Electrical Conductivity in Dynamically Orientationally Disordered Systems: ac and dc Measurements in Ferromagnetic Single Crystals of TDAE-C_{60}

A. Omerzu and D. Mihailovic
Jozef Stefan Institute, Jamova 39, 61111 Ljubljana, Slovenia

S. Tomic, O. Milat, and N. Biskup
Institute for Physics, University of Zagreb, P.O. Box 304, HR-10 000 Zagreb, Croatia

(Received 24 January 1996)

In spite of a metallic C_{60} molecular ground state, electrical conductivity measurements performed on single crystals of ferromagnetic TDAE-C_{60} fail to show evidence of metallic behavior. Instead, the material appears to be an insultor exhibiting conductivity of the form $\sigma(\omega, T) = \sigma_{\mathrm{dc}}(T) + \sigma_{\mathrm{ac}}(\omega)$. Phonon-assisted activated polaronic hopping and interbuckyball tunneling, respectively, are proposed as the mechanisms for the two processes. The transition from a dynamically disordered state (rotating buckyballs) to a quasiordered state (frozen buckyballs) is clearly visible as a change in activation energy in the conductivity at $T_0 = 150$ K. [S0031-9007(96)01107-6]

PACS numbers: 72.20.Jv

When the ferromagnetic behavior in tetrakis-(dimethylamino)ethylene-[60]fullerene (or TDAE-C_{60}) was originally reported [1] it was thought that because of the relatively high room-temperature conductivity ($10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$) of the powder samples and the Pauli-like temperature-independent dc susceptibility between 16 and 300 K, the material is a metal. Since TDAE transfers one electron to C_{60}—a fact confirmed by numerous measurements [2]—the highest occupied molecular orbital (HOMO) t_{1u} level of C_{60} is partially filled, and a metallic ground state could well be expected. The magnetism was therefore originally attributed to itinerant electrons. More recently, however, it was found that the susceptibility behavior above the magnetic transition (16 K) is actually rather complex and is strongly dependent on the degree of merohedral disorder of the C_{60} molecules [3]. The Pauli-like behavior originally observed could thus no longer be taken as evidence of a metallic ground state. Furthermore dc conductivity measurements of thin films and powders as a function of temperature have shown Arrhenius behavior [4] with activation energies in the range 0.3–0.5 eV. The insulating behavior of powders was confirmed in measurements of microwave conductivity by Schilder *et al.* [5], optical [6], and infrared studies [7], the latter suggesting a limit of $\sigma_{\mathrm{dc}}^{300\,\mathrm{K}} < 2\ \Omega^{-1}\,\mathrm{cm}^{-1}$.

However, powder grains of TDAE-C_{60} samples are typically rather small (typically 50 nm in size), so the surface-to-volume ratio is very large, and, combined with the high sensitivity of the material to oxygen, it is clear that unequivocal evidence for either an insulating or metallic ground state would come only from measurements on high quality single crystals. And only once the electronic ground state is determined, can a microscopic theoretical understanding of the spin ordering in this new class of organic ferromagnets be reached. In this paper we report for the first time transport measurements on ferromagnetic single crystals. We unambiguously confirm the insulating behavior and find that the measurements give new insight into the ground state properties related to the orientational dynamics of the C_{60} buckyballs.

The single crystals of TDAE-C_{60} were grown by the diffusion method from solutions of C_{60} and TDAE in toluene. The resulting crystals were found to grow in a number of different morphologies: (i) rhombohedral crystals which show ferromagnetic behavior at low temperatures (α phase), (ii) needles (β phase), which have been found to be nonferromagnetic and insulating with a larger lattice constant than in the powder [8], and (iii) rhombohedral crystals with antiferromagnetic properties at low temperature (α' phase) which transforms into the α phase upon annealing at room temperature or higher [9].

