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Quantum interference effects in nanostructured Ag

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Abstract. We present results for the measured low temperature magnetoresistance of nanostructured Ag produced by inert gas phase condensation. The Ag particles are typically between 2 and 100 nm in diameter and the material is in the form a network of chains of particles. The magnetoresistance is negative and consistent with the presence of quantum interference effects similar to that seen in disordered metals. From the field dependence of the resistance we can infer characteristic length scales associated with the network of connected Ag particles.

1. Introduction

Nanostructured materials are a very attractive class of materials and have a wide range of potential applications. This is due to their many unique and remarkable properties which are not found in conventional bulk materials [1]. Because the scale of the grain size in nanostructured materials is less than the inelastic mean free path of electrons we can expect to see effects from coherent interference of electrons in the electron transport properties of these materials. These quantum interference effects have been widely studied in metallic glasses [2] and thin disordered metal films [3]. Bruynseraede *et al* [4] and Sauer *et al* [5] discussed the possibility of quantum interference effects in nanostructured metals when the length scale of the disordered structure matched the inelastic scattering length suggesting the possibility of a minimum in the temperature dependence of the resistivity. In this paper, we report the quantum interference effects in the temperature and magnetic field dependence of the resistivity of nanostructured silver produced by inert gas phase condensation dispersed in a polymer matrix.

2. Experimental details

Silver nanoparticles were synthesized by inert gas condensation and loosely compacted to form a disc approximately 2 mm thick and 1.5 cm in diameter. This disc was then infiltrated under pressure with a two component epoxy resin system (Araldite 2020, Ciba–Geigy) and cured giving a volume fraction of silver in the nanocomposite of only 7%—this was determined using a pycnometer to measure the actual density of the composite and then assuming the Ag density was 10.5 g cm^{-3} and the epoxy resin was 1.2 g cm^{-3} . The microstructure of the nanocomposite was characterized by transmission electron microscopy using a Philips CM20 TEM in bright field and dark field modes: samples for TEM observation were prepared by ultramicrotomy using a diamond knife.

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The resistance measurements were made by a d.c. four probe technique in a conventional helium cryostat for temperature between 2 and 70 K. Magnetoresistance was measured in fields up to 6 T. Samples were cut into rods 1.5 cm long and 2 mm square. The current used to make the d.c. resistance measurements had to kept below 10 μA. If a larger current was used the sample would become insulating (resistance >10 MΩ at room temperature). The use of such a low current meant the noise in the resistance measurement was a few parts in 10^5. Since the sample is a complex network of chains of Ag particles it is likely that the chains could not support the higher currents because of the joule heating.

3. Theory

The sample is extremely disordered and the measured resistivity is 71.8 $\mu\Omega$ cm at 4.2 K. It is difficult to estimate the mean free path because the samples are made of a network of chains of particles. However disordered metals which exhibit a small positive temperature coefficient of resistivity down to 20 K and then a resistivity minimum typically have an electron mean free path of the order of a few atomic spacings. This means that the mean free path is approaching the scale of the Fermi wavelength and we have to concern ourselves with interference effects. One way to picture the importance of this is to consider electron paths which form closed loops. Electron waves which traverse the path in opposite directions have the same path length and interfere constructively enhancing the probability of back scattering and increasing the resistivity. Phonon scattering and magnetic fields destroy the phase coherence between these paths and reduce the resistivity [2–6].

A simple expression for the conductivity in a disordered metal when $k_f \ell$ is of the order of unity is [7]

$$\sigma(T) = \frac{k_f^2 l_e e^2}{3\pi^2\hbar}\left[1 - \frac{l_e}{l_i(T)} - \frac{3}{(k_f l_e)^2}\left(1 - \frac{l_e}{L_i(T)}\right)\right] \tag{1}$$

where l_e and $l_i(T)$ are elastic scattering and inelastic scattering lengths, respectively and

$$L_i = \sqrt{\tfrac{1}{2} l_e l_i}. \tag{2}$$

The temperature dependent part of equation (1) can be written as

$$\sigma^T(T) = \frac{e^2}{\pi^2\hbar}\left[\frac{1}{L_i(T)} - \frac{(k_f l_e)^2}{3}\frac{1}{l_i(T)}\right]. \tag{3}$$

