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Insulating and conducting phases of RbC_{60}

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Optical measurements were performed on thin films of Rb_xC_{60}, identified by x-ray diffraction as mostly $x = 1$ material. The samples were subjected to various heat treatments, including quenching and slow cooling from 400 K. The dramatic increase in the transmission of the quenched samples, and the relaxation towards the transmission observed in slow-cooled samples, provides direct evidence for the existence of a metastable insulating phase. Slow cooling results in a phase transition between two electrically conducting phases.

The Rb_xC_{60} system seems to have a very rich phase diagram. The $x = 0, 3, 4$, and 6 phases[1] were identified shortly after the discovery of superconductivity in intercalated C_{60}.[2] More recently a phase with one alkali-metal atom per fullerene ($x = 1$) was discovered.[3,4] With the exception of the superconducting $x = 3$ material, little is known about the electrical properties of the compounds; in fact the exact composition of the nominally $x = 3$ material is also debated.[5]

The present work has been motivated by the conduction-electron spin-resonance (CESR) experiments of Jànossy *et al.*[6] and by the NMR studies of Tycko *et al.*[7] Jànossy *et al.* studied a two-phase sample of Rb_xC_{60}, and decomposed the CESR signal into two contributions. They argued that the broader one originates from the superconducting $x = 3$ compound, while the narrower one comes from another phase. This signal exhibited a complex, history-dependent thermal behavior, with indications of a structural phase transition in slowly cooled samples and a metastable insulating quenched phase. Earlier x-ray studies on the $x = 1$ compound by Zhu *et al.*[8] established the existence of a rocksalt structure at high temperature, with a phase transition at around 120 °C. Jànossy *et al.* tentatively assigned the narrower CESR signal to the $x = 1$ material, and argued that it is a metal at high temperatures. On the other hand, Tycko *et al.*[7] interpreted NMR results on RbC_{60} in terms of a paramagnetic insulator. We set out to explore this compound by utilizing the direct link between IR transmission and conductivity.

Optical measurements in the IR regime are helpful in the study of these compounds in two ways. First, the four IR active molecular vibrations are sensitive to the electronic state of the molecule; the $F_{1u}(4)$ mode at 1427 cm^{-1} in pure C_{60} exhibits a characteristic change in frequency and intensity as the doping proceeds.[9–11] Second, mobile electrons in a metallic phase lead to an overall reduction of the transmission t; in first approximation, $t \approx 1/\sigma_1^2$, where σ_1 is the real part of the conductivity. For frequencies below the relaxation rate of the charge carriers, the IR transmission can serve as a good indicator of the conductivity, although the accurate evaluation of $\sigma(\omega)$ requires performing full Kramers-Krönig analysis of the data.

The two thin film samples used in this study were prepared in sealed chambers, made to allow for controlled doping and for cooling and heating over a wide temperature range.[12] The pristine C_{60} was deposited on high resistivity silicon substrates. The thicknesses of the films were $d = 2.5$ μm for sample I and $d < 1$ μm for sample II. The doping was performed in a Bomem MB-155 FTIR spectrometer allowing *in situ* infrared transmission measurements at 2-cm^{-1} resolution during doping. In order to achieve the best homogeneity the films were kept at an elevated temperature (125 °C, to increase the Rb diffusion rate) throughout the process. Rb was added in small quanta over several days, and the dc resistivity and the infrared transmission spectra were monitored. As demonstrated both experimentally[10,11] and theoretically,[13] the position of the intramolecular $F_{1u}(4)$ vibrational mode is a good indicator of the electronic composition of the doped fullerene film. The appearance of a single dominant resonance in the present sample (measured at 125 °C, see Fig. 1, top panel) indicates homogeneity of composition; the position of the peak, 1393 cm^{-1}, is clearly different from the position of the $F_{1u}(4)$ peak in pristine C_{60} (1427 cm^{-1}). The resistance of the sample dropped by several orders of magnitude, and the transmission dropped by more than a factor of 10, indicating that the doping produced an electrically conducting phase.

