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Magnetic resonance in the antiferromagnetic and normal state of $NH_3K_3C_{60}$

Ferenc Simon, András Jánossy,* Ferenc Murányi, and Titusz Fehér
Technical University of Budapest, Institute of Physics, PO Box 91, H-1521 Budapest, Hungary

Hideo Shimoda† and Yoshihiro Iwasa
Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923-1292, Japan

László Forró
Laboratoire de Physique des Solides Semicristallins, IGA Department de Physique, Ecole Polytechnique Federal de Lausanne, 1015 Lausanne, Switzerland

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We report on the magnetic resonance of $NH_3K_3C_{60}$ powders in the frequency range 9–225 GHz. The observation of an antiferromagnetic resonance below the phase transition at 40 K is evidence for an antiferromagnetically ordered ground state. In the normal state, above 40 K, the temperature dependence of the spin susceptibilty measured by electron-spin resonance agrees with previous static measurements and is too weak to be explained by interacting localized spins in an insulator. The magnetic-resonance linewidth has an unusual magnetic-field dependence which is large and temperature independent in the magnetically ordered state and decreases rapidly above the transition. These observations agree with the suggestion that $NH_3K_3C_{60}$ is a metal in the normal state and undergoes a Mott-Hubbard metal to insulator transition at 40 K.

The superconducting transition temperature, T_c, of cubic alkali metal A_3C_{60} fullerides has a simple relation to the lattice constant:[1] T_c increases with the ionic size of the alkali. This motivates the quest to synthesize large lattice parameter fullerides with C_{60} in the $(C_{60})^{3-}$ charge state. The intercalation of ammonia into Na_2CsC_{60} increased T_c by nearly 20 K, from 10.5 K to 29.7 K.[2] In contrast, superconductivity was not detected at ambient pressure in $NH_3K_3C_{60}$, the ammonia intercalated stable phase of K_3C_{60}.[3] According to Raman scattering in $NH_3K_3C_{60}$, the charge state is $(C_{60})^{3-}$ and, at least along some directions, the nearest-neighbor interball separation exceeds substantially that of Rb_2CsC_{60}, a superconductor with one of the highest transition temperatures.[4] The two materials differ in that NH_3 intercalation expands the lattice without changing the cubic symmetry in Na_2CsC_{60} while $NH_3K_3C_{60}$ has a face-centered orthorhombic structure. Zhou *et al.* questioned the importance of lower symmetry since superconductivity is recovered under hydrostatic pressure at a relatively high temperature (28 K at 14.8 kbar) without any change in the crystallographic structure.[4] They suggested that the smaller transfer integrals at ambient pressures suppresses superconductivity and favors a Mott-Hubbard transition to an insulating ground state. The observation by Iwasa *et al.*[5] and by Allen *et al.*[6] of a phase transition with no structural change[7] at about 40 K and ambient pressure reinforces this view. The electron-spin resonance (ESR) intensity at 9 GHz disappeared below 40 K but the static susceptibility, χ, measured by superconducting quantum interference device (SQUID), and the ^{13}C NMR (Ref. 5) changed little. In spite of these somewhat contradictory results, Iwasa *et al.*[5] concluded that the ground state is an antiferromagnet. Initially it was thought that the ordered magnetic moment is unusually small, $\sim 0.01\mu_B$. Recently, Tou *et al.*[8] found that the ^{13}C line is significantly broadened below the transition, indicating an antiferromagnetically ordered ground state of $NH_3K_3C_{60}$, with an ordered moment of $1\mu_B/C_{60}$. In the interpretation of the ^{13}C NMR (Ref. 8) it was assumed that spins lie perpendicularly to the external field and the spin-flop (SF) field is small, less than 1 T. The recent detection of damped oscillations in zero-field μSR (Ref. 9) is a further signature of static magnetic moments below 40 K. Just like the ground state, the normal state of $NH_3K_3C_{60}$ is also poorly understood. In particular, it is unknown whether above 40 K it is metallic or insulating. Initially, the temperature variation of χ and ^{13}C NMR T_1 of Ref. 5 were interpreted assuming a narrow-band metallic normal state. Recent NMR data[8] were analyzed assuming localized spins on the C_{60} ions above 170 K. A further complication arises from the recently found structural transition[7] due to the ordering of the K-NH_3 pairs at $T_S = 150$ K.