When the temperature is low, $l_i(T) \gg l_e$ so the second term can be ignored. As the temperature is increased, we cannot ignore this term. The inelastic mean free path decreases as the temperature increases so that for the first term $\mathrm{d}\sigma/\mathrm{d}T$ is positive while for the second term $\mathrm{d}\sigma/\mathrm{d}T$ is negative. The first term will be dominant at low temperature but when the temperature is increased there will be some temperature at which will $\mathrm{d}\sigma/\mathrm{d}T$ change sign. So there will be a minimum resistivity at some temperature. As we see in figure 1 the minimum resistivity is 10 K for our sample of nanostructured Ag which is consistent with a mean free path of a few nanometres.

The relationship between conductivity and magnetic field in disordered metals is given by [8]

$$\sigma(B) = -\frac{e^2}{2\pi^2\hbar}\sqrt{\frac{eB}{\hbar}}\, f\left(\frac{B}{B_i}\right) \tag{4}$$

where

$$f\left(\frac{B}{B_i}\right) = \frac{1}{48}\left(\frac{B}{B_i}\right)^{3/2} \qquad \left(\frac{B}{B_i}\right) \ll 1 \tag{5}$$

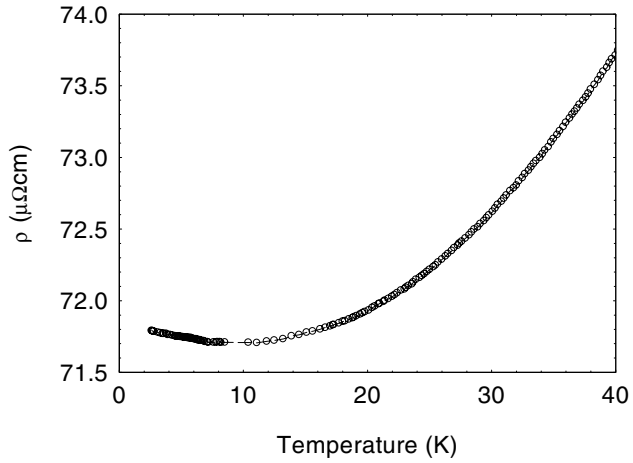


Figure 1. Temperature dependence of the resistance of the Ag nanocomposite at low temperatures showing a resistance minimum around 10 K.

and

$$f\left(\frac{B}{B_i}\right) = 0.605 \qquad \left(\frac{B}{B_i}\right) \gg 1 \tag{6}$$

and

$$B_i = \frac{3\hbar}{8e}\frac{1}{L_i^2}.$$

So the magnetoconductivity is proportional to B^2 at low field and $B^{1/2}$ at high field. The characteristic field at which there is a crossover from the quadratic to square root behaviour is determined by the inelastic mean free path.

However our samples are not disordered metals in the same manner as metallic glasses. There is substantial disorder but we have a complex network of chains of particles along which the electrons are directed. The mean free path is about 10 nm while the particle size, as we shall show below, is between 2 and 100 nm so the electron closed loops are directed and contained within the loops created by the network. Now there is another characteristic length in the problem—the average diameter of the loops created by the network, L_N. In equations (5) and (6) the diffusion length L_i acts as a cutoff so that closed loops longer than L_i do not contribute to the interference effect. It is not possible to carry out a detailed quantitative analysis of the data on the nanostructured Ag using equations (5) and (6) because they assume the electron samples all of the space within a distance L_i whereas in these samples they are directed along the chains of the network of the porous Ag. Now the average size of the loops in the network plays the role of a cutoff restricting the size of the loops which contribute to the interference effect so that now B_i is not associated with inelastic scattering but with the characteristic length of the network.

$$B_i = \frac{3\hbar}{8e}\frac{1}{L_N^2} \tag{7}$$

and the crossover from quadratic behaviour should correlate with the diameter of the loops in the network of Ag chains.

