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Quantum interference effects in nanostructured Au

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Abstract

We present results on the magnetoresistance and temperature dependence of the resistivity for nanostructured Au produced by chemical means. The magnetoresistance was typical of highly disordered metals exhibiting quantum interference effects. We fitted the data and were able to determine the spin–orbit scattering relaxation time to be 10^{-12} s and we found the inelastic scattering time at 10 K to be 10^{-11} s. The inelastic scattering rate varied as T^3 between 4 and 20 K, which is typical for electron–phonon scattering in disordered metals.

1. Introduction

Nanostructured materials are very attractive materials with many interesting properties and applications [1] which are not found in conventional bulk materials. As the scale of the grain size in nanostructured material is less than the inelastic mean free path, and often approaches that of the elastic mean free path, quantum interference effects (QIE) [2] can be observed in these materials. These effects occur in metals with a relatively high resistivity of between 100 $\mu\Omega$ cm and a metal–insulator transition. Typically the temperature coefficient of resistivity is negative and in the absence of strong spin–orbit scattering there is a negative magnetoresistance. In the presence of spin–orbit scattering the magnetoresistance is positive. In this paper, we report on quantum interference effects in nanostructured Au films, produced by chemical methods, which have a substantial resistivity and exhibit interference effects with strong spin–orbit scattering. Previously we reported on (QIE) in Ag produced by inert gas-phase condensation. These results were complicated because the microstructure was not homogeneous but instead was a sponge-like network of chains of Ag particles. Here the Au microstructure is still complex but more homogeneous; however, the grain size was small enough to produce significant disorder.

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2. Experimental methods

Au nanoparticles stabilized with mercaptobenzoic acid were formed using a wet chemical approach. Hydrogen tetrachloraurate ($HAuCl_4{\cdot}3H_2O$) was reduced in the presence of the stabilizing ligand mercaptobenzoic acid ($HS–C_6H_4–COOH$) to yield discrete particles [4] with an average diameter of 2.9 nm. The particles were dispersed colloidally in water.

Patterned electrodes were produced by sputtering a gold film onto a glass substrate using a contact mask. Nanostructured Au films were deposited by placing ten droplets onto this glass substrate and allowing the solvent to evaporate. Once dry, these films were placed in an oven at 350 °C for 60 min. During this annealing process it is likely that some of the stabilizing ligand will be lost and that fusion of particles will occur.

The electrodes were configured to allow dc four-probe resistance measurements to be made. We measured the resistance as a function of magnetic field up to 6 T at temperatures of 2, 4, 8, 10, 15 and 20 K. We also measured the temperature dependence of the resistivity between 2 and 30 K in zero field.

The microstructure of the nanostructured films was determined using transmission electron microscopy (TEM). Suitable specimens were prepared by physically removing the sample from the glass substrate and embedding it in epoxy resin. Cross-sections were then cut using an ultramicrotome to produce a very thin, electron-transparent cross-section of about 50 nm thickness. This was placed on a Cu grid ready for the TEM.

3. Theory

In the presence of disorder, electron scattering is such that the electrons follow a diffusive random walk. Electron waves, from electrons whose path forms a closed loop, traverse the path in opposite directions with the same path length and interfere constructively, enhancing the probability of back-scattering and increase the resistivity. Inelastic scattering destroys the phase coherence of electron paths and so the resistivity is reduced as the temperature rises. The magnetic field enclosed by the closed path shifts the phase of the electron waves and also destroys the coherence, leading to a negative magnetoresistance. Spin–orbit scattering changes the constructive interference to destructive and so the magnetoresistance changes sign. All these effects are now well known and discussed in a number of publications [2].

An expression for the magnetoconductivity in the presence of both spin–orbit and inelastic scattering is [5, 6]

$$\Delta\sigma(B) = \frac{e^2}{\pi^2\hbar}\sqrt{\frac{eB}{\hbar}}[3f(B/B_{so}) - f(B/B_i)] \tag{1}$$

where

$$B_i = \frac{\hbar}{4eD\tau_i}, \qquad B_{so} = \frac{\hbar}{eD([\tau_{so}/2]^{-1} + [4\tau_i]^{-1})^{-1}}$$

and

$$f(x) = \sum_{n=2}^{\infty} 2\left(\sqrt{n+1+1/x} - \sqrt{n+1/x} - \frac{1}{\sqrt{n+1/2+1/x}}\right)$$

where τ_i is the inelastic scattering relaxation time, τ_{so} is the spin–orbit relaxation time—i.e. the time over which the electron loses memory of its spin direction owing to scattering—and B is the magnetic induction. D is the diffusion constant such that $\sigma = e^2DN(E_F)$ where N is the density of states at the Fermi energy.

