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Transport phenomena in polymer-graphite composite materials

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The dc electrical resistance of a polymer-graphite composite has been studied in high magnetic fields (<10 T) and at low temperatures for different concentrations of graphite. The resistivity of the composites for the high graphite concentrations was much greater ($>10^4$) than that of pure graphite, and above a critical concentration of graphite a percolative behavior occurred. In addition to the ordinary positive magnetoresistance, an anomalous negative magnetoresistance at low fields was observed in the composite, but not in pure graphite. The data are explained in terms of contact resistances between adjacent graphite particles, with a special emphasis on the bidimensional aspect of graphite.

The interest in composite materials has grown for a few years because of the large diversity of their physical properties and their applications in many domains. Among them, polymer–carbon-black composites are used widely in electronics, antistatic materials, records, magnetic shieldings, etc.[1] A few studies have already been done on systems like granular metals[2,3] and polymer–carbon-black composites[4,5] where the temperature dependence of the resistivity was explained in terms of hopping or thermally assisted tunneling between the conducting particles. We have investigated a composite material containing graphite, which is much purer and crystallographically better defined than carbon black. The magnetoresistance measurements have been used to study the electrical-transport problem of conducting particles (graphite) dissolved in an insulating medium (polystyrene). The resistance is determined not only by the percolation path through the sample, but also by the contacts between particles. It will be shown that the magnetoresistance data give information about the type of contact between particles. Pierre and Deltour[6] have studied a composite made up of a polymer (polystyrene) and copper particles, and have also found that the contacts between the particles are determinative in the transport properties.

The samples investigated were made of a polymer matrix (polystyrene) containing dispersed graphite particles (KS6, Lonza A.G., Siens CH5643, Switzerland) ranging from 1 to 8 μm in size, with an average of 3 μm. Each particle consisted of a few flakes of graphite (mean size $1\times1\times0.1$ μm^3) held together by van der Waals forces, and each flake contained single-crystalline domains larger than 60 nm. The samples were prepared by dissolving the polystyrene in xylene and then mixing in the graphite powder. This solution was poured onto a glass slide; evaporation of the solvent left films with a thickness of about 250 μm. All resistivity measurements were done at liquid-helium temperature using the four-probe method. The magnetic field was generated by a 10 T superconducting coil. To characterize the starting material, we also did resistivity measurements on pressed pellets of pure graphite.

In Fig. 1 we have plotted the electrical resistivity of the samples as a function of the volumetric concentration of graphite. The resistivity shows a percolation transition with an infinite value at low concentrations of graphite where the particles form small isolated clusters, and with finite values at higher concentrations due to the occurrence of conducting paths. The percolation transition is a phase transition and, hence, has its own critical exponents. Close to the transition the resistivity ρ can be written[7] as

$$\rho(c)=a(c-c_0)^{-Q}\quad(c\geq c_0)\ , \tag{1}$$

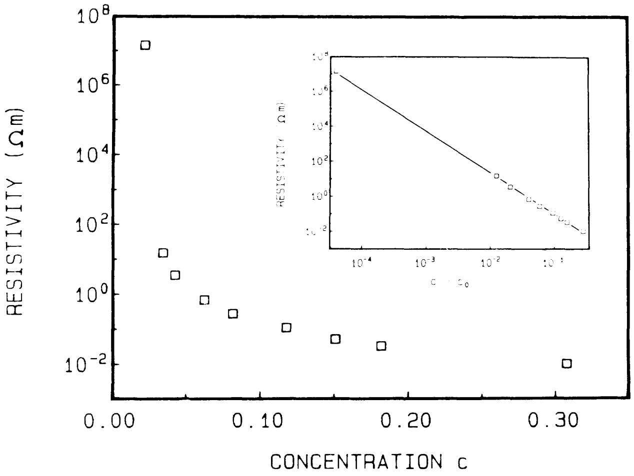

FIG. 1. Resistivity ρ of polystyrene-graphite composites as a function of the volumetric concentration c of graphite. A percolation transition occurs at $c_0\simeq0.02$. The inset shows the resistivity ρ vs $c-c_0$ on a double-logarithmic scale. The straight line has a slope with $Q=3.5$ [see Eq. (1)].