The doping method employed does not allow accurate determination of the sample stoichiometry. Therefore it is important to show that the conducting phase seen in the IR transmission is not the $x = 3$ material. To this end x-ray diffraction experiments were performed at the X3B1 beamline of the National Synchrotron Light Source, at Brookhaven National Laboratory on the very same specimens used in the IR studies. The incident wavelength was 0.764 Å with the diffracted beam collimated by 0.1° Soller Slits. Spectra were taken at 125 °C and room temperature in the angular range covering the (220), (311), and (222) reflections of the cubic unit cell of lattice spacing $\sim$ 14 Å. The small quantity of the sample and the thick silicon windows limited the structural information available, but we established unambiguously that the predominant phase in our specimens is identical to the rocksalt phase seen by Zhu *et al.*[8] At 125 °C two peaks are observed at $2\theta = 8.8°$ and $2\theta = 10.3°$. These correspond to the (220) and (311) peaks, respectively,

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of the rocksalt phase.[8] Similar diffraction peaks of the $x = 3$ material are at 8.6° and 10.1°; these peaks were very weak or totally absent in the two samples we studied. After slow cooling to room temperature the peak height decreased, and the width broadened, indicating that the sample had transformed in accordance with the observations of Zhu *et al.*[8] Our results are also in agreement with measurements on a slow cooled sample of RbC_{60} in a more recent x-ray study by Chauvet *et al.*[14]

In the IR experiments the samples were subjected to three thermal treatments (A, B, and C). In (A) the specimen was thermalized at 225 °C and it was slowly cooled to room temperature at an average rate of 5 °C/h, stopping at several fixed temperatures for taking the full IR spectrum. Treatment (B) was the inverse of (A), slowly heating from room temperature to 225 °C. In treatment (C) the sample was quenched from 225 °C by pouring liquid N_2 on it. After a few minutes of thermalization at low temperature, the sample was quickly warmed to a preset temperature below 60 °C. At each of these temperatures many IR spectra were recorded, and the relaxation from the quenched metastable phase to the equilibrium phase was studied.

The top panel of Fig. 1 shows spectra taken on sample I at 125 °C and at −10 °C during heat treatment (A). The top panel of Fig. 2 shows the temperature dependence of the transmission for treatments (A) and (B) at a fixed wave number, chosen to be 900 cm^{-1} to represent the broad band behavior, far away from the sharp vibrational resonances. Upon heating, treatment (B), the specimen exhibits a phase transition around 120 °C. The temperature hysteresis suggests that the transition is of first order. As confirmed by our x-ray data, this is the structural transition observed by Zhu *et al.*,[8] although the transition temperature seems to be sample dependent [120 °C,[8,4] 140 °C,[6] 70 °C,[7] and 90 °C (Ref. 14)].

The detailed evaluation of these transmission data indicates that the material is an electrical conductor. Reasonable plasma frequency and relaxation rate values can be deduced in a Drude fit, but the two parameters cannot be determined independently. For the high temperature phase a resistivity of $\rho = 18$ mΩ cm was obtained, approximately independent of the frequency in the measured range. At low temperature the conductivity is increased by about a factor of 2. Less than ideal film quality can conceal the metallic character in the measured dc resistivity,[15] but the magnitude of the resistivity indicates that, although electrically conducting, neither of the two phases is an ordinary clean metal.

Tycko *et al.* argue that in the high temperature phase the ^{87}Rb NMR data can be understood in terms of a paramagnetic insulator, with electron spins localized to C_{60} molecules.[7] The dc resistivity measurements on sample I seem to support this picture: it has a high dc resistance, and decreases at higher temperatures. How-