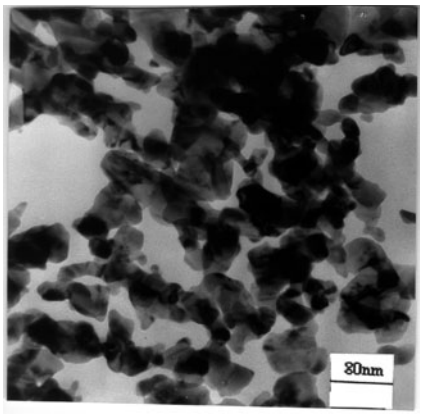

Figure 1. A bright-field TEM micrograph of the Au thin film.

In our Au samples, at very low temperatures, τ_i^{-1} is small compared to τ_{so}^{-1} and thus $\Delta\sigma(B)$ is negative because the magnetoconductivity is dominated by $f(B/B_i)$. At higher temperatures where τ_i^{-1} is large compared to τ_{so}^{-1}, $f(B/B_{so})$ is equal to $f(B/B_i)$ and the magnetoconductivity is positive. At intermediate temperatures the magnetoconductivity starts negative and changes sign at a field where B is approximately equal to B_{so}.

4. Results and discussion

Figure 1 shows the microstructure of a section of the Au thin film. From this micrograph, it may be seen that the particle size covered a range from approximately 10 to 100 nm. The individual gold nanoparticles appear to have packed closely together in a disordered manner when water was evaporated from the film during drying and subsequently formed into chains and rings within the thin film due to the loss of the stabilizing ligand on annealing at 350 °C. From this micrograph, it may also be seen that most of particles are polycrystalline, having been formed from this coalescence of fine particles.

In a previous paper [3] we examined QIE in Ag–epoxy nanocomposites, where the Ag nanoparticles were produced by inert gas condensation. These results were complicated by the inhomogeneity of the microstructure consisting of a loose network of chains of Ag nanoparticles. We believe that this resulted from fusion of individual Ag nanoparticles during the condensation process. In this work, the use of a stabilizing ligand keeps the colloidal Au nanoparticles from coalescing. Thus, a high-density, close-packed structure can result when the water is removed from the colloid without fusion of individual particles taking place. The result is that when the ligand is finally removed and the particles fuse together, a much more homogeneous film is produced. Such a highly disordered film has a high resistivity and exhibits electrical properties similar to those of metallic glass alloys.

In figure 2 we show the temperature dependence of the resistivity. The resistivity is approximately 75 $\mu\Omega$ cm. This is not high enough to produce a negative temperature coefficient of resistivity (TCR) since in disordered metals negative TCRs are usually observed for homogeneous metals with a resistivity over 150 $\mu\Omega$ cm—the Mooij correlation [2]—but the much reduced positive temperature coefficient is consistent with the Mooij correlation. The resistivity is high enough for the QIE to be observed in the magnetoresistance. This is similar to the behaviour of amorphous metal alloys such as MgAl and MgZn [7] which have a similar resistivity and small positive TCR but a negative magnetoresistance due to QIE.

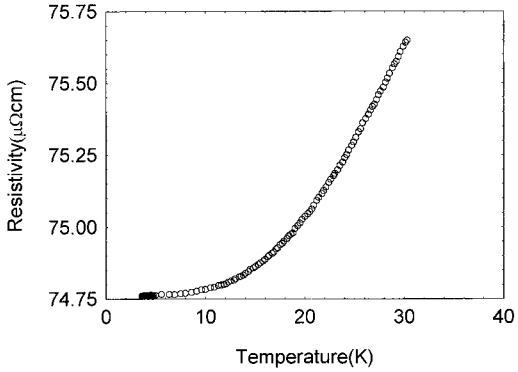

Figure 2. The temperature dependence of the resistivity.

