

Frequency dependent ESR study of the magnetic phase transition in $\text{NH}_3\text{K}_3\text{C}_{60}$

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Abstract. $\text{NH}_3\text{K}_3\text{C}_{60}$ undergoes a magnetic ordering phase transition below 40K which is probably the reason that this system is not a superconductor at ambient pressure. We measured the magnetic field dependence ($H = 0.3, 2.7, 5.4$ and 8.1 T) of the electron spin resonance of $\text{NH}_3\text{K}_3\text{C}_{60}$. Below 40 K the resonance broadens and shifts as the magnetic order develops. The broadening and shift are much larger at 0.3 T than at higher fields, but do not follow the $1/H$ dependence expected for an antiferromagnetic order. The magnetic spin susceptibility measured by the ESR intensity changes only little, if at all, through the transition. At 9 GHz (0.3 T) results depend on the cooling rate from ambient temperatures to temperatures below 50K.

$\text{NH}_3\text{K}_3\text{C}_{60}$, a fulleride first synthesized by Rosseinsky et al.[1] is at the borderline of a magnetic insulator and a superconducting metal. The crystal structure at ambient pressure has an orthorhombic distortion and a 6% volume expansion with respect to the fcc K_3C_{60} parent compound. Lattice expansion of A_3C_{60} superconductors with the same crystal structure increases the density of states and the superconducting transition temperature[2]. $\text{NH}_3\text{K}_3\text{C}_{60}$ has a unit cell volume of 3054 \AA^3 and a T_c higher than 30 K is expected from an extrapolation of the T_c vs lattice parameter diagram of fcc compounds. Instead, at ambient pressures it has a magnetic ground state as evidenced from low field ESR[3] and μSR [4]. The lack of superconductivity at ambient pressures is not due to the non cubic structure since under pressures larger than 10 kbar it is a superconductor[5] with $T_c=28$ K.

In this paper we present the magnetic field dependence of the electron spin resonance spectrum at 9, 75, 150 and 225 GHz (resonance fields of about $H_r = 0.3, 2.7, 5.4$ and 8.1 T) of $\text{NH}_3\text{K}_3\text{C}_{60}$. The aim was to find the antiferromagnetic resonance (AFMR) in the ground state. In a previous study of the 9 GHz ESR of $\text{NH}_3\text{K}_3\text{C}_{60}$ the onset of a magnetic order appeared as a rapid decrease of the resonance intensity. We were motivated by the recent observation[6] of the AFMR of orthorhombic RbC_{60} in which the width and shift of the resonance follows a $1/H_r$ dependence characteristic of the antiferromagnetic powder spectrum.

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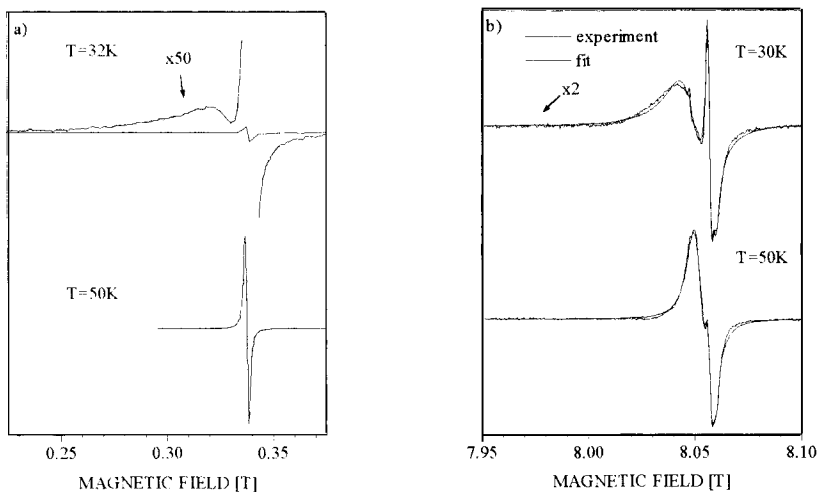


FIGURE 1. Broadening of the electron spin resonance spectra of $\text{NH}_3\text{K}_3\text{C}_{60}$ due to static internal fields below the transition at 40 K. Resonance frequency a) 9 GHz, b.) 225 GHz. The broadening is more important at low applied fields. The residual low temperature narrow lines are from a small amount of minority phase.

Samples were prepared following standard methods. X-ray diffraction showed a high phase purity. Purity was confirmed by the low temperature ESR spectra in which residual unbroadened lines had low intensities. Sample A was sealed under helium atmosphere into a quartz tube and ESR was measured at all fields. Sample B (synthesized independently from A) was mixed with vacuum grease in the dry-box under argon atmosphere and measured at the higher fields (2.7 - 8.1 T). Results for Samples A and B were similar although Sample A showed broader lines and somewhat larger shifts at low T. X-band ESR was recorded on a Bruker spectrometer in Lausanne, high frequency ESR was recorded at Budapest.