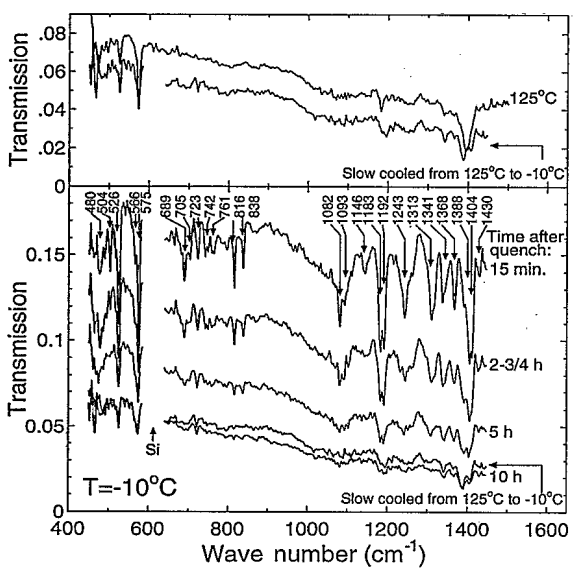

FIG. 1. The infrared transmission spectra of an RbC_{60} film (sample I) with various cooling histories. Top panel shows the spectrum at 125 °C and slow cooled [treatment (B)] to −10 °C. For the bottom panel, the sample was quenched [treatment (C)] from 125 °C to −50 °C. The temperature was then stabilized at −10 °C and spectra were obtained as the sample slowly relaxed from the quenched state into its equilibrium state. The labels beside each curve indicate the time passed since the quench. For comparison, the slow-cooled [treatment (B)] spectrum is also reproduced here. The 590 − 650-cm^{-1} region has a strongly temperature-dependent Si feature which is omitted. Positions of the vibrational absorptions are indicated.

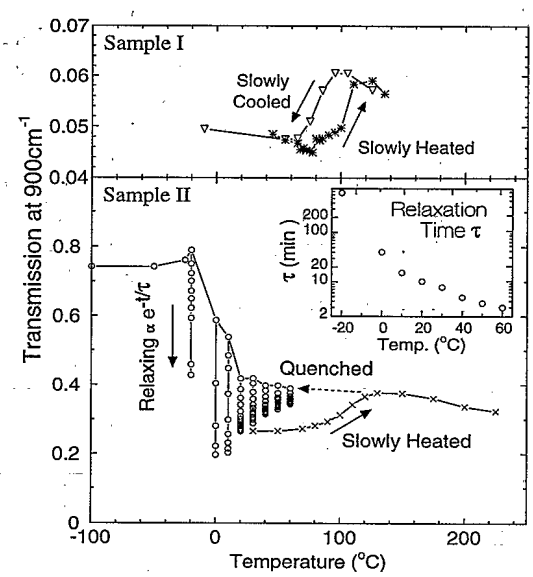

FIG. 2. Infrared transmission at a fixed energy (900 cm^{-1}) for slow cooling [treatment (A)], slow heating (B), and for the quenched state (C). The upper panel shows the hysteresis between (A) and (B) for sample I. The lower panel presents the temperature dependence of the quenched state (C) for sample II and its relation to the the slowly heated (A) data. The inset shows the relaxation time, τ (plotted on a logarithmic scale in minutes), at various temperatures. The overall transmission difference between the two samples is due to their different thickness.

ever, the dc resistivity can easily be dominated by grain boundaries. [The resistance seems to be very high even for the slow cooled state, for which the NMR (Ref. 7) and CESR (Ref. 6) data agree on the metallic character.] The IR transmission is less sensitive to grain boundaries. Above 120 °C the transmission was found to be slightly decreasing (sample II) as the temperature was raised.

In the slow-cooled phase, close inspection of the $F_{1u}(4)$ line shows it is split by about 16 cm^{-1} (1388 cm^{-1} and 1404 cm^{-1}). We believe that the splitting is due to crystal field effects. According to the NMR results[7] the rapid rotation of the C_{60} molecules (characteristic of the high temperature phase) stops below the phase transition. In pristine C_{60} the single $F_{1u}(4)$ line splits to three lines (separated by $\sim$ 3 cm^{-1}) when the molecular rotation ceases.[16] The doublet seen in our measurement can be due to stronger crystal fields with appropriate symmetry, related to the new low temperature structure,[14] such that two of the three $F_{1u}(4)$ modes are left degenerate. Another possible explanation is separation into x=0 and x=3 phases. However, the splitting we observe is not consistent with the x=0 and x=3 IR $F_{1u}(4)$ peak positions (1427 and 1363 cm^{-1}, respectively). Furthermore, Poirier *et al.*[4] have shown that RbC_{60} does not phase separate, even though KC_{60} does.[17]