The motivation for the present work is twofold: following Ref. 10 on RbC_{60} and CsC_{60} we observe the antiferromagnetic resonance (AFMR) in $NH_3K_3C_{60}$ using a multifrequency spin-resonance technique. Our less detailed earlier work[11] was inconclusive in this respect. Below 40 K the 9 GHz resonance spectrum of $NH_3K_3C_{60}$ is broad, and good sensitivity and a high-purity material are required for its detection.[11] The AFMR in powders becomes narrower at higher fields and is an unambiguous evidence for the antiferromagnetic (AF) ground state. Second, we gain information about the normal state from the ESR measured in a large frequency range. Our normal-state ESR susceptibility data agree with the static susceptibility data of Ref. 5 and point to a metallic system rather than an insulator with interacting localized moments.

Several $NH_3K_3C_{60}$ powder samples were prepared following methods described elsewhere.[5] Samples were sealed in quartz ESR tubes under low-pressure He. Powder x-ray diffraction showed them to be of high purity. The small re-

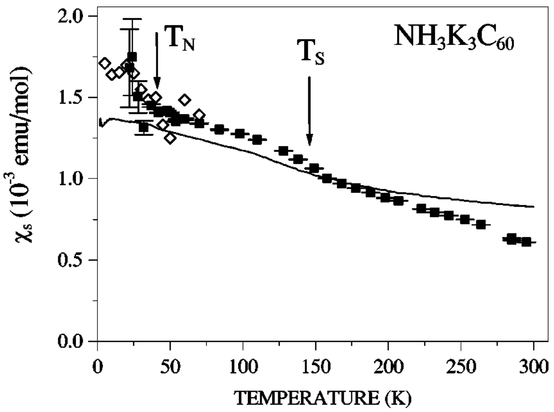

FIG. 1. Spin-susceptibility of $NH_3K_3C_{60}$ measured by ESR at 9 GHz (■ 0.3 T) and 225 GHz (◇ 8.1 T). The solid curve is the SQUID data from Ref. 5 measured at 1 T after core electron diamagnetic susceptibility correction. T_S is the structural, T_N the magnetic ordering, temperature.

sidual K_3C_{60} content was unobservable by x-ray diffraction but increased the noise of the 9 GHz ESR spectrometer below 19 K. The main features of the ESR spectra were identical for all samples studied, and we show in our figures the results from two samples. The 9 GHz ESR spectra were recorded on a commercial Bruker spectrometer. The 35, 75, 150, and 225 GHz ESR were studied at the Budapest high-frequency spectrometer. Samples were slowly (~50 K/h) cooled from 300 K to 5 K. At 9 GHz only data between 20 and 300 K are shown, as below 19 K residual K_3C_{60} distorted the spectra. ESR intensities and *g* factors were measured with respect to standard calibrating samples.

In Fig. 1 we show χ determined from the ESR intensity together with χ measured in Ref. 5 by the SQUID technique. χ of $NH_3K_3C_{60}$ varies little through the 40 K transition for all ESR frequencies, *f*, between 9 (0.3 T) and 225 GHz (8.1 T). Our χ data are in remarkable agreement with that of the SQUID results of Iwasa *et al.*[5] in the full temperature range. The SQUID measurements were corrected for the core electron contribution. ESR measures the spin susceptibility in the paramagnetic state and, if the applied field is large compared to the SF field, in the AF state also. Only the perpendicular AF susceptibility is observed in such large fields. The (molar) susceptibility below T_N is $\chi_\perp = N_A \mu_{\mathrm{eff}}^2/(6k_B T_N)$, where N_A is the Avogadro number. From Fig. 1, $\chi_\perp \simeq 1.3 \times 10^{-3}$ emu/mol and the ordered moment is $\mu_{\mathrm{eff}} = 0.9\mu_B/C_{60}$.

