiny Al grains ($d \simeq 20$ Å), which form the clusters and filaments on the Al backbones, normal. A field in excess of 3 T returns the resistivity to the normal high-temperature ρ–T line (extrapolated from measurements above T_c). We interpret this type of behaviour as characteristic of metallic films. More details of this type of measurement can be found in the article by Eytan *et al* (1993). ϕ_c was defined as midway between the last sample to show Josephson junction coupling and the first to show zero resistivity in all fields below 1 T at 0.5 K. This definition is in line with classical percolation which deals only with 'metallic' contacts and does not take quantum mechanical tunnelling into account. Note also that $\rho(m) = 0$ is the definition of ϕ_c implied by equation (1*b*). These criteria allow one to estimate, to within ± 0.007, the following ϕ_c values (4) 0.559, (8) 0.568, (9) 0.507, (12) 0.549, and (5) > 0.557 (the highest ϕ of the series). An examination of table 1 shows that different ϕ_c values observed for different series is a major reason for the very different ρ values observed for the same ϕ. The mean ϕ_c for series 4–12 is taken to be 0.554, in remarkably good agreement with the ϕ_c values of 0.559 and 0.560 obtained from the GEM and percolation fits of the data at 295 K respectively. Earlier studies of this nature were performed by Shapira and Deutscher (1983) who also observed that some of their Ge–Al samples with a negative temperature coefficient of resistivity become superconducting. Near ϕ_c our samples consist of an intimate mixture of linked Al networks, probably with a negative temperature coefficient of resistivity due to localization and interaction effects, and an Al-doped amorphous Ge matrix which has an exp $(T_0/T)^n$ resistivity–temperature dependence at low enough temperatures. The observation of both Josephson junction behaviour and a peculiar temperature-dependent quasi-particle tunnelling behaviour (Eytan *et al* 1993, Adkins *et al* 1980) when the Al is superconducting, conclusively shows that a wide range of barrier thicknesses are present near ϕ_c. Therefore, in this region, it is not clear whether the resistivity is primarily determined by the metallic connectivity of the Al matrix and/or whether quantum mechanical tunnelling between the Al grains and clusters dominates. It is obvious that no model exists which takes all these effects into account.

The parameters obtained by fitting the series 0, 11, and 4–12 data at 295 K, with ϕ_c fixed at the superconducting value of 0.544, are given in column 3 of table 2. As the data at lower temperatures are fitted for series 4–12 using the fixed ϕ_c values obtained from superconductivity measurements, δ increased from 1.18 at 295 K to 3.3 at 5 K for series 4–12. A plot of the GEM equation fitted to the 5 K data of series 4–12 with $\phi_c = 0.554$ is shown by the broken curve in figure 2. The parameters in this case are $\rho(\text{Ge}) = 4.34 \times 10^3\ \Omega$ cm, $\rho(\text{Al}) = 4.65\ \mu\Omega$ cm (measured value), $\phi_c = 0.554$ (measured value), $t = 3.42$ and $\delta = 3.3$. From this curve and the experimental results shown in figure 2, the fitted value of ρ(Ge), which must represent some mean value for all samples in the series, is obviously far too low for the low-ϕ samples of this series. Similar behaviour is observed for series 3 and 8. Therefore, as ϕ_c is the correct value at 5 K, if the relationships given in equation (3) and (5) are even semi-qualitatively correct, the only conclusion is that the resistivity of the