Typical ESR spectra are shown in Figure 1. The 9 GHz results are in good agreement with Ref. 2. The ESR intensity is proportional to the magnetic spin susceptibility and increases by a factor of 2 as the temperature decreases from 300 K to 50 K (Figure 2). This is a large variation for a simple metal, but is far from the Curie dependence of an insulator with localized moments. The linewidth increases linearly with field as $\Delta H = \Delta H_0(T) + a(T)H_r$. The X band linewidth (the half width at half height of the best fit Lorentzian absorption line) has a peak at 125 K where the intensity has also a small anomaly (Figure 2). $a(T)$ increases as the transition is approached, $a(200\text{K}) = 1 \times 10^{-4}$ while $a(60\text{K}) = 5 \times 10^{-4}$. On the other hand the resonance field, H_r , changes less than 100 ppm from 50 to 300 K. Thus the field does not smear the transition since static fields not only broaden but usually also shift the resonance.

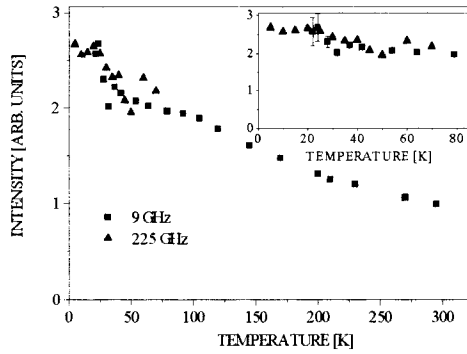


FIGURE 2. The ESR intensity is proportional to the magnetic spin susceptibility. The contribution of impurity phases is negligible. Insert: surprisingly, there is little change of the spin susceptibility through the transition.

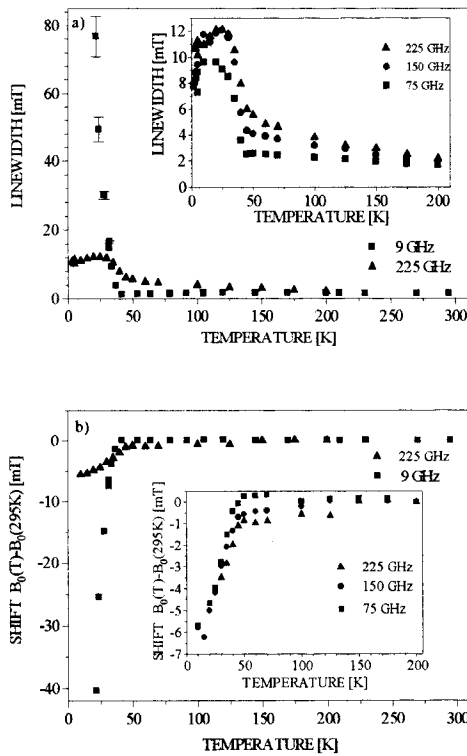


FIGURE 3. a) ESR linewidth and b) resonance field shift versus temperature at various frequencies. Above the transition the line broadens linearly with applied field. Internal static fields shift and broaden the resonance below the transition. The line is much more shifted and broadened at 9 GHz than at higher frequencies.

Below 40 K the resonance broadens and shifts to lower fields rapidly for all frequencies. These effects are quite different at 9 GHz than at higher frequencies (Figure 3). The linewidth and shift are field independent from 75 to 225 GHz and saturate as a function of temperature at 20 - 30 K. At 9 GHz the broadening and shift are much larger than at higher frequencies and depend on sample cooling rate. In samples cooled within a few minutes from ambient T to below 50 K the resonance broadened so rapidly that it could not be followed. For these samples only a decrease in the intensity of the narrow line was observed, like in previous report[3]. In slowly cooled samples a broad component carrying most of the intensity appears below 40 K. Below 22 K and at 9 GHz the line is too broad to be observed. At higher frequencies we did not detect any difference between slowly and rapidly cooled samples. The resonance intensity is unchanged both at 9 and 225 GHz within experimental accuracy through the transition. We searched in vain for magnetic field and thermal hysteresis effects between 0 and 9 T and 2.5 to 55 K.

The low temperature state is magnetically ordered as evidenced by the large field dependent broadening and shift. The order is most probably antiferromagnetic. We may rule out ferromagnetism or ferrimagnetism as there is no increase of the resonance intensity through the transition. Although the magnetic order is certainly not perfect since μ SR revealed a large distribution of fields[4], the system is not a spin glass since in that case we would observe a magnetic and thermal history dependence.

In powders, the antiferromagnetic resonance (AFMR) width is of the order of $\Delta H = (H_r H_a)/H_r$ if H_r is larger than the spin flop field, $(H_r H_a)^{1/2}$ but smaller than the exchange field H_E . The broadening of the AFMR is proportional to the square of the sublattice magnetization. A shift of similar magnitude as the broadening is expected. The anisotropy field, H_a , in fullerenes is due to dipolar fields and is of the order of $H_a = 10$ mT for a the magnetic moment of $1 \mu_B$ per fullerene molecule. At $H_r = 0.3$ T and 22 K we measure $\Delta H = 0.1$ T and with the above values the exchange field is of the order of $H_E = 3$ T. The assignment of the observed resonance to an AFMR is uncertain since we do not observe the $1/H_r$ narrowing with applied field expected for the AFMR of a powder. Instead of an $1/H_r$ dependence, a residual shift and width persists up to high fields after an initial narrowing between 0.3 and 2.7 T. We have no consistent explanation for the observed behavior.

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