Antiferromagnetic Resonance in the Linear Chain Conducting Polymers RbC_{60} and CsC_{60}

A. Jánossy,[1] N. Nemes,[1] T. Fehér,[1] G. Oszlányi,[2] G. Baumgartner,[3] and L. Forró[3]
[1]*Institute of Physics, Technical University Budapest, H-1521 Budapest, Hungary*
[2]*Research Institute for Solid State Physics, H-1525 Budapest, POB. 49, Hungary*
[3]*Département de Physique, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland*

(Received 28 April 1997)

Antiferromagnetic resonance has been observed in powders of the conducting alkali fulleride linear polymers, RbC_{60} and CsC_{60}, at high frequencies (75, 150, and 225 GHz). This is proof for an antiferromagnetically ordered ground state and shows that these systems are not spin glasses. The sublattice magnetization is independent of applied magnetic field up to at least 8 T. Magnetic fluctuations are observed between 35 and 50 K. Comparison with the spin-density-wave system $(\mathrm{TMTSeF})_2\mathrm{PF}_6$ clearly shows that these polymers are also quasi-1D spin-density-wave systems with 3D ordering at low temperatures, as suggested previously. [S0031-9007(97)04146-X]

PACS numbers: 71.30.+h, 75.30.Fv, 76.50.+g

Recently Chauvet *et al.* [1] suggested that the conducting alkali fulleride linear chain polymers, orthorhombic RbC_{60} and CsC_{60}, are quasi-one-dimensional conductors, and the phase transition below 50 K is the three-dimensional (3D) ordering of spin-density waves (SDW). At present, both the dimensionality of the electronic structure and the nature of the low temperature phase remain open questions. The polymers have a relatively simple crystal structure [2] with parallel running chains of covalently bonded C_{60} molecules. The electronic structure calculated for a single chain [3] has a very narrow conduction electron band for which correlations must be important. Mele *et al.* [4] proposed, however, that interchain overlap may be important, and the electronic structure may be 3D with large bandwidths both along and perpendicular to the chains. On the other hand, the physical properties are suggestive of a quasi-1D conductor. Above 50 K the polymers are metals with a large, weakly temperature dependent spin susceptibility and low frequency conductivity [5]. Magnetic fluctuations measured by NMR spin lattice relaxation [6] and the observation of a narrow ESR line in the metallic phase [3] support the idea of a quasi-1D metal. Above the transition, precursor effects are observed: Magnetic fluctuations increase dramatically [6], and a gradual development of a gap [5] has been inferred from the microwave and far infrared conductivities. Both NMR [6] and μSR (muon spin rotation) [7–9] studies confirm the development of static magnetic moments on the fullerene chains at low temperatures. Cristofolini *et al.* [7] and MacFarlene *et al.* [8] interpreted μSR data as indicative of a strongly disordered magnetic state developing gradually as the temperature is lowered, while Uemura *et al.* [9] believe that the μSR data do not exclude an antiferromagnetic or SDW order. On the other hand, Brouet *et al.* [6] interpreted the ^{133}Cs and ^{13}C NMR as indicative of a spin-flop transition. Both molecular and crystalline orientational disorder broaden the NMR, but a spin-flop transition is only possible in an antiferromagnetically ordered system.

In this paper we present evidence for an antiferromagnetically ordered state below 35 and 30 K for the Rb and Cs polymers, respectively. We report on the antiferromagnetic resonance below the ordering transition for both polymers. In RbC_{60} the static susceptibility is depressed, and the electron spin lattice relaxation is enhanced by magnetic fluctuations between 35 and 50 K. There is a strong similarity between the fulleride polymers and the quasi-1D organic charge transfer salt, $(\mathrm{TMTSeF})_2\mathrm{PF}_6$ in which spin density waves have been extensively studied [10]. In $(\mathrm{TMTSeF})_2\mathrm{PF}_6$, the first unambiguous evidence for a magnetically ordered ground state came from the observation of the antiferromagnetic resonance [11], and in this system 3D fluctuations above the phase transition depress the static susceptibility, similar to the case of fulleride polymers.