The conductivity measurements on 1–2 mm^3 size α-phase (ferromagnetic) crystals with flat faces (~1 mm^2 in size) were performed using either pressure contacts or gold contact paste contacts. The crystals were determined to be monoclinic with lattice constants matching the published structural data [10]. The present measurements were performed on 5 single crystals, all showing qualitatively the same behavior, although the data presented is on one particular sample, whose x-ray analysis showed that the conductivity was measured to within a few degrees of the crystallographic a axis (the differences between samples will be discussed later). Two contacts were made to two opposite faces of the crystal [11], giving a capacitance of ~50 pF at room temperature. The resistance measurements were performed using a Keithley 617 electrometer in *V-I* mode. The ac conductivity was measured with a HP 4284A precision LCR meter, whose phase accuracy was sufficient to reject the effects of sample and lead capacitances for all measured frequencies. The temperature dependence of the resistance was measured between 300 and 4 K with different cooling rates ranging from quenching at $>30\ \mathrm{K\,min}^{-1}$ to a slow cool at $<0.1\ \mathrm{K\,min}^{-1}$.

0031-9007/96/77(10)/2045(4)$10.00

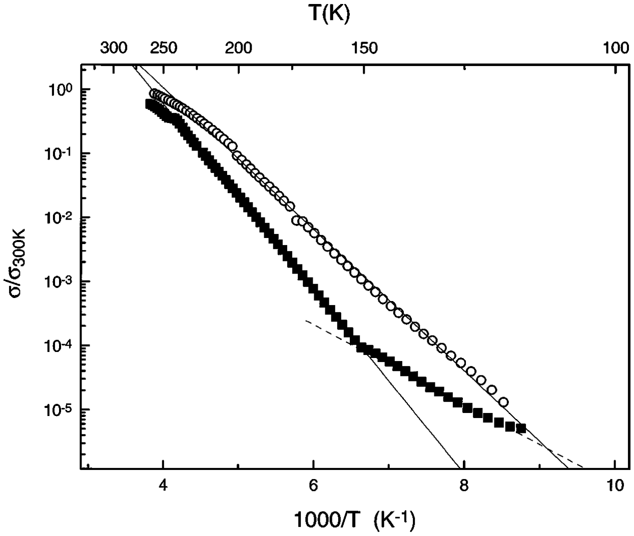

FIG. 1. The dc conductivity $\sigma/\sigma_{300\,\mathrm{K}}$ of TDAE-C_{60} single crystal as a function of temperature. $\sigma(0, T = 300\ \mathrm{K}) = 5 \pm 1 \times 10^{-5}\ \mathrm{S\,cm^{-1}}$. The squares were measured for cooling at $\sim 0.1\ \mathrm{K\,min^{-1}}$, while the circles were measured in near-quench condictions, cooling at $\sim 33\ \mathrm{K\,min^{-1}}$.

The dc single crystal conductivity σ is shown in Fig. 1 as a function of temperature for $300 > T > 100$ K. The two curves represent two different cooling rates. The data are described well by activated temperature dependence, whereby

$$\sigma_{\mathrm{dc}} = \sigma_0 \exp(-E_a/k_B T)\,, \tag{1}$$

where for the slow cooling experiment,

$$E_a' = 0.3\ \mathrm{eV} \quad \text{for } T > T_0$$

and

$$E_a'' = 0.14\ \mathrm{eV} \quad \text{for } T < T_0\,,$$

where $T_0 = 150$ K. The typical sample to sample variations in E_a', E_a'' and T_0 are ~ 0.05 eV and ~ 10 K, respectively. Superimposed on the slow-cooled conductivity data in Fig. 1 we have plotted a measurement in a rapid-cool measurement sequence, where the total cool time from 300 to 100 K was 6 min. Whereas there is a clear discontinuity in the slow-cooled measurement at T_0, the quench measurement shows no discontinuity and no change of slope at all at T_0. Below 100 K the conductance becomes immeasurable in both cases. (No evidence of a low-temperature reentrant rise in conductivity was observed down to 4.2 K.) We also note that temperature cycling tends to smear the observed kink and that it is reliably seen mainly in fresh samples. (These effects are attributed to the fact that C_{60} orientational disorder changes with temperature cycling.) The value $\sigma_{300\,\mathrm{K}} = 5 \times 10^{-5}\ \mathrm{S\,cm^{-1}}$ in our measurements on single crystals is significantly smaller than reported previously on powder samples. Since the conductivity of powder samples is known to increase significantly in thermally degraded samples [5], we attribute the increased conductivity in the powders to degradation.

