Metal-Insulator and Structural Phase Transition Observed by ESR Spectroscopy and X-Ray Diffraction in KC_{60}

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We have performed electron spin resonance (ESR) spectroscopy and x-ray diffraction experiments at low temperature on KC_{60} single crystals. ESR data reveal the occurrence of a metal-insulator phase transition at about 50 K. In the same temperature range, we observe the stabilization of a superstructure which doubles the volume of the unit cell. We suggest that displacements of the K atoms and a modulation of the C_{60} charge may be involved in the mechanism of this phase transition. These results shed new light on the subtle interplay of structure, dimensionality, and electronic properties in the AC_{60} fullerides.

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The recently discovered alkali fullerides AC_{60} ($A =$ K, Rb, Cs) have been extensively studied in the past few years but a clear understanding of their properties is still lacking. In these materials, the C_{60} molecules form polymer chains organized in an orthorhombic structure [1–3]. At room temperature, single crystal x-ray diffraction has revealed similar chain orientation angles (~45°–50°) but different relative chain orientations in KC_{60} and RbC_{60}, described in Pmnn and I2/m space groups, respectively [4]. Moreover, the chain orientations have been found to be nearly the same in the Rb and Cs salts [5]. These structural results were recently analyzed in terms of competing quadrupolar interactions [6].

The chain orientations may be of importance to discuss the electronic properties of these salts. RbC_{60} and CsC_{60} are usually described as quasi-one-dimensional materials [7,8]. Their X-band electron spin resonance (ESR) susceptibility drops below 40 K [7], indicating a different electronic ground state at low temperature. Despite extensive studies, the nature of this ground state remains controversial [9]. In contrast, KC_{60} is described as a three-dimensional (3D) metal, and a flat spin susceptibility has been reported from X-band ESR down to 4 K [7]. Electrical measurements confirm the high temperature metallic behavior although a broad upturn of the resistivity was reported at about 50 K [10,11]. Furthermore, preliminary NMR results, which suggest the opening of a gap in the spin excitations below 40 K, remain unexplained [12].

We report here on a combined study of the electronic and structural properties of KC_{60}. The main finding is the presence of a previously unobserved phase transition at low temperature. The vanishing asymmetry of the ESR signal at 50 K shows that it is a metal-insulator phase transition. Moreover, the appearance of new x-ray reflections below 65 K demonstrates the condensation of a superstructure with reduced wave vector components $(0.5, 0, 0.5)$.

The experiments were performed on two single crystals, noted Nos. 1 and 2 (size about 10^{-2} mm^3). They were prepared by stoichiometric insertion of potassium in C_{60} single crystals at 400 °C for 10 days, followed by slow cooling (10 hours) to room temperature [10]. Upon cooling, the C_{60} molecules form polymer chains at about 100 °C. Both crystals were characterized by x-ray diffraction methods. The mosaic spread of the crystals is rather large (about 2°), probably due to the insertion process. Because of the symmetry lowering from cubic to orthorhombic induced by the polymerization, 12 orientation variants coexist at room temperature. In principle, the variants should have equal weights but, as mentioned previously [4], we have observed significant differences, possibly due to some external anisotropic effects during the formation of the polymer chains. The unusual complexity of these crystals (variants producing split or overlapping reflections, mosaic spread) preclude standard structure determination. Crystal No. 1 had been used for the previous detailed determination of the chain orientation, shown to correspond to the Pmnn space group, in Refs. [4,13]. Precession photographs on crystal No. 2 also revealed the presence of reflections characteristic of a primitive lattice, in agreement with Pmnn. The diffraction patterns presented here were obtained using the monochromatic (Cu$K\alpha$) fixed-crystal, fixed-film technique and recorded with x-ray films and imaging plates. They were scanned to extract quantitative diffracted intensity data. The ESR data were obtained with a Bruker ESP 300E X-band spectrometer (9.3 GHz) equipped with an ESR 900 Oxford Instrument cryostat.