The lower panels of Figs. 1 and 2 summarize the temperature- and time-dependent responses in heat treatment (C). Below 20 °C the quenched sample is an insulator, but it exhibits thermally activated relaxation towards the stable (conducting) phase. The relaxation is illustrated in the lower panel of Fig. 1, where spectra taken on sample I quenched to −10 °C are plotted. The temperature dependence of the transmission in the quenched state is better seen in the lower panel of Fig. 2. Here the transmission of sample II at 900 cm^{-1} is plotted as a function of temperature. The relaxation towards the slow-cooled state was recorded at several temperatures, repeating treatment (C) each time. The relaxation is well described by an exponential time dependence with relaxation time τ. The inset in the lower panel of Fig. 2 shows the relaxation time at several temperatures. For $T < -30$ °C, the relaxation is very slow and the quenched phase is metastable. Above the critical temperature of $T_c = 20$ °C the quenched state seems to be identical to the high temperature conducting phase, and exhibits a (fast) relaxation towards the slow-cooled conducting state.

Immediately after quenching the transmission is high and vibrational modes barely visible in the metallic state become pronounced. The four symmetry allowed IR active modes (F_{1u}) for the $x = 1$ phase appear at 526, 575, 1183, and 1404 cm^{-1}. The resonances in Fig. 1, lower panel, at 1430, 1368, and 1341 cm^{-1} correspond to the $F_{1u}(4)$ mode at $x = 0$, $x = 3$ or 4, and $x = 6$, respectively,[10,11] corresponding to a small amount of these phases in our film. The $F_{1u}(2)$ line at 566 cm^{-1} also originates from the $x = 6$ phase. These modes remain visible in both the high temperature and the slow-cooled metallic phases. The $F_{1u}(3)$ mode around 1183 cm^{-1} seems to be split, but this mode is not sensitive to doping[10,11] or crystal field effects.[16]

In the quenched state, a number of new modes are visible in addition to the four IR active vibrations allowed by the icosahedral symmetry of the C_{60} molecule. Many of these modes can be assigned to Raman active H_g and A_g modes seen in Rb doped C_{60}.[18,19] The resonances around 480, 742, 838, 1080, 1192, 1243, and 1313 cm^{-1} are near neutron scattering peaks[20] and were identified as fundamentals in a study on pristine C_{60} single crystals.[21] In contrast to the resonances due to the $x = 3$ and $x = 6$ impurity phases, all of these lines disappear as the relaxation proceeds, suggesting that they belong to the metastable $x = 1$ compound. The Raman and other optically silent modes may acquire IR activity if there is a symmetry breaking in the solid state as, for example, in the neighborhood of impurities. Other possibilities include the dimerization seen in organic charge transfer salts[22] or the charged phonon effect observed in low dimensional solids.[23]

For wave numbers corresponding to energies higher than the gap in the electronic spectrum, the IR transmission of an insulator is expected to be similar to its metallic state transmission. In our measurement the transmission of the quenched insulating state stayed high up to 4000 cm^{-1}, indicating a large band gap. If the phase transition is driven by an instability of the electronic system, the gap should be related to the critical temperature by a factor on the order of unity. In conjunction with a transition temperature around 290 K, the gap in this metastable insulating material seems to be large, $2\Delta > 8k_BT_c$.

In conclusion, we have established that the high temperature rocksalt structure of the $x = 1$ phase is electrically conducting. Upon cooling, a structural phase transition occurs leading to the splitting of the $F_{1u}(4)$ intramolecular vibrational line. The slow-cooled material is a better conductor. When the sample is quenched to low temperature, a metastable insulating state develops at temperatures below $T_c = 290$ K. In this phase the gap in the electronic excitation spectrum is rather large, for it does not show up in the measured frequency range extending up to 4000 cm^{-1} (320 meV).

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