Is the Ground State of A_1C_{60} (A=Rb,Cs) Antiferromagnetic?

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Abstract. EPR measurements in the metallic and the low-temperature orthorhombic phases of Rb_1C_{60} and Cs_1C_{60} powder samples have been performed at 9, 34, and 94 GHz. Detailed analysis reveals that all line features emerging in the low-temperature phase can be assigned to paramagnetic defects. We conclude that, in contrast to previous interpretations of the data, no signs of antiferromagnetic resonance (AFMR) have been observed. Furthermore we report on 94 GHz measurements of Rb_1C_{60} single crystals which show a clear angular dependence in the metallic regime.

INTRODUCTION

It is well established that upon cooling the polymer phase of the alkali fullerides Rb_1C_{60} and Cs_1C_{60} undergoes a metal-to-insulator transition in the temperature range of 50 to 25 K. Despite considerable effort that has been put into the investigation of the insulating ground state, its nature is yet not fully understood. Chauvet *et al.* were the first to propose a magnetic ground state in analogy to the spin-density-wave (SDW) ground state of the Bechgaard salt $(TMTSF)_2PF_6$ [1]. Myon spin rotation (μSR) experiments [2,3] confirmed the notion of a magnetic ground state by proving the existence of internal static magnetic fields. On the other hand μSR oscillations which are characteristic of SDW materials like $(TMTSF)_2PF_6$ have not been observed in Rb_1C_{60}. This result led to the assumption of a high degree of magnetic disorder in the ground state. Despite this disorder Alloul *et al.* interpreted their observations of the temperature-dependent linewidths and relaxation times of ^{13}C, ^{87}Rb, and ^{133}Cs in Rb_1C_{60} and Cs_1C_{60} as indicative of an antiferromagnetic spin-flop phase [4]. This interpretation has received further support by the direct observation of antiferromagnetic resonance (AFMR) using high field EPR at 75, 150, and 225 GHz by Jánossy *et al.* [5].

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Nontheless the proposition of a magnetic ground state remains under debate. Investigations of EPR intensity, lineshape, and relaxation behavior on Rb_1C_{60} powder at 9 GHz by Atsarkin *et al.* favor a nonmagnetic ground state that could be the result of a spin-Peierls transition or the development of a charge-density-wave (CDW) [6]. A discussion of several ground state scenarios can be found in [7].

Here we present a detailed analysis of the EPR signal of Rb_1C_{60} and Cs_1C_{60} powder samples in Q (34 GHz) and W band (94 GHz) as well as measurements on Rb_1C_{60} single crystals in W band.

Before proceeding to experimental details, the following section outlines the signal behavior expected of magnetically ordered systems in EPR.

THEORY

Similarly to an antiferromagnet, a spin-density-wave ground state shows a very distinctive EPR behavior. The characteristic electron-spin-resonance features of the former are known as antiferromagnetic resonance [8]. For applied static fields H_0 larger than the spin-flop field H_F, which is a characteristic measure of the strength of the antiferromagnetic coupling, the anisotropy of the AFMR signal scales inversely with H_0. For powder samples this means an inverse scaling of the AFMR linewidth with H_0. If, on the other hand, the linewidth of a powder originates in g anisotropy, it scales linearly with the applied static field. Thus, these two cases can be discriminated by measuring the signal at different H_0 fields, i.e., different microwave frequencies.

An important feature of magnetically ordered systems is the strong exchange coupling of neighboring spins. This implies fast spin relaxation and thus saturation of AFMR line components is not expected at common microwave powers.

EXPERIMENTAL

EPR measurements at 34 and 94 GHz have been performed using standard Bruker spectrometers equipped with cylindrical cavities. All spectrometers allow the adjustment of signal and reference phase so that mixing of absorptive and dispersive signal components can be minimized. Measured spectra are the derivatives of absorption signals due to the application of lock-in technique for noise suppression.

Powder samples were prepared by K.-F. Thier following the standard route. Rb_1C_{60} single crystals were kindly provided by J. Hone of the Zettl group in Berkeley.

MEASUREMENTS

While in the conducting polymer phase Rb_1C_{60} and Cs_1C_{60} powder samples show only the conduction-electron-spin-resonance (CESR) peak, the signal turns into a

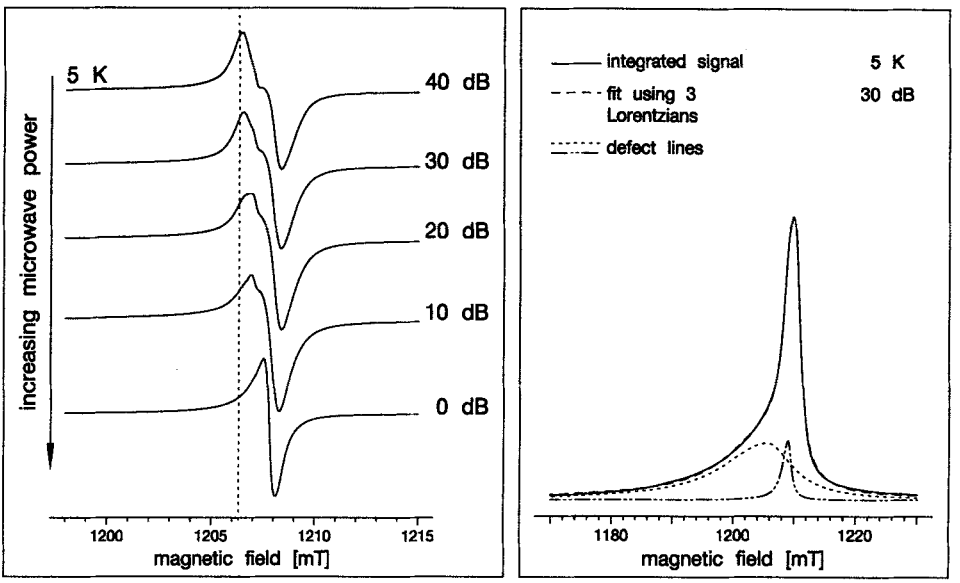

FIGURE 1. Low temperature spectra of Rb_1C_{60} at 34 GHz applying increasing microwave power, as measured (left). The spectra are labelled with the corresponding microwave attenuation values in decibel. Increasing the irradiated microwave power leads to the saturation of the line component indicated by the dashed line. The right figure shows the integrated spectrum at 30 dB fitted with three Lorentzians. Only the two line components that emerge at low temperatures are shown separately. The third component is a residual CESR signal. Note the different scaling of the field axes.