Above 50 K, the ESR signal is composed of a single narrow Dysonian line with an almost isotropic g-factor

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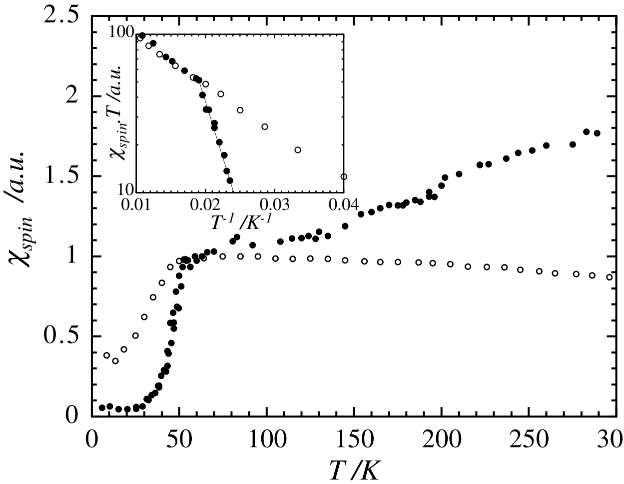

FIG. 1. Temperature dependence of the normalized ESR spin susceptibility in KC_{60}. A semilog plot of $\chi_{\rm spin}T$ as a function of $1/T$ is given in the inset to show the activation energy (solid symbols: crystal No. 1; open symbols: crystal No. 2).

($g = 2.0000$). A careful examination of the rotation patterns gives a small but detectable anisotropy of the peak-to-peak linewidth (between 3.9 and 4.5 G). Some anisotropy of the g-factor is probably also present but hardly detectable (possibly due to the orientational averaging effect of the variants). We shall first describe the data obtained on crystal No. 1. Its spin susceptibility decreases smoothly with temperature and drops rapidly below 50 K (Fig. 1) [14]. Below this temperature, a weak signal is superimposed to the main line which, however, still gives the main contribution to the susceptibility above 20 K. In this temperature range, the data show the occurrence of a gap in the spin excitation spectrum (i.e., $\ln(\chi_{\rm spin}T)$ versus $1/T$ gives a straight line with a slope of about -300 K, as shown in the inset of Fig. 1). Moreover, Fig. 2 gives the anisotropy A/B of the line (as defined in the inset). The observed Dysonian line is consistent with a highly conducting crystal [15]. The ratio A/B being an increasing function of the electrical conductivity, these data confirm the metallic behavior of the crystal above 100 K. Below this temperature, A/B decreases to reach a value close to 1 at 40 K, below which the composite nature of the signal prevents any accurate determination of A/B. In summary, the spin susceptibility and the line anisotropy indicate the presence of a metal-insulator phase transition. Moreover, Fig. 3 gives the temperature dependence of the ESR linewidth. The rapid increase below 50 K confirms the occurrence of a phase transition. Crystal No. 2 also shows an anomaly below 50 K albeit with a quantitatively different behavior: (i) in the high temperature region ($T > 50$ K), the spin susceptibility is roughly constant (Fig. 1), and the line asymmetry is less pronounced (Fig. 2); (ii) below 50 K, the susceptibility drop is incomplete without clear activited behavior (inset of Fig. 1). Additionally, the linewidth increase at low temperature is somewhat smeared out.

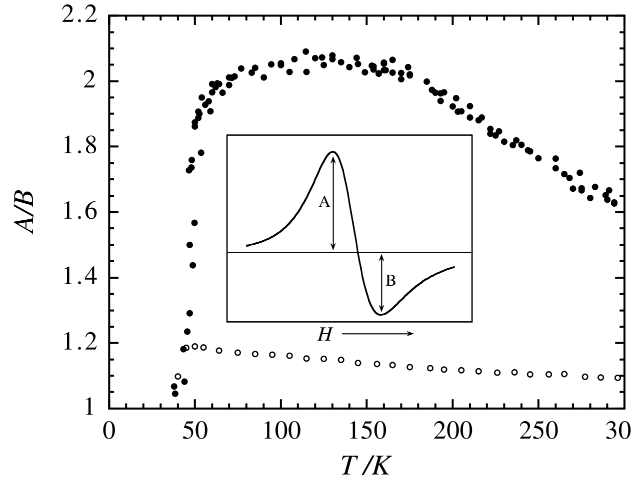

FIG. 2. Temperature dependence of the anisotropy A/B of the ESR line (solid symbols: crystal No. 1; open symbols: crystal No. 2). The definition of A and B is given in inset.