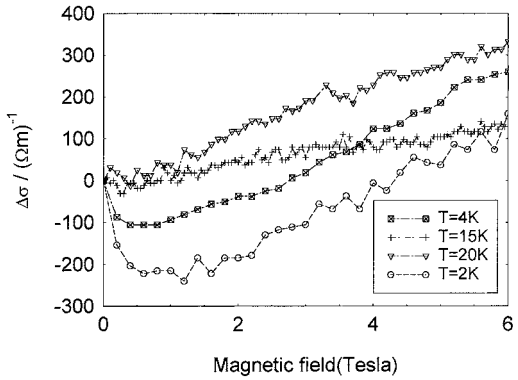

Figure 3. The magnetoresistance at 2, 4, 15 and 20 K.

We have measured the magnetoconductance at several temperatures and, for clarity, show the data for 2, 4, 15 and 20 K in figure 3. The noise level is a little high at about 2 parts in 10^5 and is attributable to the poor contact resistance of approximately 100 Ω between the Au contacts and the deposited colloid which was unavoidable. For temperatures below 15 K there is a negative magnetoconductance at low fields which crosses over to positive at higher fields. The crossover field increases as the temperature is lowered. As discussed above, this is typical for samples with spin–orbit scattering for which τ_i and τ_{so} are similar in magnitude.

In figure 4 we show magnetoconductance fits made using equation (1). The only fitting parameters are B_i and B_{so} which depend on τ_i and τ_{so} but also on D. We have estimated D from the Einstein relationship $\sigma = e^2 DN(E_F)$ and we estimate N using the free electron approximation and assuming that the density is close to that of normal Au. τ_{so} is temperature independent so we did a global fit keeping τ_{so} constant for all temperatures. Doing this we find that τ_{so} is approximately 10^{-12} s.

In figure 5, we show the values of inelastic relaxation rate, τ_i^{-1}, for our nanostructure Au. For comparison we also show the values determined for the amorphous metal alloy Cu–Ti–Au [5, 6]. These data suggest that in the temperature range 4–20 K, $\tau_i^{-1} \propto T^{-3}$. This kind of behaviour is predicted for disordered metals; it is Bloch–Grüneisen-like but with the relaxation of phonon scattering selection rules typical for a disordered metal [8].

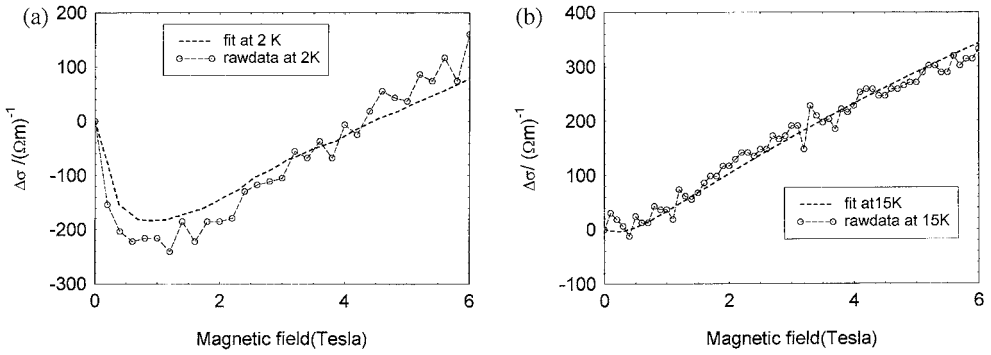

Figure 4. The magnetoconductances at 2 and 15 K fitted using equation (1).

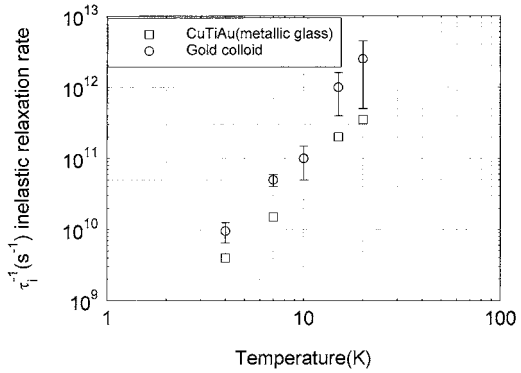

Figure 5. The inelastic relaxation rate for nanostructure Au and that for the amorphous metal alloy Cu–Ti–Au for comparison.

5. Conclusions

We found QIE in nanostructured Au, produced by a chemical method, similar to those found in metallic glasses and used the magnetoresistance to determine the spin–orbit and inelastic scattering rates.

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