ESR experiments at 9 GHz ($g = 2$ resonance field $H_0 = 0.3$ T) were performed with a Bruker 300 spectrometer. For experiments at 75.0, 150.0, and 225.0 GHz ($H_0 = 2.7$, 5.4, and 8.0 T, respectively), a spectrometer with a quartz-stabilized 75 GHz oscillator followed by a frequency doubler or tripler was used. The powder samples (typically 5 mg) were mixed into vacuum grease to reduce microwave electrical losses.

For the three RbC_{60} samples studied, the linewidths and intensities normalized to their 50 K values have the same temperature and frequency dependence, but the absolute values of the linewidths depend on sample preparation. We present detailed data for a RbC_{60} sample prepared by solid state reaction. One of the RbC_{60} samples and the CsC_{60} sample were parts of the samples studied by NMR [6]; another RbC_{60} sample was synthesized by coevaporation of Rb metal and C_{60}.

Figure 1 presents the resonance intensities of RbC_{60} determined from the integration of lines at 9 and 225 GHz and normalized to 100 K. We distinguish three temperature ranges: (i) Above 50 K, there is a nearly constant spin susceptibility χ. (ii) Below 50 K, χ decreases; the ESR intensity is still frequency independent. (iii) Below 35 K, the observed resonance intensities are frequency

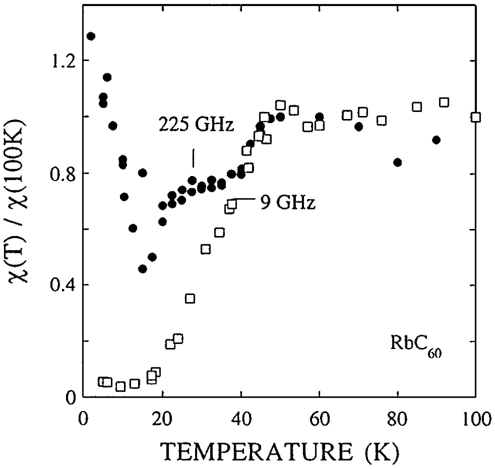

FIG. 1. Magnetic spin susceptibility of RbC_{60} derived from magnetic resonance intensities. The susceptibility is depressed between 35 and 50 K by 3D fluctuations. Below 35 K the intensity at 225 GHz ($H_0 = 8$ T) is proportional to the susceptibility of the antiferromagnetically ordered state above the spin-flop field, while the 9 GHz resonance intensity is not a measure of χ.

dependent. We assign the ESR above 35 K to the conduction electron spin resonance (CESR) of the quasi-1D metal. Between 35 and 50 K, 3D fluctuations decrease the susceptibility and relaxationally broaden the CESR. At high frequencies we observe the antiferromagnetic resonance of the 3D ordered system below 35 K.

We first discuss the paramagnetic regime above 35 K, where the frequency and temperature dependence of the linewidth, $\Delta H(f,T)$, may be simply separated: $\Delta H(f,T) = \Delta H_0 + \Delta H_T + \Delta H_f$. Here ΔH_0 and ΔH_T are homogeneous broadening while ΔH_f results from a partially averaged g-factor anisotropy. In normal metals, ΔH_0 and ΔH_T arise from spin-lattice relaxation, T_1^{-1}, due to structural disorder and phonons, respectively [12]. $\Delta H(f,T)$ has a broad minimum at 50 K and the increase above 50 K is the usual phonon term ΔH_T. In a quasi-1D metal, spin-orbit scattering is reduced because of the reduction of momentum space into which electrons can scatter. The small value of ΔH_0 (0.05–0.15 mT in RbC_{60}) is indicative of a quasi-1D metal.

In RbC_{60}, ΔH_f increases linearly with frequency f and arises from the g-factor anisotropy which is expected for the orthorhombic polymers. In the paramagnetic region, RbC_{60} is metallic, and the g-factor anisotropy broadening is reduced by the diffusion of electrons through boundaries of differently oriented crystallites.

