Electron localization in a percolating network: An ESR study of carbon-black/polymer composites

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The electronic susceptibility χ_e of conducting composites of carbon-black particles embedded in a nonconducting polymer matrix has been measured over a wide concentration and temperature range by electron-spin resonance (ESR). The onset of an extra Curie contribution to χ_e below 10^2 K is seen as evidence for electron localization, as is the narrowing of the ESR line below 50 K. We show that Coulomb interactions have to be taken into account to explain these data and that the magnitude of the interaction is consistent with the value found previously from dc-conductivity data. [S0163-1829(97)00515-8]

In carbon-black/polymer composites a conducting carbon-black (CB) filler is embedded in an insulating polymer matrix.[1,2] In such a material electronic transport proceeds via variable range hopping of charge carriers between localized states.[3,4] Previously,[5] we have studied the dc conductivity of a series of CB/polymer composites with an extremely low percolation threshold p_c of 0.03 vol %.[6,7] Up to the highest CB concentration of $33p_c$, the experimental data could be described[5] by a generalized variable range hopping expression, i.e., $\sigma(p,T) \propto \exp[-(T_0/T)^{0.66}]$. $T_0 = 112 \pm 15$ K was found to be independent of concentration and shown to be inversely proportional to the localization length of about 100 nm.[5] The value of T_0 is of the order of the Coulomb energy needed to create two charges with opposite sign on neighboring CB particles (charge disproportionation energy). Because Coulomb interactions between carriers and localization of carriers are not only of importance in the transport behavior but also in the susceptibility of composite materials,[8,9] we performed electron-spin resonance (ESR) measurements on samples of the same batch as used in the dc measurements. We show how the temperature dependence of the electron spin susceptibility χ_e and linewidth can be understood and stress the importance of localization due to Coulomb interactions.

Our experiments concern 15 composites consisting of different concentrations of carbon-black as filler material in an insulating thermoset polymer, which are numbered CB1 ($p = 33p_c$) through CB15 ($p = 1.3p_c$) in order of decreasing CB concentration. The CB particles are hollow semispherical particles with a diameter of about 30 nm, composed of two to four turbostratic graphitic layers. We measured the susceptibility of CB1 with a superconducting quantum interference device magnetometer and found that at high temperatures the paramagnetic spin contribution is too small to be resolved from the diamagnetic term. This made us use ESR experiments to study the electronic susceptibility of the CB composites.

The ESR experiments were performed by means of a JEOL X-band spectrometer equipped with an Oxford Instruments flow cryostat. For accurate temperature readings, an extra thermocouple was mounted very close to the sample. The ESR signal always had a single Lorentzian line shape, down to the lowest temperatures. The susceptibility was calibrated[10] with a diphenylpicrylhydrazyl (DPPH) standard with a known number of free spins with pure Curie behavior, i.e., $\chi_C = C/T$.

In Fig. 1 the electronic susceptibility χ_e is plotted versus temperature T. For clarity we show the data of a representative selection of samples covering the whole range of CB concentration. The room-temperature values of the susceptibility, when normalized to the amount of CB, are for all samples the same. This proves that only the susceptibility of the carbon-black itself contributes significantly to the ESR

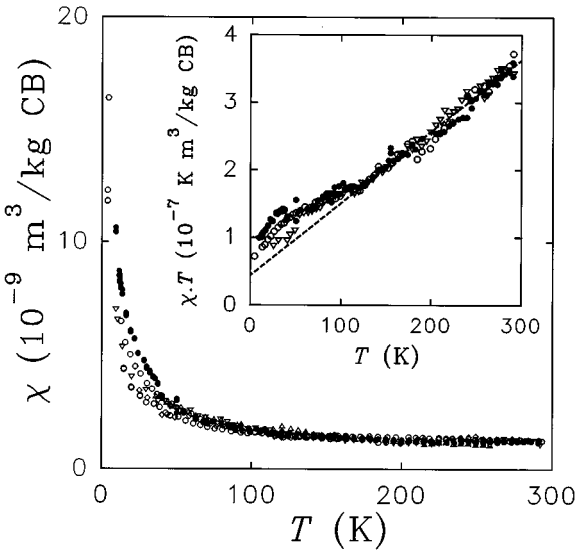

FIG. 1. T dependence of the normalized susceptibility of six representative CB samples: ○, $33p_c$; ●, $25p_c$; ◇, $16p_c$; □, $12p_c$; △, $7.3p_c$, and ∇, $3.5p_c$. In the inset $\chi_e T$ is plotted versus T for three samples with $p \geq 16p_c$; the dashed line is a straight line fit to the high-T data (see the text).