broad powder spectrum at low temperatures [5,7]. In order to determine whether this signal is composed of overlapping line components, the relaxation behavior was studied in saturation and by pulsed EPR experiments.

The left hand side of Fig. 1 displays cw EPR spectra of Rb_1C_{60} obtained at 5 K in Q band. The irradiated power differs by a factor of 10 between neighboring spectra. The signal component at the position of the dashed vertical line can be saturated by increasing the applied microwave power while the adjacent component at higher field values shows no signs of saturation. The broad wing to lower field values that is visible in the integrated spectrum in the right part of Fig. 1 also shows a decrease of intensity at an attenuation of 0 dB which corresponds to an irradiated power of roughly 135 mW. Hence, three different line components can be discriminated by their differing saturation behavior.

For this reason a fit using three Lorentzians to match the three line components in the integrated EPR signal has been applied (Fig. 1, right). It yields g factors of g=2.0072 for the broad component, g=2.0024 for the intermediate component, and g=2.0010 for the strongest component. A similar fit done on the cw spectrum at 94 GHz leads to the same g factors. By its position the strong component

can be identified as a residual signal of the CESR above the metal-to-insulator transition. The g factor of the intermediate line lies close to the g factor of free electrons. Therefore, this signal is attributed to electrons localized at intrinsic defect structures such as chain ends or broken C_{60} balls. For the third component a strongly coupled spin cluster is assumed to account for the broadness of the signal.

From Cs_1C_{60} powder samples similar spectra have been obtained, except that in this material the g factor of the broad component is 2.0037, and the residual CESR signal is much weaker than in Rb_1C_{60}.

Two-pulse experiments, which in general are sensitive to rather long-lived spin species only, show two line components at g=2.0025 and g=1.9993 for both Rb_1C_{60} and Cs_1C_{60}. The first component, also visible in the cw spectra, is the one previously assigned to localized radicals; the second is too weak to be seen in the cw spectrum. It is attributed to C_{60}^- ions since its g factor is close to that of C_{60}^- ions in solution [9].

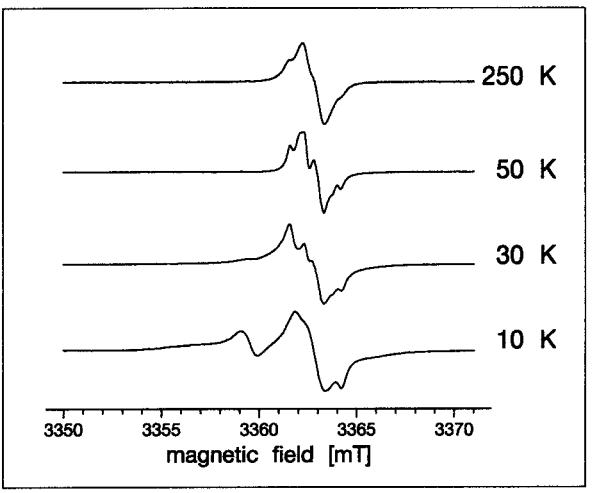

FIGURE 2. Rb_1C_{60} single crystal EPR signal for different temperatures at 94 GHz. At 50 K and above the signal exhibits an angular dependence that is not observed below the metal-to-insulator transition.

Beside the powder samples, Rb_1C_{60} single crystals have been investigated. At above approximately 400 K, these samples are true single crystals with a cubic lattice structure. Upon cooling to the orthorhombic polymer phase, domains with differently oriented polymer chains develop. There are six possible orientations of the orthorhombic cell within the crystal. Figure 2 shows a cw EPR signal of this crystal sample at different temperatures in W band. At 50 K a structured line is visible that can be fitted by six Lorentzians. The structure arises from the six CESR signals of the different domains that appear at different field values because of g anisotropy. Upon rotation of the crystal an angular dependence of the line pattern is observed. At higher temperatures an increased scattering rate of the

conduction electrons leads to a broadening of the CESR line components and thus to smoothening of the line pattern that can be observed in the 250 K spectrum in Fig. 2. At low temperatures the metal-to-insulator transition changes the signal significantly. The sixfold pattern disappears and broader components arise. This low-temperature signal is isotropic.

DISCUSSION

For the cw spectra in Q band as well as in W band all line features can be assigned to paramagnetic spins. None of the signal components shows characteristics of AFMR. In the Rb_1C_{60} crystal, an angular dependence of the signal was observed in the metallic phase. At low temperatures this angular denpendence vanishes. This is in contrast to the expectations for a single crystal AFMR signal, that should have a strong angular dependence.

These observations might be explained by assuming that the AFMR is too broad and thus too weak to be detected in powders. In the crystal sample, interactions between different domains could also broaden a possible signal beyond detectability. Another explanation might be that there is no antiferromagnetic or spin-density-wave ordering in these alkali fullerides. This would imply that the metal-to-insulator transition leads to a spin-Peierls or charge-density-wave ground state.

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