4. Results and discussion

In figure 1 we show the temperature dependence of the resistivity is very small and positive above 10 K and exhibits a minimum at about 10 K. Both of these features are unusual in a noble metal system like Ag but are typical of a disordered metal alloy or noble metal ultra-thin film when the mean free path is comparable with the Fermi wavevector. The only other possible cause of a minimum in this region is the Kondo effect from magnetic impurities: this is unlikely. ICP analysis showed that the main impurity was Cu at 200 ppm. Fe was below the detection limit for Fe of 10 ppm while Ni was below 5 ppm and Co below 1 ppm, and this would not explain the small magnitude of the positive coefficient above 10 K which results from the high level of disorder in the system.

Figure 2 shows the microstructure of a thin section of the nanocomposite. The silver nanoparticles have formed a three-dimensional interconnected structure of chains and rings in a matrix of epoxy resin. Both phases form a continuous network and thus this material can be considered to be a 3–3 composite. It was found that the particle size covered a relatively wide range from approximately 2 nm to 100 nm. Observation reveals that the larger particles are polycrystalline having been formed from coalescence of finer particles during the inert gas condensation process. Due to the size of the particles forming the silver chains, only partial coalescence has taken place and the prior particle boundaries may be clearly seen. Figure 2 also indicates that there is a high density of twinned particles present in the silver network.

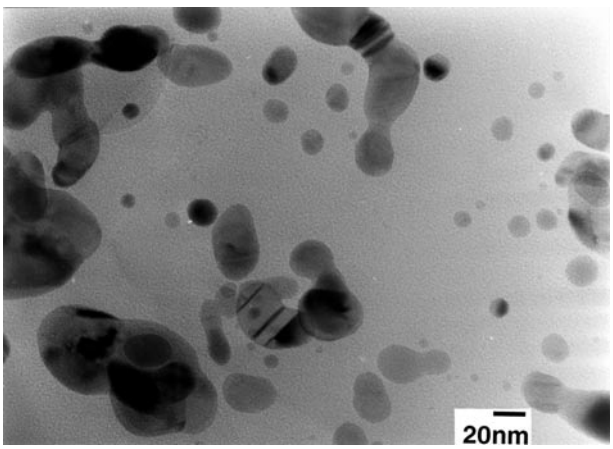
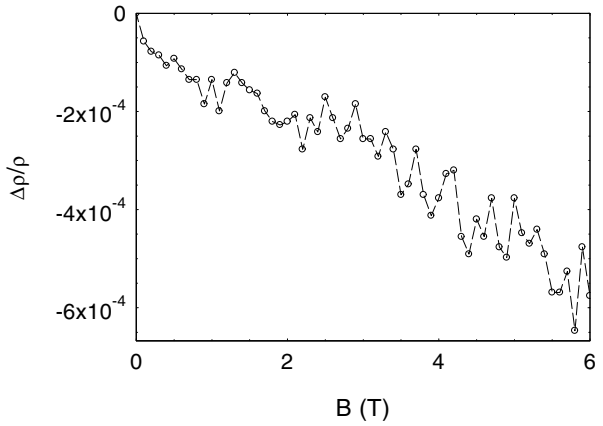
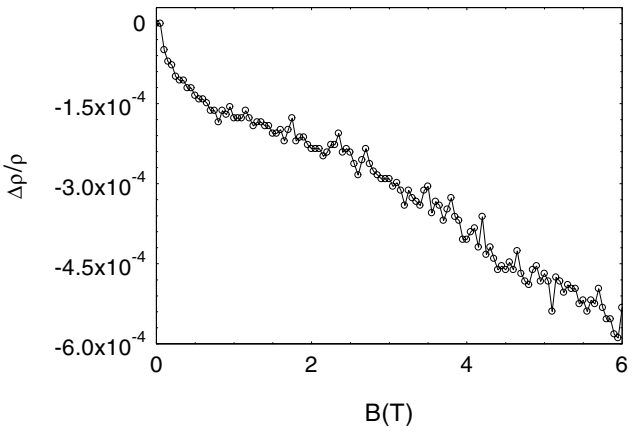


Figure 2. Microstructure of a thin section of the Ag nanocomposite.

