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ESR and heat capacity studies of phase transition in Rb_1C_{60}

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Abstract

Rb_1C_{60} is studied by ESR as a function of frequency from several tenth MHz to 26 GHz and by heat capacity, to reveal the nature of the phase transition around 50 K. Above the transition temperature, the electronic states are consistent with a metallic state. Below it, the ESR linewidth increases linearly with decreasing T, which is ascribed to a development of short-range order (SRO) based on its frequency dependence. Furthermore, the present analysis of the EPR spectra suggested a *distribution* of the linewidth that was consistent with broadly distributed transition temperatures of the spin density wave (SDW) or antiferromagnetism. The heat capacity shows a broad anomaly from 50 K down to 30 K. The apparent entropy change of such a magnetic anomaly suggests that only one fourth of spins are in the ordered state at 30 K, which is consistent with the reported intensity of AFMR.

Keywords: Electron spin resonance, Metal-insulator phase transitions, Magnetic phase transitions, Fullerenes and derivatives

One of the fascinating compounds of C_{60} is A_1C_{60} that shows a variety of physical properties. It is known that above 350 K the structure of A_1C_{60} is fcc and below it an orthorhombic polymer phase (Fig. 1) is the stable one.[1-3] On the other hand, presence of metastable monomer and dimer phases was confirmed by quenching from the high-T fcc phase.[4-6] In addition to this, presence of the alternative six independent axes for development of polymer chains from the high-T fcc phase makes the polymer phase disordered in chain length. This issue could play an important role to understand the physical properties of the polymer phase.

K_1C_{60} shows a metallic behavior in magnetic susceptibility and electric and optical conductivities.[1,7,8] Besides, Rb_1C_{60} and Cs_1C_{60} show a transition around 50 K that is interpreted as the transition from a metallic to an insulating state as reproduced in Figs. 2 and 4.[1,7,9] In that temperature region the conductivity shows a definite change and an indication of antiferromagnetic (AF) ordering were suggested.[10,11] However, the nature of this transition is still open so far. Further, a disordered nature was suggested by probing internal field by NMR and μSR.[11-15] It should be noted that the reported AF ordering temperatures spread over 20 K centering at 25 K,[10,11,14-16] which implies a dominant role of the disorder in chain length.

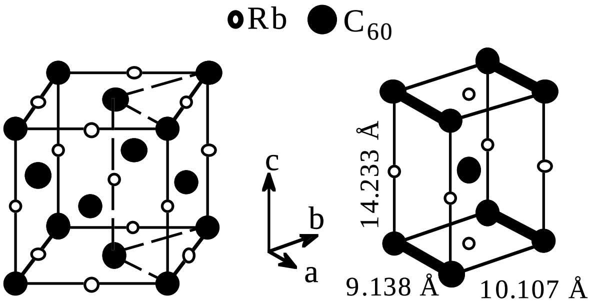

Fig. 1 The left: the high-T phase, fcc, above 350 K and the right: orthorhombic polymer phase stabilized by slow cooling from the fcc phase. The thick lines represent polymer chains.

The present report demonstrates that the *spread* of the transition temperature T_c and the development of SRO have a dominant importance to interpret the experimental data.

The sample was prepared by the reported procedure.[6] ESR spectra were taken by home built spectrometers [17] and analyzed with a least-squares fit to Lorentzians. The heat capacity was measured by adiabatic technique.[18]

Figure 2 shows the temperature dependence of Electron Paramagnetic Resonance (EPR) intensities. This demonstrates that a rapid heat treatment (square-dot), which increases defects, and contamination of impurity compounds (circle-dot) affect the manner of disappearance of the EPR intensity, that is, decrease the transition temperature, T_c. The other four data sets show a similar dependence which is activation type with an activation temperature of 100 K on average. There are two possibilities to interpret this. One is to ascribe to an opening of spin gap, that is, triplet excitation is observed. The other is to take as an accidental result aris-

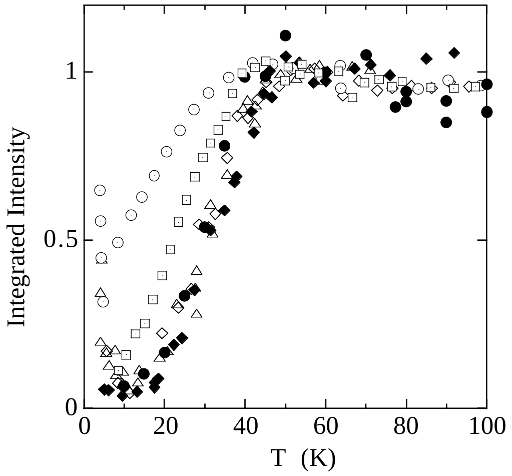

Fig. 2 The temperature dependence of the integrated intensity of EPR spectrum normalized at 60 K together with the reported data. Almost data sets converge to an universal curve that decrease exponentially below 50 K. At enough below 50 K, Curie contribution whose magnitude depends on the data sets, becomes dominant. Two data sets deviating from the others have their reasons; the one was measured from the fcc high-*T* phase at 500 K, and the other includes several % of Rb_3C_{60} phase. Solid circle: the present data, closed diamond: ref.[10], square dot: ref.[7], diamond: ref.[1], circle-dot: ref.[20], triangle: ref.[21].

ing from a wide *spread* of the transition temperatures in SDW or AF transition. Take account of the metallic nature above the transition, it does not seem to be a spin-Peierls transition, which could be realized in a system with a large on-site Coulomb repulsion *U* as in insulating materials, accompanied by AF ordering in the vicinity of impurities/disorders as found in $Cu_{1-x}Zn_xGeO_3$ systems.[19] Thus, it is reasonable to take the observed decrease of EPR intensity to be due to the *spread* in T_c.