We interpret the decrease of the spin susceptibility (Fig. 1) and the increase of T_1^{-1} with decreasing T below 50 K [Fig. 2(a)] as arising from precursor effects to a 3D magnetic ordering at about 35 K. The pseudogap due to 3D fluctuations reduces the magnetic susceptibility and also explains that below 60 K the 9 GHz electrical conductivity falls rapidly [5]. Three-dimensional antiferromagnetic fluctuations at the Larmor frequency are responsible for the homogeneous increase of the linewidth as the transition is approached. Above 40 K the line is homogeneous [13] and the linewidth measures T_1^{-1}. Once ΔH_f, the temperature independent inhomogeneous broadening, is subtracted, the line broadens by the same amount for all frequencies between 9 and 225 GHz [Fig. 2(a) inset]. The frequency independence shows that there are no internal static fields and thus no static moments above 35 K. Fields fluctuating slower than $\gamma \Delta H$ (of the order of 10^7 Hz) are sensed as "static" and would give rise to an inhomogeneous line. This interpretation is consistent with the strong enhancement of magnetic fluctuations observed in the nuclear spin relaxation rates [6].

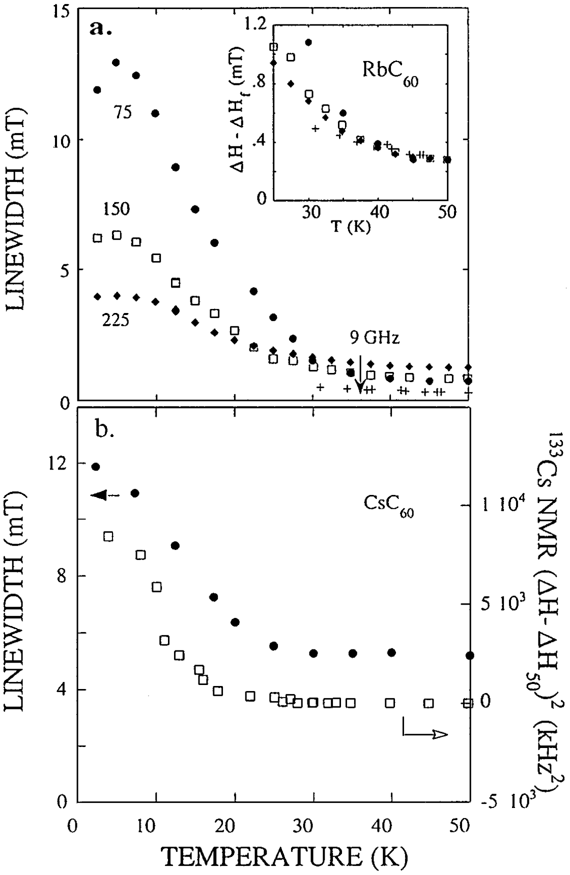

FIG. 2. (a) Below the ordering temperature of 35 K, the increase of the resonance width (with respect to the high T value) is inversely proportional to the resonance frequency. (b) The antiferromagnetic resonance linewidth of the CsC_{60} polymer and the square of the ^{133}Cs NMR linewidth (corrected for the value at 50 K, ΔH_{50}) are both proportional to $[M(T)]^2$, the square of the sublattice magnetization (NMR data: Ref. [6]). Inset: the linewidth corrected for g-factor anisotropy is increased by 3D magnetic fluctuations.

Below the ordering temperature of 35 K, a strong increase of the linewidth is found for both RbC_{60} and CsC_{60} which, for a given temperature, *decreases* with increasing frequency (Fig. 2). This behavior is in sharp contrast with the linear increase with f observed above 35 K. The line also shifts below 35 K, and the shift is proportional to the increase of the linewidth. The intensity at 225 GHz shows a minimum at about 20 K and increases with further decreasing of the temperature. The intensity at 9 GHz continues to decrease, but at this frequency the anisotropy of the internal fields broadens most of the magnetic resonance beyond detectability and the apparent intensity is no longer a measure of χ.