Following the ESR study, low temperature x-ray experiments were conducted on both crystals. They were found to exhibit essentially the same structural behavior and we present here the results obtained with crystal No. 1. Figure 4 shows a portion of a typical x-ray photograph taken at low temperature ($T = 12.5$ K). The spots are split due to the juxtaposition of reflections originating from the 12 orientation variants. These data were analyzed with the help of computer simulations, taking into account the contribution of the variants. Besides the main reflections, several additional ones can be observed with reduced wave vector components of the type $(0.5, 0, 0.5)$. These additional reflections originate from different orientation variants and they can be traced back to their parent variant. This is illustrated in Fig. 4, where the crystal orientation is such that the extra reflections $(2.5, 1, 1.5)$, $(2.5, 1, 0.5)$, and $(2.5, 1, -0.5)$ happen to proceed from a single variant. Upon heating, the intensity of these extra reflections

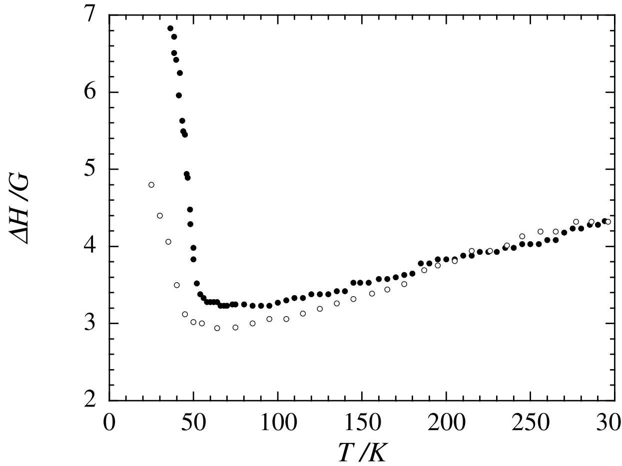

FIG. 3. Temperature dependence of the ESR linewidth (solid symbols: crystal No. 1; open symbols: crystal No. 2).

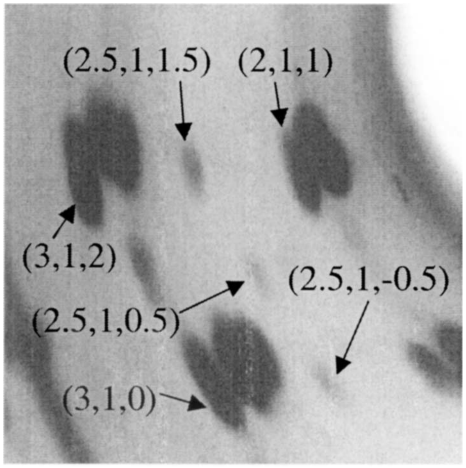

FIG. 4. Selected area from an x-ray photograph (monochromatized CuKα radiation, stationary sample and photograph) of KC_{60} single crystal No. 1 at $T = 12.5$ K. This area corresponds to a q range of about 0.2–0.4 Å^{-1} ($q = 2\sin\theta/\lambda$). The indices of some main and superstructure reflections originating from a single orientation variant are indicated.

(typically 10^2–10^3 times weaker than the main Bragg spots) diminishes continuously and becomes undetectable above about 70 K, as shown in Fig. 5. The reflection profiles can be fitted reasonably well with a Gaussian function, and the inset of Fig. 5 shows the temperature dependence of the intensity and width of a selected reflection, as deduced from the fits. The width stays practically constant up to 60 K, where it broadens, suggesting the possibility of precursor effects, though in a narrow temperature range. The temperature dependence of the intensity supports this conclusion. From our data, the transition temperature T_c is estimated to be in the 60–65 K range. Our results show that the fluctuations above T_c exhibit no sign of anisotropy.

Both ESR and x-ray data show that the nature of the KC_{60} ground state changes at low temperature. While the occurrence of a superstructure is clearly established, for both crystals, below approximately 60 K, ESR shows the presence of a gap in the spin excitation spectrum for crystal No. 1 associated with a loss of the metallic electrical conductivity below 50 K only. At the present stage, we have no clear explanation for these two slightly different estimations of T_c.