The variation of $\chi(T)$ with *T* is difficult to explain with a "textbook" metallic or localized spin susceptibility. The variation is too weak to originate from a Curie-Weiss temperature dependence of localized spins. The three-dimensional (3D) AF order sets in at a Neél temperature of $T_N \simeq 40$ K. Between 40 and 300 K $\chi(T)$ decreases by a factor ~2.3 whereas a factor 4.25 would be expected from a Curie-Weiss behavior of antiferromagnetically correlated spins $\chi(T) = C/(T+T_N)$, where *C* is the Curie constant. The fit of $\chi(T)$ to a Curie-Weiss behavior with T_N left as a free parameter leads to $T_N \geqq 120$ K in contradiction with the observed long-range 3D order at 40 K. On the other hand, the variation of χ is larger than usually found in metallic systems. Nevertheless, strong correlation effects in a narrow-band metal may lead to the observed variation of $\chi(T)$ as it was originally suggested in Ref. 5. Electron-electron correlation effects are needed to explain the large value of χ of the K_3C_{60} parent compound[1] also. The larger lattice constants of $NH_3K_3C_{60}$ suggest a narrower band and even more important correlation effects. There is a slight anomaly in $\chi(T)$ at the structural transition, T_S. The transition is of second order and affects χ in the range 50–150 K. The sensitivity of $\chi(T)$ to the structural transformation is readily understood if the material is a metal with strong electron correlations since the freezing of molecular rotation is certainly accompanied by a change in electronic structure. In summary, above T_N the material is more likely a strongly correlated metal than an insulator with localized spins. Unfortunately, a definite answer is not possible from the χ data alone.

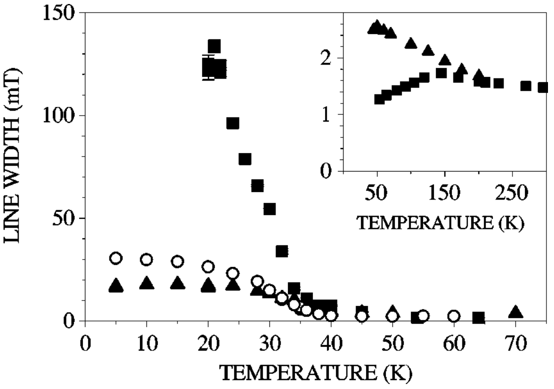

FIG. 2. Temperature dependence of the linewidth, ΔH, at various frequencies (■ 9 GHz, ○ 35 GHz, ▲ 75 GHz). The inset shows ΔH (in mT) above 40 K.

Figure 2 shows the variation of the resonance linewidth (ΔH) with temperature at various frequencies. The 40 K transition is marked by a sharp increase of ΔH with decreasing *T*. The 9, 35, and 75 GHz spectra below 40 K are characteristic of an AFMR of a powder in applied fields larger than the SF field:[10] the linewidth narrows and the resonance field shifts proportionally to the inverse of the applied field. This is in contrast with paramagnetic systems where (excluding crystal-field effects) ΔH is either independent of *f* or increases with *f*. We rule out a spin-glass ground state, proposed in Ref. 12 for RbC_{60}, since we observed no thermal or magnetic history dependence. Also, were the ground state a spin glass, there would be no simple explanation for the scaling of the line shape. As shown in Fig. 3, the 24 K line shapes are identical at 9 and 35 GHz if the magnetic field axis is multiplied by the resonance field, H_0. The close similarity of the scaled line shapes is a characteristic feature of AFMR in powders and implies a $1/H_0$ ($1/f$) dependence of ΔH below 40 K. As expected, below $T = 40$ K the resonance field shift (not shown), $H_0(T) - H_0(40\,\mathrm{K})$ scales also with $1/H_0$ at 9 and 35 GHz.

Between 75 and 225 GHz the linewidth depends little on *f* and does not follow the $1/H_0$ field dependence (Fig. 4). To explain this, we assume that in this range the $1/f$ narrowing of the AFMR line is compensated by a *g*-factor anisotropy broadening linear in *f*. The *g*-factor anisotropy is a consequence of the orthorhombic crystal structure of $NH_3K_3C_{60}$.[3] For simplicity, we assume in the following a uniaxial anisot-