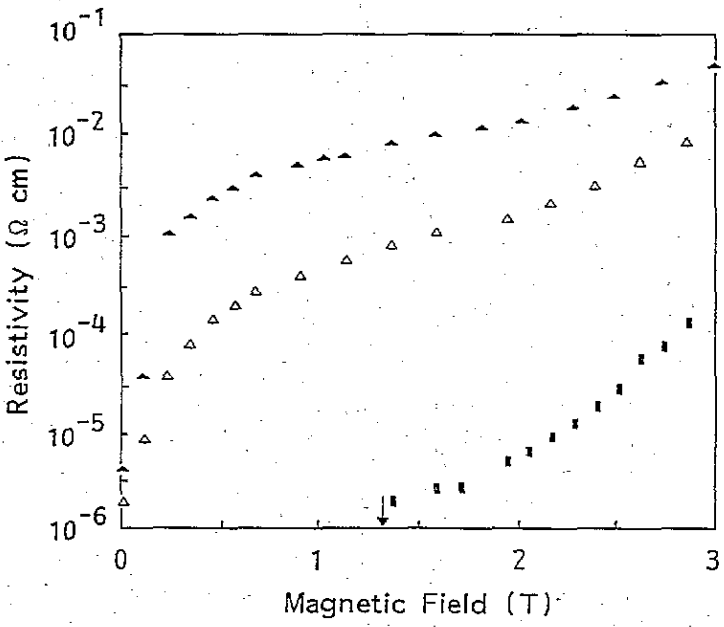

Figure 6. This figure shows a plot of the resistivity versus magnetic field at 0.5 K for the sample 4–7 (54.3% Al) (filled triangles), sample 4–6 (55.4% Al) (open triangles), and sample 4–5 (56.5% Al) (filled rectangles). Note that the 56.5% Al sample remains completely superconducting up to fields of 1.35 T. The sharp contrast between insulating samples that exhibit finite resistivities and metallic samples that exhibit zero resistivities in modest magnetic fields clearly identifies ϕ_c (the metal–insulator transition composition) for this series.

Al-doped amorphous Ge component is increasing with decreasing ϕ. This means that the percentage of Al incorporated into the Al-doped amorphous Ge depends on the relative rates of arrival of the Al and Ge at the substrates, which is not too surprising as the samples are made by quenching and not under thermodynamic equilibrium conditions. This also means that the Al-doped amorphous Ge in each and every sample of all the series has a unique temperature dependence.

The only way known to the authors to extract the ρ–T curve for the Ge component is to solve the GEM equation for ρ(Ge) at all temperatures using the known ρ(Al, T) data and ϕ_c from superconductivity measurements (0.554 for series 4–12) and a suitable exponent t. As the values of t obtained by fitting series 3, 4–12 and 8 at temperatures between 295 K and 5 K, with ϕ_c fixed by the superconductivity measurements, are remarkably constant ($t(3) = 4.64 \pm 0.58$, $t(4\text{–}12) = 3.495 \pm 0.06$ and $t(8) = 3.55 \pm 0.22$), these are the obvious t values to use. Shown in figure 7 are the log ρ(Ge) versus T curves obtained by this procedure for the samples 5, 7, 9, 14, and 20 from series 4, using the known ρ(Al; T) data; $\phi_c = 0.554$ and $t = 3.495$. The values of ρ(Ge) calculated in this way are in semi-quantitative agreement with the values obtained by Chopra and Nath (1976) for homogeneous and amorphous Ge–Al films, with concentrations of Al in the range 2–10 at.%, between 300 K and 125 K. Chopra and Nath (1976) observed that all samples in this range have the same resistivity at about 180 K. Figure 7 shows that ρ(Ge) is reasonably constant for all samples in the series near room temperature but not at lower temperatures. This is probably the reason why the GEM equation is a reasonable model for the results near room temperature but fails at lower temperatures. Note that if the Al-doped amorphous Ge contains several per cent of Al, the absolute and to a much lesser extent the relative volume fraction of granular Al is in error.

5. Conclusions

One of the primary conclusions of this study is that the extensively studied granular Ge–

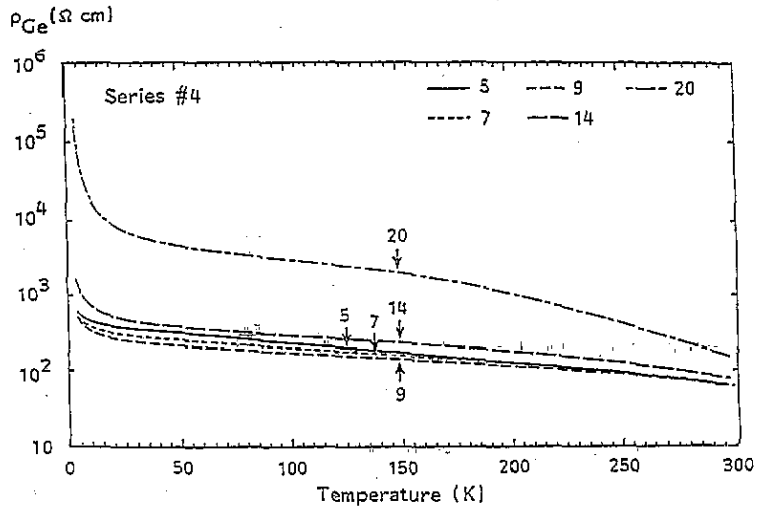

Figure 7. This figure shows theoretical plots of the resistivity of the Al-doped amorphous Ge against temperature for samples 5, 7, 9, 14, and 20, with $\phi = 0.565$, 0.543, 0.520, 0.476 and 0.423 Al respectively, from series 4. These curves are obtained by fitting the GEM equation (4) to the data shown in figure 3 using the parameters $\phi_c = 0.554$, $t = 3.495$ and the measured resistivity values for Al.