The dependence of $\sigma(\omega)$ on frequency, $\omega = 2\pi\nu$ at low frequencies ($20 < \nu < 10^6$ Hz) can serve to identify the process leading to carrier localization. In Fig. 2(a) we show $\sigma(\omega)$ measured at a number of different temperatures. We observe a clear crossover from frequency-independent conductivity at low frequencies to a power-law frequency dependence at higher frequencies. Unfortunately due to the very low value of sample conductance, we have not been able to measure the frequency response below 140 K.

A possible reason for the observed multicomponent conductivity could be the presence of additional phases in the sample. However, room-temperature x-ray analysis of a number of crystals from the same batch did not show any presence of additional phases which could account for the two-component behavior, and although in the five samples that we measured we did indeed find some variations in E_a and T_0, both the kink at T_0 and the two-component $\sigma(\omega, T)$ was always observed. Thus we assign the two-component conductivity to be an intrinsic property of TDAE-C_{60}.

The ac conductivity $\sigma(\omega, T)$ in TDAE-C_{60} single crystals over the entire temperature range can thus be expressed as the sum of two components,

$$\sigma(\omega, T) = \sigma_{\mathrm{dc}}(T) + \sigma_{\mathrm{ac}}(\omega, T)\,, \tag{2}$$

where $\sigma_{\mathrm{dc}}(T)$ is given by Eq. (1). The frequency-dependent component is *temperature independent,*

$$\sigma_{\mathrm{ac}}(\omega) = B\omega^s\,, \tag{3}$$

and B is constant. $\sigma_{\mathrm{ac}}(\omega)$ can be analyzed by subtracting the low-frequency part $\sigma_{\mathrm{dc}}(T)$ from the data. The result is shown in Fig. 2(b). We find that when this is done, all the data fall on the same straight line, with $s = 1.16 \pm 0.1$.

Unfortunately we cannot infer anything about its properties of TDAE-C_{60} from A_1C_{60} materials (A = alkali) because the latter materials exhibit polymerization [12] which does not occur in TDAE-C_{60} [13]. A possible origin of the activated behavior in conductivity could be the presence of a Hubbard gap in the excitation spectrum due to the antiferromagnetic correlations between electrons [9] below 150 K. However, although a detailed infrared study has yet to be performed on single crystals, from the data so far [7] there is no evidence of an energy gap of the order of $E_a \sim 0.2$ eV (which changes by ~ 0.1 eV or more at T_0), which would be expected for a semiconductor with a Hubbard gap. A Mott-Hubbard insulating ground state thus appears to be ruled out in TDAE-C_{60}.

Because of the strong coupling of electrons to phonons on the C_{60} molecule, an electron when added to the neutral or charged buckyball [14] gives rise to a relaxation of the equatorial bond conjugation and a reduction in energy