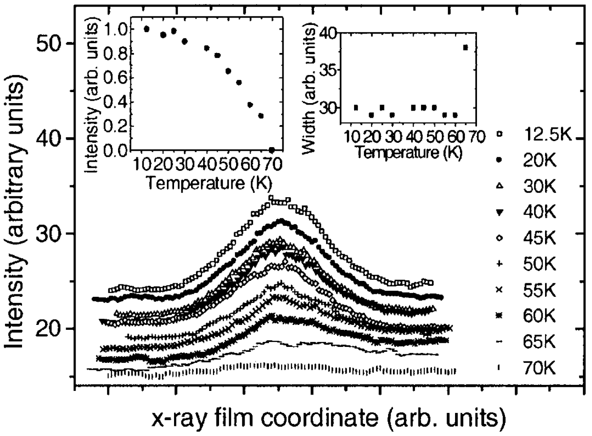

FIG. 5. Profiles of the (2.5, 1, 1.5) reflection (crystal No. 1) obtained by scanning the photographs, as a function of temperature. The curves have been shifted vertically for clarity. Temperature dependence of the intensity and width deduced from fits with a Gaussian function is shown in the insets.

Let us now discuss the possible nature of this phase transition. The (0.5, 0, 0.5) reduced wave vector components of the supplementary reflections correspond to a low temperature superstructure $(\mathbf{a} + \mathbf{c}, \mathbf{b}, \mathbf{a} - \mathbf{c})$. This superstructure could result from some atomic displacements and/or charge modulation removing the equivalence between C_{60} molecules present in the high temperature orthorhombic phase and producing some type of dimerization. At first, one may consider a displacement of the C_{60} center of mass. In this case, the intensity of the superstructure reflections would be proportional to the square of the form factor of a sphere with the C_{60} radius R (3.5 Å) and would be very weak for $q \sim 0.3$ Å^{-1}. This is in contradiction with experimental observations, because most superstructure reflections are observed around this wave vector value. The second possibility concerns the potassium sublattice. We recall that the analysis of the room temperature structure indicated anomalous Debye-Waller factors for the potassium in the **a** and **c** directions [4]. This was tentatively attributed to randomly distributed K displacements off the center of the octahedral site of cubic AC_{60}. From the values of the Debye-Waller factors these displacements are estimated to be about 0.50 and 0.55 Å along **a** and **c**, respectively, and it is possible that an ordering of these displacements be stabilized below T_c. Such large atomic displacements could effectively generate superstructure reflections in the observed low-q range. However, it is still difficult to understand that no superstructure reflections are observed for high-q values. A third possibility is a charge modulation on the C_{60} molecules, similar to a charge density wave (CDW) state. Although the diffraction satellites produced by pure CDW's are generally too weak to be detected, they have been observed recently in $(TMTSF)_2PF_6$ [16] (though 10^5 weaker than the main reflections). A distinct feature of such satellites is that they are visible at low-q values only, as is the case in KC_{60}. However, the KC_{60} superstructure reflections are only 10^2–10^3 smaller that the main ones and thus they appear to be too strong to be due, solely, to a CDW. A combination of a CDW on the C_{60} molecules with large correlated K displacements, as discussed above, is an appealing hypothesis. Further investigations would be necessary to clarify this crucial structural aspect.

In order to be consistent with the condensation of a low temperature diamagnetic ground state as seen by ESR, the mechanism of the structural phase transition should be associated with a pairing of the spins borne by the C_{60} molecules. Moreover, the loss of the electrical conductivity implies the opening of a gap at the Fermi level.

Local-density calculations [13,17,18] conclude that KC_{60} has essentially a 3D electronic band structure, though possibly anisotropic [18], so that nesting properties are not expected unless exact half band filling [19]. These calculations are thus difficult to reconcile with the observed metal-insulator phase transition. However, calculations performed for different chain orientations [13,20] show how they can strongly influence electronic band structures. This illustrates how the AC_{60} electronic properties may be sensitive to subtle structural parameters. Consequently, it would be useful to have band structure calculations analyze the influence of possible displacements of the potassium atoms and/or dimerization of the C_{60} chains, as suggested by our findings. Furthermore, the nesting properties of the Fermi surface and the possible role played by the $(0.5, 0, 0.5)$ wave vector should be analyzed.

Previous reports concerning a resistivity upturn [10,11] and the opening of a gap in the ^{13}C NMR relaxation rate [12] below approximately 50 K are in agreement with the present ESR data. Although we have observed some differences between the two crystal studied, both behaviors differ significantly from that observed by Bommeli *et al.* [7]. These authors report that KC_{60} is metallic with a flat spin susceptibility in the orthorhombic phase down to 4 K. Moreover, the reported ESR linewidth at room temperature (6.5 G) is larger than in our study. Differences in the thermal treatment may be responsible for these discrepancies. Actually, the resistivity anomaly in the KC_{60} single crystals was previously reported to be sample dependent [10]. This may be related to the very complicated phase transformations and thermodynamics of the AC_{60} compounds and in particular of KC_{60}, as revealed by the analysis of differential scanning calorimetry data [21]. In this context, our data suggest that sample No. 1's behavior is close to ideal, whereas the transition in sample No. 2 is not fully developed.