We suggest that the resonance at high fields below 35 K is a $q = 0$ mode antiferromagnetic resonance (AFMR) broadened by orientational disorder of the powder. The main reason for this suggestion is that the line shapes are scaled precisely as $1/H_0$. The $T = 5$ K RbC_{60} resonance line shapes shown in Fig. 3 as a function of $(H - H_0)H_0$ (instead of the usual $H - H_0$) are the same for the three frequencies. The increase of linewidths below 35 K with respect to the 50 K values follows a $1/H_0$ dependence within experimental error. A similar $1/H_0$ dependence is found for the shift of the average resonance position. The $1/H_0$ dependent width and shift are observed for both RbC_{60} and CsC_{60} at high frequencies. Such a behavior is unusual, e.g., in paramagnetic systems the line shapes are normally independent of or proportional to the field. In ferromagnets the resonance of a powder broadened by demagnetization effects is independent of the field for small magnetization. In a spin glass a complex magnetic and thermal history dependent behavior is expected. We found no hysteresis; the spectra of RbC_{60} cooled from 50 K to low temperatures in zero field or in 8 T field are identical. On the other hand, the $1/H_0$ dependence is a natural feature of an AFMR in a powder at high values of H_0, as illustrated for simplicity for a uniaxial antiferromagnet [14] in Fig. 4. The figure shows the $q = 0$ spin-wave modes observable at high fields and frequencies with the magnetic field aligned along the easy and hard axes. The $q = 0$ spin-wave mode frequencies are given by $\omega^{\pm} = \gamma(H_0^2 \pm H_{\mathrm{sf}}^2)^{1/2}$, where the $(+)$ $[(-)]$ sign corresponds to field in the hard (easy) direction. For illustration, we assume, in Fig. 4, $H_{\mathrm{sf}} = 1$ T for the spin-flop field. In the polymers the symmetry is orthorhombic, and there is a further mode for fields in the intermediate direction which lies between the modes for easy and hard directions. Typically, the resonance of an arbitrarily oriented single crystal falls between the easy and hard axis branches, and in a powder the line shape and average line position scale as H_{sf}^2/H_0 for large fields, just as we observe in the polymers.

In a sample of isolated randomly oriented single crystals, the AFMR linewidth would be equal to H_{sf}^2/H_0 (Fig. 4). At 5 K we find $K = (\Delta H \times H_0)^{1/2} = 0.2$ T for RbC_{60}, and 0.3 T for CsC_{60}. K measured in a polycrystalline sample underestimates H_{sf}, the spin-flop field of a single crystal. As shown for the polymer [15] KC_{60}, the polymer chains follow a zigzag pattern, and it is natural to assume that differently oriented neighboring domains are magnetically coupled. Strongly coupled domains have a single resonance, and the AFMR is narrowed. (The narrowing of the ferromagnetic resonance in thin polycrystalline films of anisotropic ferromagnets is a well-known phenomenon.) Another consequence of the coupling of domains will be that the usual divergences of powder spectra are smeared, and the line is not strongly asymmetric. The narrowing of the AFMR is related to the narrowing of the g-factor anisotropy in the paramagnetic state and depends on the morphology of the grains. Both the AFMR linewidth and the g-factor anisotropy broadening are larger in the coevaporated RbC_{60} sample than in the samples made by solid state reaction.

Although the AFMR of a powder of grains consisting of coupled domains is narrower than that of uncoupled single crystals, the linewidth ΔH is still proportional to H_{sf}^2, and we may determine the temperature dependence of the

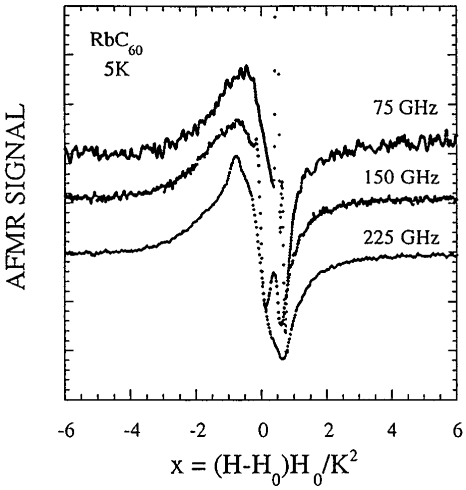

FIG. 3. The antiferromagnetic resonance line shape scales with the inverse of the resonance field H_0. The scaling constant $K = 0.2$ T is the spin-flop field reduced by coupling between differently oriented domains. The impurity lines near $x = 0.5$ are more visible at lower frequencies.