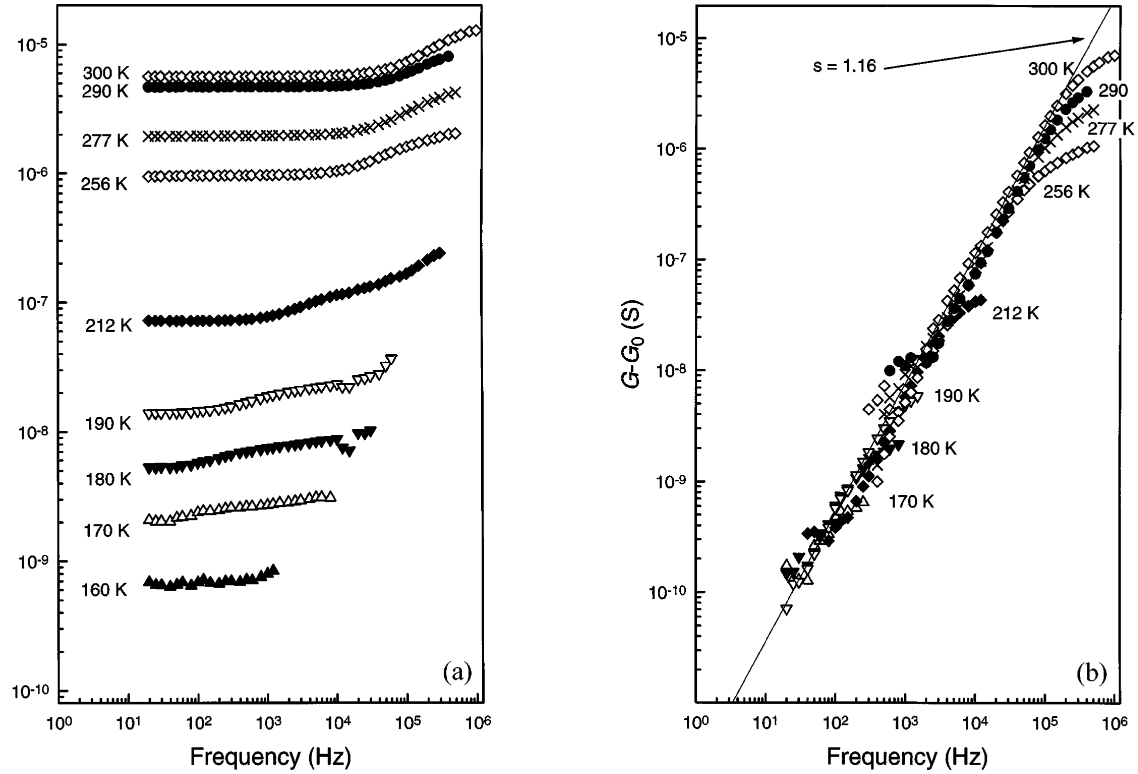

FIG. 2. (a) The conductance $G(\omega, T)$ as a function frequency in TDAE-C_{60} single crystal for a number of different temperatures. (b) The conductance $G = G(\omega, T) - G_0$ as a function of ω.

of such a "polaronic" state of $E_b \sim 0.1$ eV. Thus each electron on the buckyball should be considered as a small polaron confined to the C_{60} molecule, and we should expect classic thermally activated phonon-assisted (or polaronic) conductivity [15] $\sigma \sim \omega \exp(-E_b/kT)$, where E_b is the polaron binding energy and ω should probably signify the rate of rotation of the molecule, rather than a phonon frequency [15] [possibly explaining the rather low measured value σ_0 in Eq. (1)]. We can thus suggest that the conductivity given in Eq. (2) in terms of a crossover from interbuckyball tunneling (T-independent, high frequencies) to phonon-assisted hopping (T-dependent, low frequencies), the former not expected to have any temperature dependence. Since $E_a \gg \omega$, we do not expect any significant frequency dependence in the hopping in the polaronic model, while for the tunneling, the orientational disorder introduces a degree of randomness giving rise to frequency-dependent behavior similar to pseudorandom systems. As expected, the vibrational frequency of the strongly coupled intra-C_{60} mode $\hbar\omega = 1470$ cm^{-1} = 0.18 eV is close to the value found for the activation energy E_a' and is not much different to the polaronic binding energy E_b calculated by Harrigaya [14].

The values of the exponent s found here are not very different from some random systems like chalcogenide glasses, for example, a-As_2S_3 and a-As_2Te_3 and close to that observed in amorphous semiconductors in general [16], implying the hopping between balls has some degree of disorder associated with it. Since there is no disorder associated with the TDAE-C_{60} crystal lattice itself, orientational disorder of C_{60} molecules is a natural explanation for introducing a degree of randomness in the interball hopping probability. Not surprisingly, the temperature T_0 coincides with the orientational ordering transition in TDAE-C_{60} which occurs in the range 150–180 K (depending on sample and on measurement frequency) [3]. The molecular orientational ordering in crystals of C_{60} has been shown to have glasslike behavior and a range of relaxation times extending to subhertz frequencies, so by quenching the sample we can to some extent freeze a disordered merohedral state. The abrupt break in the activation energy at T_0 shows that we can clearly distinguish between the disordered state from the ordered phase in the dc conductivity. On slow cooling below T_0 the C_{60} molecules start freezing into preferential relative orientations [3,17] and a change in E_a.