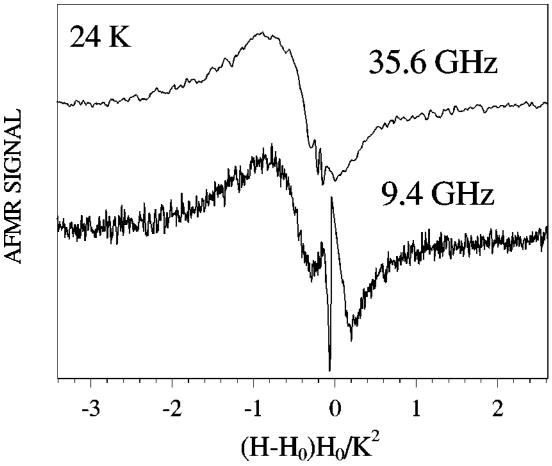

FIG. 3. Antiferromagnetic resonance at 24 K. Line shapes at 9 and 35 GHz are identical if the magnetic field scale is multiplied by the resonance field, H_0. (Low intensity narrow impurity lines are subtracted from the spectra.) We chose the normalizing constant $K = 0.17$ T, the spin-flop field H_{SF} measured at 5 K.

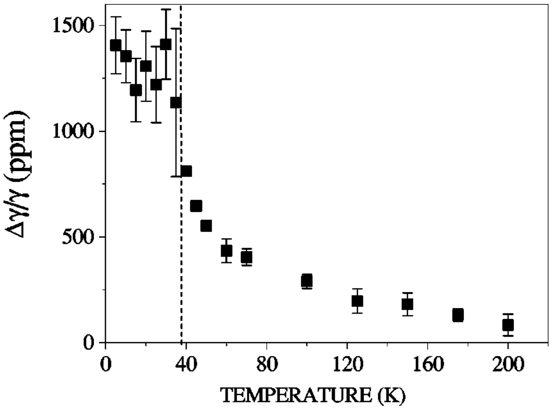

FIG. 5. Temperature variation of normalized linearly f-dependent contribution. (Dashed line indicates T_N.) $\Delta\gamma/\gamma$ is assumed to be due to partially resolved g-factor anisotropy in both the AF and paramagnetic state.

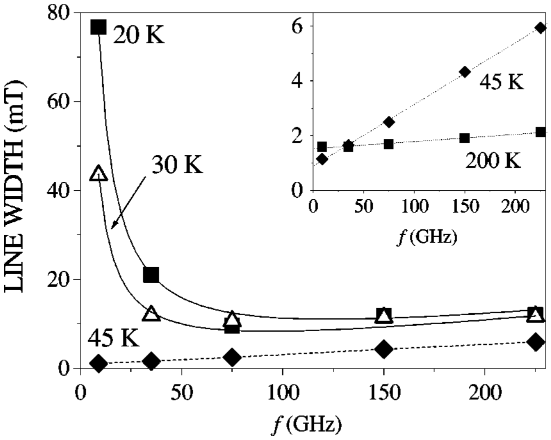

FIG. 4. ΔH as a function of f at various temperatures. The narrowing of the AFMR is compensated at high frequencies by a g-factor anisotropy broadening. (Solid lines: fit, explained in text.) Inset: ΔH (in mT) is linear in f due to partially resolved g-factor anisotropy. (Dashed lines: linear fit.)

ropy and that the principal axes of the g tensor coincide with the easy and hard axes of the AF state. In a single crystal the resonance field depends on the alignment of the external field with respect to the magnetic axes of the antiferromagnet. The hard and easy axis modes correspond to external fields perpendicular and parallel to the easy axis, respectively.[13] If H_0 is larger than the SF field, H_{SF}, the modes are[13] $\omega_\pm = \gamma_\pm\sqrt{H_0^2 \pm H_{SF}^2}$. The $+(-)$ sign corresponds to the hard (easy) axis mode, $\gamma_\pm = \gamma \pm \Delta\gamma/2$, where $\gamma = g\mu_B/\hbar$, $\Delta\gamma$ measures the anisotropy. In a powder of independent single crystals the spectrum has extrema at $H_{AFMR}^{\pm} = \sqrt{\omega^2/\gamma_\pm^2 \mp H_{SF}^2}$, $(\omega = 2\pi f)$. We assume that the measured linewidth $\Delta H = H_{AFMR}^{-} - H_{AFMR}^{+}$. A fit to this formula (Fig. 4) with the free parameters H_{SF} and $\Delta\gamma$ is in good agreement with experiment. We find $\Delta\gamma = 1300 \pm 200$ ppm independent of T below 40 K and $H_{SF}(5\text{ K}) = 0.17$ T. The anisotropy in $NH_3K_3C_{60}$ is large in comparison with $\Delta\gamma/\gamma \simeq 80$ ppm in the orthorhombic fulleride polymer RbC_{60} at T_N. On the other hand, H_{SF} in $NH_3K_3C_{60}$ is close to values in the RbC_{60} and CsC_{60} fulleride antiferromagnets.[10] The SF field is $H_{SF} = (2H_EH_A)^{1/2}$, where H_E and H_A are the exchange and anisotropy fields, respectively. $NH_3K_3C_{60}$ is composed of light elements where spin-orbit interactions are small and H_A arises from dipolar fields and is of the order of 1 mT. Since $g\mu_BH_E$ is of the order of kT_N, we expect H_{SF} is of the order of 0.1–1 T.