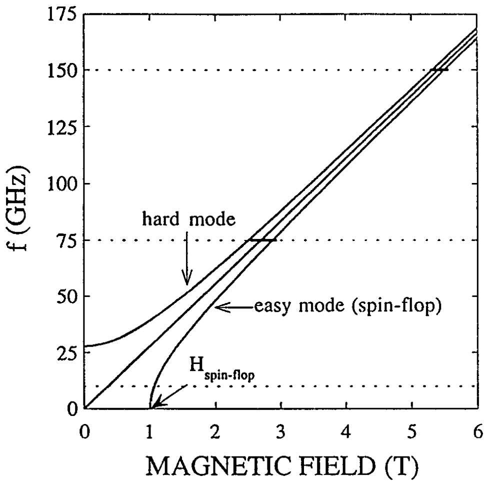

FIG. 4. Resonance modes of a uniaxial antiferromagnet for magnetic fields along and perpendicular to the easy magnetization direction. Only modes relevant to the experiment are shown. At high frequencies, the linewidth of the AFMR of a powder (heavy lines) is inversely proportional to the frequency.

sublattice magnetization $M(T)$ from the AFMR linewidth. In the mean field approximation $H_{\mathrm{sf}} = (2H_a H_E)^{1/2}$, where H_a and $H_E = 2JM/(\gamma\mu_B)^2$ are the anisotropy and effective exchange fields, respectively. In the polymers, magnetic moments reside on molecules of light elements for which spin-orbit coupling related anisotropy is negligible, and H_a is determined [16] by dipolar fields proportional to M. Thus the AFMR linewidth is proportional to $[M(T)]^2$. Figure 2 shows that the temperature dependence of the AFMR linewidths of RbC_{60} and CsC_{60} is similar to the square of the ^{133}Cs NMR linewidth measured by Brouet *et al.* [6]. The NMR and AFMR were measured on the same CsC_{60} material. The agreement is remarkable since the AFMR is a collective mode arising from strongly coupled domains, while NMR measures local dipolar fields and is broadened by disorder. The ^{133}Cs NMR linewidth is directly proportional to $M(T)$, while the AFMR width is affected by both the exchange and dipolar fields. The AFMR width is larger in CsC_{60} than in RbC_{60} and this, together with the larger alkali NMR broadening [6], indicates a larger sublattice magnetization for CsC_{60}. From AFMR alone one cannot determine the magnitude of $M(T)$; however, the value of $0.5\mu_B$ at low T as estimated by Brouet *et al.* [6], assuming a commensurate antiferromagnetic structure, is consistent with our findings.

The temperature dependence of the sublattice magnetization is characteristic of a magnetically ordered system. The linewidths scale with $1/H_0$ in a broad temperature range, and this shows that $M(T)$ is not dependent on the applied magnetic field. The onset of the static magnetic order is well defined, and the magnetization saturates below 7.5 K. These features are in contrast with a gradual transition from a nonmagnetic state to a magnetic state at low temperatures as suggested by MacFarlane *et al.* [8].

Finally, we stress the similarity between the alkali fulleride polymers and the prototype SDW material, $(\mathrm{TMTSeF})_2\mathrm{PF}_6$. In the latter material the opening of a pseudogap due to 3D fluctuations decreases appreciably the static susceptibility below 20 K. Below the ordering temperature of 11.5 K, the susceptibility measured in fields above spin flop rises again [17]. This behavior is remarkably similar to that of RbC_{60} shown in Fig. 1. In both materials the antiferromagnetic resonance is evidence for a magnetically ordered ground state. The magnetic fluctuations in the alkali polymers above the ordering temperature (for which further evidence is given between 35 and 50 K in this paper) indicate that there is only a very small energy gap in the fluctuation spectrum. A gap is expected if the antiferromagnetic lattice is commensurate with the crystal lattice. Our results suggest that the fulleride polymers are incommensurate quasi-1D SDW systems, as is $(\mathrm{TMTSeF})_2\mathrm{PF}_6$. It is difficult to detect the magnetic order in an incommensurate system, and this may explain the failure by neutron diffraction [18] and μSR [7–9]. Clear μSR oscillations have been observed [19] in $(\mathrm{TMTSeF})_2\mathrm{PF}_6$, but oscillations in $(\mathrm{TMTSeF})_2\mathrm{ClO}_4$ are nearly completely smeared by a small structural disorder.