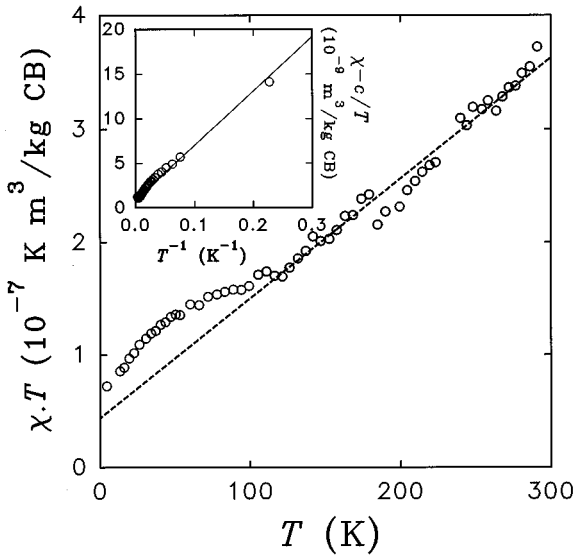

FIG. 2. $\chi_e T$ vs T for CB1 as a typical example shows the growth of a second Curie contribution between 100 K and 50 K; the dashed line is the same as in Fig. 1. The inset with χ_e vs $1/T$ stresses the low-T Curie tail (after subtraction of the first Curie contribution). The solid line is a fit to the Kamimura model (see the text).

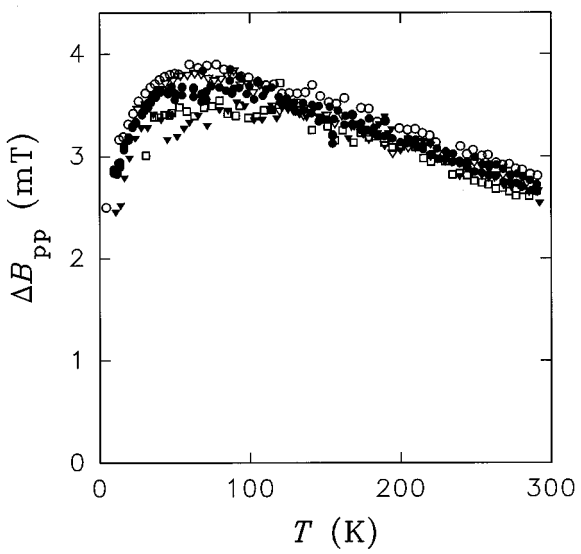

FIG. 3. T dependence of the linewidth of a representative set of CB samples ranging from $33p_c$ to $3.5p_c$; symbols are the same as in Fig. 1.

data. Only in CB15 with p very close to p_c (omitted) does the additional contribution from the matrix become of importance. At high temperatures χ_e is T independent (Pauli-like), which is typical for delocalized electrons, while a Curie-like contribution, characteristic for localized states, dominates at low temperatures. In the inset we show the data for three samples with $p \geqslant 16p_c$ in a $\chi_e T$ vs T plot. A Pauli susceptibility (χ_P) will give a straight line through the origin, a Curie term (χ_C) a horizontal line. The dashed line is a straight line fit to the high-T data. In Fig. 2 the data set of CB1 ($p = 33p_c$), which due to the highest CB-concentration has the best signal-to-noise ratio, is presented in the same way. By plotting the data versus $1/T$ (inset), low temperatures get more emphasis. The drawn line is a theoretical fit, discussed below. Figure 3 illustrates the temperature dependence of the peak-to-peak linewidth ΔB_{pp}. The data clearly show a maximum in ΔB_{pp} around 50 K of about 1.5 times the room-temperature and low-temperature value of 2.5 mT.