where c is the concentration of metallic particles in the insulating matrix and c_0 the concentration at the percolation threshold. Q is the critical exponent for the resistivity and lies between 1.6 and 1.7 in a three-dimensional system. In the inset of Fig. 1, the resistivity data are plotted on a double-logarithmic scale, yielding $Q = 3.5 \pm 0.3$ according to Eq. (1) with $c_0 \simeq 0.02$. This is not the theoretically expected value for a percolation problem. Obviously, more data points close to the threshold have to be taken into account for a proper estimation of the critical exponent. Moreover, the contacts between particles play an important role in the measured resistance. This can be seen in the high-concentration domain of Fig. 1, where the resistivity is 10^4 times that of pure graphite which, in our case, has a resistivity of 5.9×10^{-7} Ω m at 4.2 K. The increased resistance of concentrated samples is explained by contact resistances (tunneling or metallic constriction) between the particles. In the high-concentration region (far beyond the critical threshold where percolation can be neglected) the value of this contact resistance will be roughly 10^4 times greater than the resistance R_G of a single graphite particle. From the measured resistance of the pure-graphite pellet, we get $R_G \simeq 0.2$ Ω for a particle size of 3 μm. The contact resistance R_{contact} is then of the order of 2 kΩ. These contact phenomena depend on the volumetric concentration and are difficult to include in a theory of percolation.[7]

In view of the following magnetoresistance data, let us briefly discuss the various types of contacts that can take place between two graphite particles in the composite. To give a quantitative estimate of the contact dimensions, we will consider the most concentrated samples, where the contact resistance is of the order of 2 kΩ. The transport of current between particles can occur via a tunneling (or hopping) process or through a metallic constriction. Both contact phenomena will have a different behavior in a magnetic field. A tunneling resistance is not expected to be dependent on the magnetic field, whereas the resistance of a metallic constriction can depend on the magnetic field because of the resistivity of the material forming the contact. The relevant expression for the resistance of a metallic contact depends on the values of the mean free path l of the electrons and the contact dimension (radius a for a circular contact) with respect to each other. For a contact in the dirty limit ($l \ll a$), the resistance R_M is obtained from the Poisson equation, yielding[8] $R_M = \rho/2a$. For a clean contact ($l \gg a$), the resistance R_S is given by the Sharvin formula[9] $R_S \simeq \rho l/a^2$. For a contact resistance of 2 kΩ and with $\rho l \simeq 3 \times 10^{-14}$ $\Omega\,\text{m}^2$ for pure graphite, we obtain, with the latter expression, a contact radius $a \simeq 4$ nm. As the mean free path of the electrons in the graphite is greater (50 nm) than this value, only the Sharvin term is of importance for the contacts between graphite particles, and the Maxwell term can be ignored. The Sharvin expression is independent of the electronic scattering ($\rho \propto l^{-1}$) and, therefore, is independent of the magnetic field. The resistance of both a metallic contact in the clean limit and of a tunneling contact is constant in a magnetic field. However, it must be remembered that the conductivity in crystalline graphite is highly anisotropic. Indeed, due to the layered structure of graphite,[10] the conductivity is roughly a factor 10^3 greater in the planes than perpendicular to the planes. Near a small contact on a graphite sample, the pattern of the current is very anisotropic with most of the electrical current flowing only in the first layer of graphite. In such a situation, the contact resistance can be modeled by the resistance of a thin slab with one contact in the middle of the slab and another at the boundary. For such a Corbino geometry,[11] the resistance is of the order of the square resistance $R_{\text{sq}} = \rho/d$. The relevant thickness is given by the interplanar distance $d = 3.35$ Å. With the measured bulk resistivity (mainly determined by the in-plane conductivity for the polycrystalline graphite) we obtain $R_{\text{sq}} \simeq 2$ kΩ. The occurence of this two-dimensional contact phenomenon is especially important for contact dimensions smaller than 300 nm (interplanar distance times conductivity anisotropy). This quantitative analysis to model the contact between graphite particles in the composite is only a rough estimate. The total metallic contact resistance will be a combination of a Sharvin resistance and a square resistance. In the composite, a graphite particle can have more than one contact with the other particles, which can be tunnel junctions or metallic contacts, or even a combination of both. The measured (magneto)resistance of the samples is an average of the whole composite system (which depends on the concentration of graphite particles) with, in addition, a percolative problem. However, even for a tunneling junction between particles, the contact resistance includes a series resistance given by the square resistance R_{sq}.