Our ESR and x-ray results provide clear evidence for coupled electronic and structural effects at low temperature in KC_{60} and they add to the rich spectrum of physical properties displayed by the AC_{60} series. In particular, new perspectives are open through possible relationships between the metal-insulator transition in KC_{60} and the behavior of RbC_{60} and CsC_{60}, where the nature of the low temperature ground state is still debated. Moreover, for the first time in the AC_{60} series, a low temperature superstructure, $(\mathbf{a} + \mathbf{c}, \mathbf{b}, \mathbf{a} - \mathbf{c})$, is found. We recall that there is no evidence for any low temperature lattice or magnetic ordering [22], or structural anomalies in RbC_{60}, so far. On the other hand, a spontaneous lattice contraction observed by powder x-ray diffraction and attributed to magnetoelastic coupling effects [5], has been associated with the transition to a spin singlet state at 13.8 K in CsC_{60}, deduced from NMR studies [23].

In conclusion, the present results strengthen the view that the variety of properties exhibited by the AC_{60} series results from a complex interplay of structural and electronic characteristics.

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[1] O. Chauvet *et al.,* Phys. Rev. Lett. **72**, 2721 (1994).
[2] S. Pekker *et al.,* Solid State Commun. **90**, 349 (1994).
[3] P.W. Stephens *et al.,* Nature (London) **370**, 636 (1994).
[4] P. Launois *et al.,* Phys. Rev. Lett. **81**, 4420 (1998); P. Launois *et al.,* Synth. Met. **103**, 2354 (1999).
[5] S. Rouzière *et al.,* Europhys. Lett. **51**, 314 (2000).
[6] K.H. Michel and A.V. Nikolaev, Phys. Rev. Lett. **85**, 3197 (2000).
[7] F. Bommeli *et al.,* Phys. Rev. B **51**, 14 794 (1995).
[8] V. Brouet *et al.,* Phys. Rev. Lett. **76**, 3638 (1996).
[9] (a) J. Rahmer *et al.,* in *Electronic Properties of Novel Materials-Science and Technology of Molecular Nanostructures: XIII International Winterschool,* edited by H. Kuzmany *et al.,* AIP Conf. Proc. No. 486 (AIP, New York, 1999), p. 32; (b) C. Coulon *et al.,* J. Phys. IV (France) **10**, 205 (2000).
[10] J. Hone *et al.,* Phys. Rev. B **52**, 8700 (1995).
[11] W.Y. Zhou *et al.,* J. Phys. Chem. Solids **61**, 1159 (2000).
[12] B. Simovic, Ph.D. thesis, Université Paris Sud, Orsay, France, 1999.
[13] P. Launois et al., in *Electronic Properties of Novel Materials-Science and Technology of Molecular Nanostructures: XIII International Winterschool* (Ref. [9a]), p. 47.
[14] Because of the pronounced Dysonian line shape, the spin susceptibility of sample No. 1 was deduced from the normalized product of the height of the ESR signal times the square of its linewidth rather than from numerical integration. The correction to account for the line asymmetry remains negligible. The drop at 50 K is, however, independent of the method used to deduce the susceptibility.
[15] G. Feher *et al.,* Phys. Rev. **98**, 337 (1955).
[16] J.P. Pouget and S. Ravy, J. Phys. I (France) **6**, 1501 (1996); J.P. Pouget and S. Ravy, Synth. Met. **85**, 1523 (1997).
[17] S.C. Erwin *et al.,* Phys. Rev. B **51**, 7345 (1995).
[18] T. Ogitsu *et al.,* Phys. Rev. B **58**, 13 925 (1998).
[19] M. Fally and H. Kuzmany, Phys. Rev. B **56**, 13 861 (1997).
[20] T. Saito *et al.,* Synth. Met. **113**, 45 (2000).
[21] L. Gránásy *et al.,* Phys. Rev. B **53**, 5059 (1996).
[22] B. Renker *et al.,* Solid State Commun. **109**, 423 (1999).
[23] B. Simovic *et al.,* Phys. Rev. Lett. **82**, 2298 (1999)