ESR results on χ_e in carbons, like in graphite, show at low temperatures a Curie-like behavior due to localized spins (dangling bonds[11–13]) of about 10^{18} spins per gram of carbon. At high temperatures charge carriers give a Pauli-like contribution. At room temperature the ratio of the susceptibilities due to delocalized and localized spins is about 2:1 for well-pyrolyzed samples. The localized spins interact by exchange with the conduction electrons, mixing the g values and the ESR widths,[12,14] leading to a single Lorentzian line.

Also the CB particles in the CB/polymer composites contain, apart from the delocalized Pauli spins, localized Curie spins. To visualize χ_C we show in Fig. 2 $\chi_e T = (C + \chi_p T)$ vs T for CB1. Above 125 K the Curie constant C is T independent (the normalized Curie contribution is similar for all p's). The Pauli contribution to χ_e amounts to $(1.0 \pm 0.1) \times 10^{-9}$ m^3 per kilogram of CB for all samples.[15–17] This value is also cited by Mrozowski.[11] Below approximately 100 K (see Fig. 2) a second Curie-like contribution becomes prominent, not present in the data above 125 K, while the slight change in the slope indicates an enhancement of the Pauli contribution. Calibration by DPPH of the number of spins shows that this new Curie part arises from about 10^{21} spins per kilogram of CB, averaged over all samples. This value corresponds to about one spin per CB particle since there are approximately 5×10^{25} carbon atoms per kilogram and 2×10^5 carbon atoms per CB particle in the samples.

To explain this observation, we incorporate the effect of Coulomb interactions in the electronic susceptibility as done by Kamimura.[8] In the model the total number of carriers is taken to be conserved and the sites can be empty or singly or doubly occupied. Three characteristics of the carriers are presumed: (i) electronic states are Anderson localized, (ii) there exists a random distribution $P(E) = 1/W$ of the electronic site energies, with bandwidth W, and (iii) the on-site Coulomb interaction U is taken into account for the occupation of the electronic states.

At temperatures $k_B T < U$, singly occupied states give rise to a prominent Curie contribution to the electronic susceptibility. As the temperature rises above U/k_B, also states with excitation energy U can be occupied. Thus there is a coexistence of singly and doubly occupied states, whose contributions to χ_e are different:

$$\chi_e(T) = \frac{2\mu_B^2}{k_B T} \sum_i \{2 + \exp[\beta(\mu - \epsilon_i - U_i)] + \exp[-\beta(\mu - \epsilon_i)]\}^{-1}, \quad (1)$$

in which $\beta = 1/k_B T$, U_i is the average on-site Coulomb interaction, and the summation is taken over all states in the energy band W. At low temperatures the spin susceptibility, given by Eq. (1), obeys the Curie law $\chi_e \approx \mu_B^2 N_s / k_B T$. Fur-

thermore, the ratio of the number of singly occupied states N_s to the total number of carriers N is proportional to W/U.

The Curie part gives the number of singly occupied states to be $N_s \approx 10^{21}$ per kilogram of CB. Furthermore, from the temperature at which the Curie contribution becomes prominent (see Fig. 2) the on-site Coulomb repulsion is estimated to be $U/k_B \approx 10^2$ K. The final susceptibility fit by Eq. (1) is shown in the inset of Fig. 2 and gives a value for W of about $40U$. The parameter $U \sim 10^2$ K is the on-site Coulomb repulsion. This energy equals the ionization energy of a particle minus its electron affinity,[18] resulting in $e^2/4\pi\kappa R$, with R the mean radius of the particle and $\kappa \approx 4$ the dielectric constant of the composite. The calculated value for a 30-nm-diam particle is indeed 10^2 K. The singly occupied states (localized spins) in the CB system might be linked to ionized grains, expected to be present in the ground state of, e.g., granular metals.[18,19] At temperatures much lower than T_0 the value of U will be a measure for the Coulomb repulsion in a region of the size of a CB particle. For $T > T_0$ hopping will become much faster and U will become negligible by screening. So, for $T < (T_0, U/k_B)$, χ_e will be Curie-like; for $T > (T_0, U/k_B)$ the role of Coulomb energies can be neglected and χ_e will be Pauli-like.