The magnetoresistance is shown in figure 3 for various temperatures between 2 and 15 K. In the 2 K and 4 K data we can see two distinct regions, region A below about 0.5 T and region B extending to the highest field measured. For each region A and B there is characteristic field, B_i, which marks the crossover from a quadratic field dependence to a square root field dependence of the MR and values for the characteristic length scale in equation (7), L_N, can be determined for regions A and B which we will call L_A and L_B respectively. This suggests the distribution of closed loops in the network of Ag chains is bimodal with larger loops of average diameter L_A and smaller loops of average diameter L_B. For region A we do not see the crossover because it is below the field resolution of our measurements and so B_i is significantly less than 0.05 T while for region B the crossover is about 5 T. We can therefore estimate L_A and L_B using equation (7) as $\geqslant$100 nm and approximately 10 nm respectively. We also note the effects at 2 and 4 K are very similar in magnitude so that there is only a small temperature



(a)



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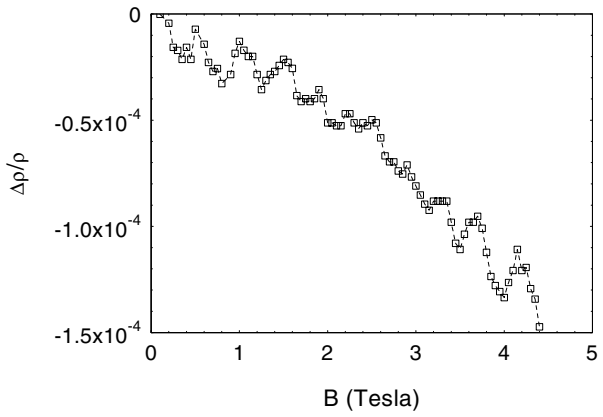
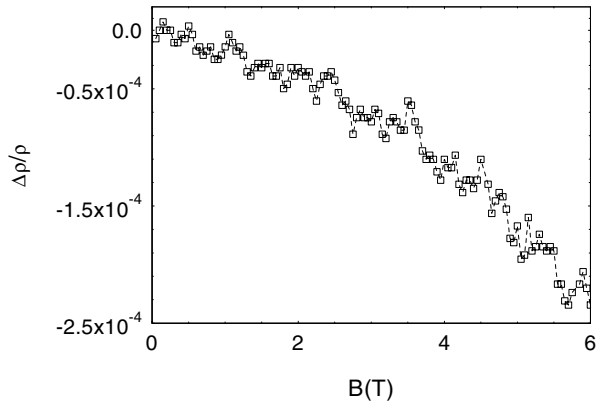


(c)

Figure 3. Magnetoresistance of the Ag nanocomposite at various temperatures, (a) 2 K, (b) 4 K, (c) 10 K and (d) 15 K. The noise in the data is the result of using a dc current of 10 μA. The chains in the Ag network cannot support a larger current than this.



(d)

Figure 3. (Continued)

dependence to the magnetoresistance. This is consistent with the idea that the characteristic length scale is L_A and L_B which are temperature independent. In conventional disordered metals the characteristic length scale is L_i which is temperature dependent. L_B is so short it probably represents electron closed paths which are within an individual Ag particle. But L_A represents paths that are comparable with the loops within the network of chains of Ag particles along which the electrons are directed.

In figures 3(c) and 3(d) we show the magnetoresistance data for 10 and 15 K. At these temperatures only region B is present. This is consistent with the a shorter inelastic diffusion length, L_i, and implies L_i is less than L_A at these temperatures. This suggests the inelastic diffusion length, $L_i(T)$, is of the order of 100 nm at 10 K and so the inelastic scattering length, $l_i(T)$, is about 1 μm at 10 K similar to values seen in other work on quantum interference in disordered metals [2].

In conclusion, the electron transport properties of nanostructured Ag produced by inert gas phase condensation are very unlike that of conventional Ag. The properties are more like metallic glasses and are dominated by quantum interference effects with the electron paths directed along the complex network of chains of Ag particles.

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