The assignment of the resonance below 40 K to an AFMR powder spectrum with a g-factor anisotropy implies that the broadening is inhomogeneous. However, although the spectra are significantly broadened, the line shapes are Lorentzian, which is characteristic of a homogeneous relaxational broadening. We do not know of any relaxational mechanism that could explain the data. It may be that the interaction at the boundaries of small domains with differing crystal orientations reduces the inhomogeneous broadening of the AFMR and renders the line shape approximately Lorentzian. In this case the values of H_{SF} and $\Delta\gamma/\gamma$ are only lower limits.

The ESR in the normal state (above 40 K) has an interesting frequency and temperature dependence (Fig. 2, inset and Fig. 5). The linewidth, ΔH, can be decomposed into $\Delta H(f,T) = \Delta H_0(T) + \Delta H_f(T)$, where $\Delta H_f(T)$ is proportional to f. The frequency independent term $\Delta H_0(T)$ has a maximum at the structural transition, T_S. This maximum is observed in the 9 GHz linewidth but is hidden at higher frequencies by the frequency dependent term (Fig. 2, inset). As the transition is approached from above, molecular rotations of the NH_3 groups become slower and fluctuations at the Larmor frequency broaden the line. Below the transition the molecular order increases gradually and the line narrows. A static or slowly fluctuating disorder is the usual mechanism for conduction electron-spin relaxation and a maximum is expected if the state is metallic.

An incompletely resolved g-factor anisotropy is the most likely origin of $\Delta H_f(T)$ in orthorhombic $NH_3K_3C_{60}$. (ΔH is independent of frequency in cubic K_3C_{60}.) $\Delta H_f(T) = H_0\,\Delta\gamma/\gamma$ is proportional to f up to 225 GHz at and above 40 K. As shown in Fig. 5, $\Delta\gamma/\gamma$ increases strongly as the temperature approaches T_N from above. The g-factor anisotropy at 40 K (i.e., slightly above T_N) is equal to the temperature-independent value in the AF state. The strong nonlinearity in the frequency dependence of the linewidth appears suddenly at temperatures slightly below 40 K. Thus fields up to 8 T do not smear the transition. Such behavior may be expected for an AF ordering with a large value of H_E but is unlikely in a spin glass where the melting temperature is smeared by magnetic fields. The g-factor broadening must be incomplete in the paramagnetic state for the same reason as in the AF state. Although at 45 K the ESR is several times broader at 225 GHz than at 9 GHz the line shape is Lorentzian in both cases. The ESR of high-purity Al is an example for an incomplete g-factor anisotropic broadening[14] in a metal. In $NH_3K_3C_{60}$, the increase of the g-factor anisotropy may be due to a gradual metal to insulator transition where the motional narrowing due to the diffusion of conduction electrons becomes less effective as T_N is approached.

The observation of an AFMR below 40 K is an unambiguous evidence for an antiferromagnetically ordered ground state. The static susceptibility and ESR are compatible with a paramagnetic metallic state at high temperature. This could happen if $NH_3K_3C_{60}$ undergoes a Mott-Hubbard metal to insulator transition. If this suggestion is true then $NH_3K_3C_{60}$ is one of the rare examples, and would be the only example among fulleride compounds, in which a Mott-Hubbard transition takes place at experimentally accessible temperatures.

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[*] Author to whom correspondence should be addressed. Electronic address: atj@power.szfki.kfki.hu

[†] Present address: Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599.

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