The existence of this square resistance has been experimentally observed with the following point-contact set up. We mounted an electrochemically edged gold point on a piezoelectric ceramic and, using a differential screw system, brought the point close to the surface of a highly oriented pyrolytic graphite (HOPG) sample (with axis of

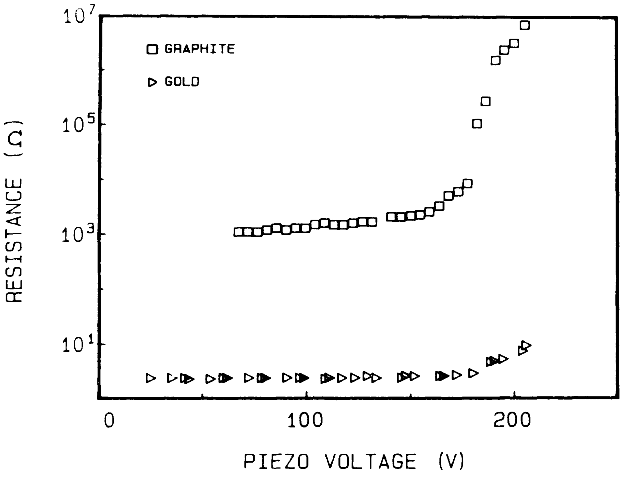

FIG. 2. Resistance of a point contact between a gold point and a HOPG single crystal as a function of the piezovoltage for adjusting the contact. The plateau is in the kΩ range. For a gold sample the plateau is in the Ω range.

the point perpendicular to the graphite planes). Upon varying the piezovoltage, we could make a slight contact between the point and the sample in controllable way. By measuring the resistance as the point approached the sample, we found that it changed from an infinite to an intermediate value, and finally reached a constant value in the kΩ range (see Fig. 2). We ascribe this value to the square resistance R_{sq}. With a gold sample, the resistance of this plateau was in the Ω range (though ρl was only 10 times smaller than in the case of graphite) and was due to a metallic constriction of the Sharvin type.

In Figs. 3 and 4 we have plotted the relative change of resistance $\Delta R(H)/R_0$ versus magnetic field for samples with different concentrations of graphite. In the high-field region of Fig. 3 the magnetoresistance is linear. The relative change in the magnetoresistance is maximal for the pure-graphite sample (solid circles) and decreases with decreasing concentration. At low fields (<3 T), a negative magnetoresistance is observed (Fig. 4), which is absent in the pressed-graphite sample.

We will discuss first the positive component in the magnetoresistance data. Because of the similar behavior of the composite material and pure graphite, the observed positive magnetoresistance in the composite materials must be due to the magnetic field dependence of the resistivity of the graphite particles themselves. Linear behavior is typical of polycrystalline materials and, in our case, is related to the randomly oriented graphite cristallites. Moreover, the observed magnetoresistance is isotropic and does not depend on the orientation of the sample with respect to the magnetic field. Upon dilution, the absolute resistance of the composite varies by 7 orders of magnitude with respect to the pure-graphite pellet (Fig. 1), but $\Delta R(H)/R_0$ is of the same magnitude for all samples. Because the ratio $\Delta R(H)/R_0$ for the relative magnetoresistance is independent of the percolation problem, the magnetoresistance of the whole sample can be considered on the basis of the magnetoresistance of the particles themselves, including the contact phenomena. We can then separate $\Delta R(H)/R_0$ into two parts:

$$\begin{aligned}\frac{\Delta R(H)}{R_0}&=\frac{\Delta R_G(H)+\Delta R_{\text{contact}}(H)}{(R_G)_0+(R_{\text{contact}})_0}\\&=\frac{\Delta R_G(H)+\Delta R_S(H)+\Delta R_{\text{sq}}(H)}{(R_G)_0+(R_S)_0+(R_{\text{sq}})_0}\\&\simeq\frac{\Delta R_{\text{sq}}(H)}{(R_S)_0+(R_{\text{sq}})_0}=\frac{(R_{\text{sq}})_0}{(R_S)_0+(R_{\text{sq}})_0}\frac{\Delta R_{\text{sq}}(H)}{(R_{\text{sq}})_0}=\alpha(c)\frac{\Delta R_{\text{sq}}(H)}{(R_{\text{sq}})_0}\ ,\end{aligned}\tag{2}$$

where R_G and R_{contact} refer to the intrinsic resistance of one graphite particle and the contact resistance, respectively, and the index 0 is given for the zero-magnetic-field values. R_S is the magnetic-field-independent contact resistance (Sharvin or tunneling type). The factor $\alpha(c)=(R_{\text{sq}})_0/[(R_{\text{sq}})_0+(R_S)_0]$ depends on the graphite concentration. Since $R_{\text{contact}} \gg R_G$, the relative magnetoresistance would be very small for a magnetic-field-independent contact resistance and not at all comparable to $\Delta\rho(H)/\rho_0$ for the pure-graphite sample (Fig. 3). Assuming a large contribution to the contact resistance from the square resistance R_{sq} of the graphite planes, the