There are a number of differences to the behavior observed in glasses, however, most notably the presence of a frequency-independent, temperature-activated component σ_0 above T_0. This conductivity process is apparently associated with rotating buckyballs, a process without any analogous behavior in glasses or other random systems investigated to date [15,16] and is more akin to thermally activated hopping in an ordered lattice.

To conclude, we find that in spite of an on-ball metallic ground state, because of the relatively small kinetic energy of the on-ball electrons the macroscopic conductivity of TDAE-C_{60} is determined essentially by the interball hopping. Frequency-dependent, T-independent tunneling and T-dependent phonon-assisted hopping are suggested to be the two mechanisms which can explain the observed behavior. The orientational disorder of the C_{60} molecules introduces a degree of randomness in the interball hopping probability giving rise to frequency-dependent ac conductivity behavior analogous to random glasses. As a consequence, when the balls start rotating above their orientational ordering transition T_0, there is a change in hopping probability and a clear change in the conductivity is observed. Although such behavior has been predicted theoretically [18], to our knowledge this is the first opportunity to directly study experimentally the molecular orientational-disorder induced localization as it crosses over into an ordered state through thermal treatment.

This work was supported in part by the EC SELMAT Network and the Joint U.S.-Slovene board. We wish to acknowledge the helpful comments of Fred Wudl regarding the anisotropy in the conductivity.

---

[1] P-M. Allemand *et al.*, Science **253**, 301 (1991).
[2] The C═C bond length in TDAE has been found by x-ray diffraction [L. Golič *et al.* (unpublished data)] to be 1.41 Å, which implies a radical $TDAE^+$ ion. Other evidence includes optical spectroscopy (see Ref. [6]), ESR and NMR (see also Ref. [3]).
[3] D. Mihailovic *et al.*, Science **268**, 400 (1995).
[4] A. Hassanien *et al.*, in *Physics and Chemistry of Fullerenes and Derivatives*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (World Scientific, Singapore, 1995), p. 489.
[5] A. Schilder, H. Koos, I. Rystau, W. Schütz, and B. Gotschy, Phys. Rev. Lett. **73**, 1299 (1994).
[6] D. Mihailovic *et al.*, in *Progress in Fullerene Research*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (World Scientific, Singapore, 1994), p. 275.
[7] F. Bommelli *et al.*, Phys. Rev. B **51**, 1366 (1995).
[8] A. Suzuki, T. Suzuki, and Y. Maruyama, Solid State Commun. **96**, 253 (1995).
[9] A. Mrzel, P. Cevc, A. Omerzu, and D. Mihailovic, Phys. Rev. B **53**, R2922 (1996).
[10] P. W. Stephens *et al.*, Nature (London) **355**, 331 (1992).
[11] The anisotropy of the conductivity could not be measured because the crystals do not grow with faces along the crystallographic directions, and special apparatus is needed for preparation of suitable crystals which was not available.
[12] O. Chauvet *et al.*, Phys. Rev. Lett. **72**, 2721 (1994); P. W. Stephens *et al.*, Nature (London) **370**, 636 (1994).
[13] The original structure in the powder was concluded to be monoclinic C2/m (Ref. [10]). Single crystal x-ray structure determination shows that the unit cell is actually doubled in the *c* direction with a room-temperature space group C2/c with four formula units per cell [L. Golic *et al.* (unpublished data)].
[14] K. Harrigaya, J. Phys. Soc. Jpn. **60**, 4001 (1991).
[15] N. F. Mott, *Conduction in Non-Crystalline Materials* (Oxford University Press, Oxford, 1993).
[16] S. R. Long, Adv. Phys. **31**, 553 (1982).
[17] W. I. F. David *et al.*, Europhys. Lett. **18**, 219 (1992).
[18] M. S. Depshpande, E. J. Mele, M. J. Rice, and H-Y. Choi, Phys. Rev. B **50**, 6993 (1994).