This work was supported by Hungarian grants OTKA T015984 and by the Swiss National Science Foundation for Scientific Research. We are indebted to S. Pekker for providing the coevaporated RbC_{60} sample, and to H. Alloul and V. Brouet for illuminating discussions. We acknowledge M. Mehring for communicating similar data for RbC_{60} at 140 GHz prior to publication.

[1] O. Chauvet, G. Oszlanyi, L. Forró, P.W. Stephens, M. Tegze, G. Faigel, and A. Jánossy, Phys. Rev. Lett. **72**, 2721 (1994).

[2] P.W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Jánossy, S. Pekker, G. Oszlányi, and L. Forró, Nature (London) **370**, 636 (1994).

[3] P.R. Surján and K. Németh, Solid State Commun. **92**, 407 (1994); S. Stafström, M. Boman, and J. Fagerstrom, Europhys. Lett. **30**, 295 (1995); K. Tanaka, Y. Matsubura, Y. Oshima, and T. Yamabe, Solid State Commun. **93**, 163 (1995).

[4] E.J. Mele, G.V. Krishna, and S.C. Erwin, Phys. Rev. B **52**, 12 493 (1995).

[5] F. Bommeli, L. Degiorgi, P. Wachter, Ö. Legeza, A. Jánossy, G. Oszlányi, O. Chauvet, and L. Forró, Phys. Rev. B **51**, 14 791 (1995).

[6] V. Brouet, H. Alloul, Y. Yoshinari, and L. Forró, Phys. Rev. Lett. **76**, 3638 (1996).

[7] L. Cristofolini, A. Lappas, K. Vavekis, K. Prassides, R. DeRenzi, M. Ricco, A. Schenck, A. Amato, F.N. Gygax, M. Kosaka, and K. Tanigaki, J. Phys. Condens. Matter **7**, L567 (1995).

[8] W.A. MacFarlene, R.F. Kiefl, S. Dunsiger, J.E. Sonier, and J.E. Fischer, Phys. Rev. B **52**, R6995 (1995).

[9] Y.J. Uemura, G.M. Luke, W.D. Wu, G. Oszlányi, O. Chauvet, and L. Forró, Phys. Rev. B **52**, R6995 (1995).

[10] See, e.g., G. Grüner, in *Density Waves in Solids*, edited by D. Pines, Frontiers in Physics (Addison-Wesley, Reading, MA, 1994).

[11] J.B. Torrance, H.J. Pedersen, and K. Bechgaard, Phys. Rev. Lett. **49**, 881 (1982).

[12] R.J. Elliott, Phys. Rev. **96**, 266 (1954); Y. Yafet, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 14, p. 1.

[13] J. Robert, P. Petit, J.-J. Andrè, and J.E. Fischer, Solid State Commun. **96**, 143 (1995).

[14] See, e.g., S. Foner, in *Antiferromagnetic and Ferrimagnetic Resonance in Magnetism*, edited by G.T. Rado and H. Suhl (Academic, New York, 1963), Vol. I, p. 384.

[15] M. Carrard, L. Forró, L. Mihaly, and S. Pekker, Synth. Met. **80**, 29–34 (1996).

[16] M. Roger, J.M. Delrieux, and E. Wope Mbougue, Phys. Rev. B **34**, 4952 (1986).

[17] J.C. Scott, H.J. Pedersen, and K. Bechgaard, Phys. Rev. Lett. **45**, 2125 (1980); K. Mortensen, Y. Tomkiewicz, T.D. Schultz, and E.M. Engler, Phys. Rev. Lett. **46**, 1234 (1981).

[18] J.E. Fischer (private communication).

[19] L.P. Le *et al.*, Phys. Rev. B **48**, 7284 (1993).