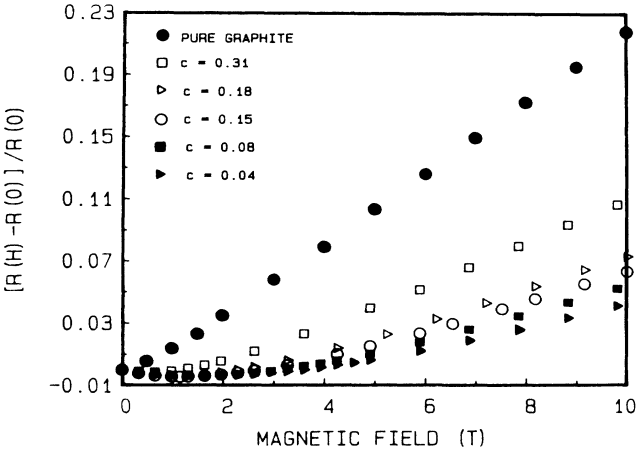

FIG. 3. Relative magnetoresistance of polystyrene-graphite composites with different graphite concentrations c. The solid circles represent the magnetoresistance of pure graphite, which is always positive.

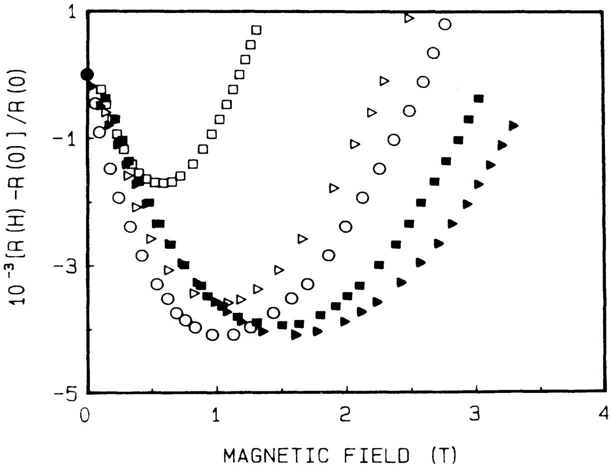

FIG. 4. Enlarged view of the low-field region of Fig. 3, showing the negative magnetoresistance of the composite for all concentrations (same symbols as in Fig. 3).

magnetoresistance data of Fig. 3 can be understood quantitatively. The decrease in the linear term of the magnetoresistance upon dilution can be explained by an additional contact resistance R_S from a Sharvin constriction (or from tunneling), the value of which increases with decreasing graphite concentration.

The observation of the negative magnetoresistance in the composite at low fields is clearly related to the contact dimension between particles. In the composite, the magnetoresistance is always negative at low fields, but is weakened as the graphite concentration increases. For a pellet of pressed graphite particles, the magnetoresistance is always positive as seen in Fig. 3 (solid circles). However, if a sharp gold point is brought into contact with this pellet, the negative effect in the magnetoresistance reappears. In the case of pure graphite, the particles are compressed against each other with large contacts between particles. For the composite, the contact dimension is of the order of 10 nm and decreases with decreasing graphite concentration. The very small size of the contacts between particles emphasizes the bidimensional structure of graphite via the additional square resistance $R_{\rm sq}$, due to one or a few layers of graphite. The negative behavior of the magnetoresistance has already been observed in pure or intercalated graphite fibers,[12–14] where it was attributed to weak localization.[15,16] Weak localization is due to a quantum interference in the elastic diffusion of the conduction electrons on the impurities (or defects) in the system.[17,18] This process amplifies the backscattering of the electrons, giving a decreased conductivity with respect to the classical case. The inelastic collisions destroy the quantum interference, and an increase in conductivity is observed with increasing temperatures. For the two-dimensional (2D) case, this results in a logarithmic temperature dependence of the conductivity at low temperatures.[17,18] In a sample with a volumetric concentration $c=0.17$ (thus, far from the threshold value $c_0 \simeq 0.02$), we indeed observed an increase of conductivity between 1 and 70 K with a logarithmic temperature dependence.[20] At higher temperatures the conductivity decreased again (metalliclike), as expected for pure graphite. If we apply a magnetic field, we introduce an extra phase which suppresses the quantum interference and the conductivity again increases; we then have a negative magnetoresistance. The magnetic field dependence of the 2D weak-localization effect can be described[19] by