Al is not an ideal system with which to investigate the percolation equations and the equations derived from percolation theory in the crossover region (equations (2) and (3)) or the GEM equation (4), as the resistivity of the Ge component is not independent of the Al concentration at all temperatures. This concentration dependence prevented the proposed study of the narrowing of the crossover region (equation (2)), and the temperature dependence of the resistivity (equation (3)) at and near ϕ_c, with decreasing temperature. This is because ρ(hi) and ρ(lo) being independent of ϕ is a basic requirement of both the percolation equations (1*a*) and (1*b*) and the GEM equation (4). However, using an independently measured ϕ_c and a reasonable value of t, it has been shown that the GEM equation can be used to extract a feasible ρ(Ge) curve from the $\rho(T)$ data for an individual sample.

The computer fits of the 295 K data, using the percolation equations (1*a*) and (1*b*) together with (2), describe the data outside the crossover region surprisingly well, especially considering the relatively small ratio of ρ(hi)/ρ(lo) ($\simeq 10^7$) and the wide crossover region ($\simeq 0.09$). The percolation fits also give very nearly the same value of ϕ_c as is obtained from the GEM equation and superconductivity measurements. Strictly speaking these results can only be true if the critical regions extend over the entire composition range on either side of the percolation threshold. In numerous experiments, where ρ(hi)/ρ(lo) is very large or infinite, which were fitted using percolation equations, the critical region is shown to lie in the range $\phi_c \leqslant \phi \leqslant 1$ (or $p_c \leqslant p \leqslant 1$) (McLachlan 1986b). However, as Dubson and Garland (1985) emphasized there is no explanation in terms of percolation theory for these unexpectedly large critical regions. It should be noted that in the current experiments there are also data for $0 \leqslant \phi \leqslant \phi_c$. A model two-dimensional percolation system with a finite ρ(hi)/ρ(lo), which can be accurately fitted by the GEM equation over the entire composition range, has been analysed by McLachlan (1988). However, the question of the validity of a

percolation approach, as used in this paper, to systems where $\rho(\text{hi})/\rho(\text{lo})$ is not extremely high, still requires further experimental work.

As shown in figure 1, even in the crossover region the GEM equation gives reasonable fits to the Al–Ge data. It also models numerous other systems, where similar sigmoid-shaped experimental resistivity ρ versus ϕ curves are observed extremely well (McLachlan *et al* 1990, McLachlan, 1986a, 1987a, 1988, Deprez *et al* 1988). Why the GEM equation, which contains only the bulk Al and doped Ge conductivities, should quantitatively fit the results in this region is not obvious. The complexity of the microstructure near ϕ_c has been previously mentioned and the different conductivity mechanisms (metallic, weak localization, electron–electron interaction in the Al matrix, hopping in the doped Ge and direct intergranular tunnelling) operating near ϕ_c have been illustrated by the temperature dependence of the resistivity in the normal and superconducting states. Any model for this region should explain the nearly linear log ρ versus ϕ behaviour in the crossover region. The extreme complexity of the resistivity in this region probably accounts for the fact that the $\rho(T)$ measurements gave no indication of the value of ϕ_c.

The fact that the ϕ_c values obtained by the percolation fit ($\phi_c = 0.560$), the GEM equation fit ($\phi_c = 0.559$) and direct measurement ($\phi_c = 0.554$) are so close is an important observation and indicates that ϕ_c is the same physical parameter in all three types of analysis. However further systems must be studied before firm conclusions can be made. The values of the exponents t and s extracted from equations (1*a*), (1*b*) and (4) are higher than those to be expected from universal behaviour. However as the system is a continuum, the universality exponents need not necessarily be observed (Halperin *et al* 1985). McLachlan (1987a) has proposed that the exponent is associated with the microstructure of the medium, and Balberg (1987) has shown that higher exponents are to be expected when tunnelling occurs, which the superconductivity measurements clearly show. Examples of $t > 2$ where the analysis is in terms of the percolation equations include the results of Carmona and co-workers (1987), McLachlan (1986b), and Deprez and McLachlan (1988), while other examples of $t > 2.0$ obtained from an analysis using the GEM equation include the PbGe system (McLachlan 1987b), cermets (McLachlan 1990) and conductor–polymer composites (McLachlan *et al* 1990).

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