The Coulomb interaction will also lead to a Stoner enhancement[20] of the Pauli susceptibility. The slight change in slope in Fig. 2 at low temperatures can be explained in this way.

Let us compare the ESR linewidth plotted in Fig. 3 to the data for graphite and carbons. Highly oriented graphite has an intrinsic linewidth of a few millitesla; the g value is anisotropic and $g_\parallel$ is found to be T dependent.[13,16] In powders such a temperature-dependent anisotropy can in itself cause the linewidth to be temperature dependent. Note that this cause of line broadening is proportional to the applied static magnetic field. In the carbon data discussed by Mrozowski[11] and Delhaes and Carmona[12] the anisotropy in g values is averaged away. The conduction electron makes a large number of hops between spin flips leading to motional narrowing. The final line becomes symmetric. The width found experimentally typically goes with $T^{-1/2}$. To determine the importance of the g-value anisotropy in our CB samples, an ESR experiment has been performed at 35 GHz at room temperature. The obtained linewidth of 2.8 ± 0.2 mT is within the experimental error identical to that at 10 GHz. Apparently, g-value anisotropy is not dominant in the broadening.

The T dependence of the linewidth with its maximum ΔB_{pp} around 50 K is different from that of graphite, but is also seen in various types of carbon blacks.[12] Qualitatively the data can be understood as follows. At high temperature there is a continuous exchange between localized and delocalized spins. This process results in an exchange narrowing of the line and a single $g_{\rm eff}$. At the lowest temperatures the ESR signal is dominated by localized spins. In the transition regime between these two extremes line narrowing becomes less effective (viewed from the high-temperature side). Viewed from the low-temperature side lifetime broadening $\Delta B \sim 1/\gamma T_1$, with γ the gyromagnetic ratio, becomes more important. In the model of Movaghar *et al.*[21] T_1 arises from a spin-flip accompanying an electron hop: $1/T_1 \sim F\sigma_{\rm ac}^{\rm hop}$. Note that we used $\sigma_{\rm ac}$ to stress that the conductivity has to be measured at frequencies where the spin flips can affect the linewidth. As a consequence,

$$\Delta B_{pp} = \Delta B_{pp}(0) + \Delta B_{pp}(T) \sim \Delta B_{pp}(0) + F\sigma_{\rm ac}^{\rm hop}(T). \quad (2)$$

We will use the difference in linewidth between 50 K and 5 K of 1 mT as a measure for the lifetime broadening and obtain $T_1 \approx 10^{-8}$ s at 50 K. Because the spin-orbit coupling in carbon is 0.7×10^{-4} eV,[22] the correlation time for hopping as estimated from T_1 (Ref. 21) is a factor 10^4 shorter than T_1. The final value of 10^{-12} s for a typical hop is in agreement with the correlation time for a hop between nearest-neigbor CB particles as measured in the ac conductivity around 1 THz.[7,23]

Above 50 K the T dependence of the linewidth can be represented by $T^{-\alpha}$, with $\alpha \sim 0.25$, which is a factor 2 smaller than the value usually found in carbons.[11] Our data shown in Fig. 1 resemble the results of Chauvet *et al.*[24] on the susceptibility and linewidth in carbon nanotubes. At low temperatures the linewidth ΔB_{pp} and the conductivity $\sigma_{\rm dc}$ show a qualitatively similar temperature dependence. The high value for the spin-orbit coupling suggested in their explanation arises from the use of the dc conductivity instead of the high-frequency conductivity as done above.

In summary, the electronic susceptibilities of the investigated CB composites normalized to the CB content are the same. An intraparticle Coulomb interaction U of about 10^2 K together with characteristic hopping energies between well-connected regions of the same order of magnitude is shown to be responsible for the Curie behavior of the electronic susceptibility at low temperatures and the Pauli-like susceptibility above 100 K. Also the linewidth can be related to electron hopping. The characteristic hopping energy of 10^2 K is found to be consistent with the value of T_0 previously deduced from the conductivity data.

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