$$\Delta R_{\rm sq}(H) = -(R_{\rm sq})_0^2 F(H,\tau) \ , \tag{3}$$

where the function F depends on the magnetic field H and on the various collision times τ for elastic and inelastic electron scattering. From Eq. (3) it is obvious that the square resistance between two particles in the composite increases the localization compared to bulk graphite. The experimental magnetoresistance data are the sum of a positive classical contribution discussed above and a negative quantum-mechanical contribution due to the localization effect:

$$\frac{\Delta R(H)}{R_0} \simeq \frac{[\Delta R_{\rm sq}(H)]_{\rm classical} + [\Delta R_{\rm sq}(H)]_{\rm quantum}}{(R_{\rm sq})_0 + (R_S)_0}$$
$$= \alpha(c) \frac{\Delta\rho(H)}{\rho_0} - \alpha(c) R_{\rm sq} F(H,\tau) \ , \tag{4}$$

where $\alpha(c) = (R_{\rm sq})_0 / [(R_{\rm sq})_0 + (R_S)_0]$ depends on the concentration. In Fig. 5 we have plotted the experimental data with the classical and quantum-mechanical contributions to the magnetoresistance for two different concentrations of graphite in the composite. The classical magnetoresistance was taken from the pressed-graphite sample (solid circles in Fig. 3) using a corresponding multiplication factor $\alpha(c)$ such that the high-field slopes of the composite and pure graphite coincide. From the difference between the experimental data and the deduced classical contribution to the magnetoresistance, we can find the quantum-mechanical contribution. We observe (Fig. 5) that the classical magnetoresistance decreases with decreasing graphite concentration, whereas the quantum-mechanical contribution increases slightly. From Eq. (4) we should expect that both contributions should decrease by the same factor $\alpha(c) = (R_{\rm sq})_0 / [(R_{\rm sq})_0 + (R_S)_0]$. It is possible that, with dilution of the composite, there is not only a decrease in the factor $\alpha(c)$, but also an increase in the averaged value of $R_{\rm sq}$ (the number of graphite planes contributing to $R_{\rm sq}$ decreases), yielding a different factor for the classical $[\alpha(c)]$ and the quantum-mechanical $[\alpha(c) R_{\rm sq}]$ contributions to the magnetoresistance.

We have studied the magnetoresistance of polystyrene-graphite composites and discussed the experimental results in terms of small contacts between graph-

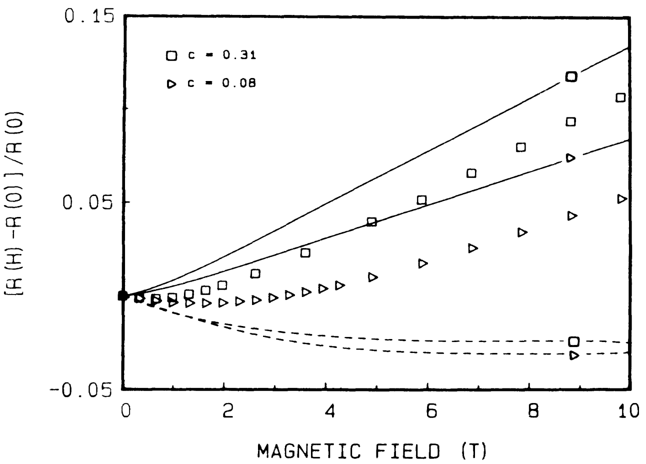

FIG. 5. Experimental magnetoresistance for two different concentrations of graphite in the composite (data points are for $c=0.31$ and 0.08). The solid lines show the positive classical contribution obtained from the pure graphite data and the dashed lines show the negative quantum-mechanical contribution, which is the difference between the experimental data and the classical effect.

ite particles. The magnetoresistance data are explained by a balance between a positive classical contribution similar to the bulk graphite and a negative quantum-mechanical effect due to a 2D localization of the electrons in the graphite planes. Both effects are enhanced by the small size of the contacts between graphite particles, because the square resistance R_{sq} of one (a few) graphite plane(s) has a dominant contribution to the total contact resistance between the graphite particles in the composite. For the graphite concentrations studied (relatively far beyond the percolation threshold) the contacts seem to be metallic and not of the tunneling type.

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