Such an effect of the *spread* in T_c appears also in the linewidth. The typical spectrum taken at 15 K and 26 GHz is shown in Fig. 3. The spectra below 40 K could be decomposed into the three parts designated as the broad, the sharp and the Curie-like part, by virtue of the higher frequency in the present report than 9 GHz in the reported. Figure 2 implies that the magnitude of the Curie part depends on the procedures for sample preparation, suggesting this part is ascribed to impurity and/or impurity phase. The linewidth of each component is plotted in Fig. 4 as a function of temperature, together with the reported. Without decomposition of the Curie-like part from the observed, the Curie contribution dominates the observed spectra enough below 20 K, because the intensity of EPR reduces down to about 10% of that at 50 K, as seen in Fig. 2. The reported EPR linewidths taken at 9 GHz would be contaminated by the Curie contribution. Therefore, the intrinsic behavior of the linewidth, as shown by the double Lorentzian; the broad and sharp, was not obtained untill such a decomposition was applied. Both of them broaden monotonically with decreasing temperature below 40 K. Then, the next issue is what are the origins of the double Lorentzian; the broad and sharp, and the monotonic broadening of the linewidth.

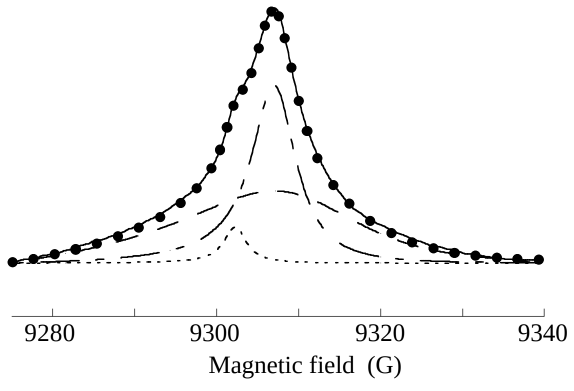

Fig. 3 An example of the EPR spectrum taken at 26 GHz and 15 K, which is decomposed into three Lorentzians; the broad (broken line), the sharp (dash-dot line), the Curie-like (dotted line). The sum of these (closed circles) is compared with the spectrum (solid line), The smallness of the Curie part represents the goodness of the sample quality.

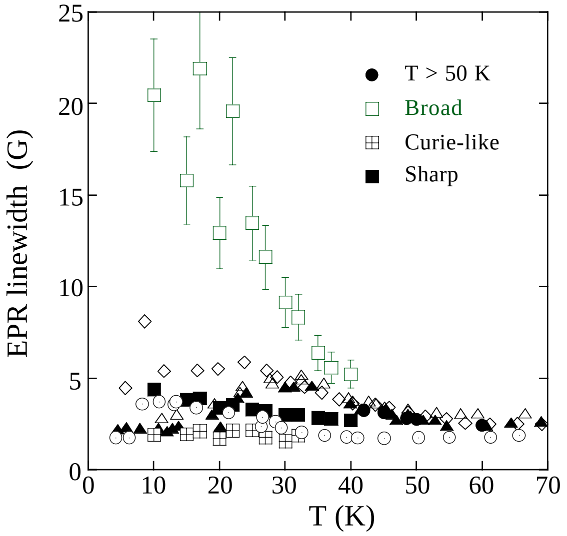

Fig. 4 The temperature dependence of peak to peak EPR linewidth: the broad, the sharp and the Curie-like, together with the reported data sets. Diamond: ref.[1], circle-dot: ref.[20], and triangles: ref.[21].

Let's try to simulate the observed double Lorentzian below 40 K. The simulated result is shown in Fig. 5 which demonstrates that there are two possibilities to interpret the double Lorentzian, the broad and the sharp. The first possibility is the presence of two independent spin species. It is, however, not likely to assume two or only two independent spin species in the present system with distributed chain-length. The second possibility of an assembly of spectra with different linewidths seems more probable for such a system. This *spread* of linewidth might be related with the origin of the slow disappearance of the EPR intensity below 50 K in Fig. 2, namely, the *spread* of T_c.

Then, the next issue is to identify the origin of the monotonic broadening of the linewidth below 50 K. In the present system, only the Rubidium nucleus is the prominent candidate for the hyperfine broadening of EPR signals, but the coupling strength with the electron spins is too weak to account for the observed linewidth enough below 50 K.[11] Therefore, a possible origin of the linewidth in the insulating state below 50 K is mag-

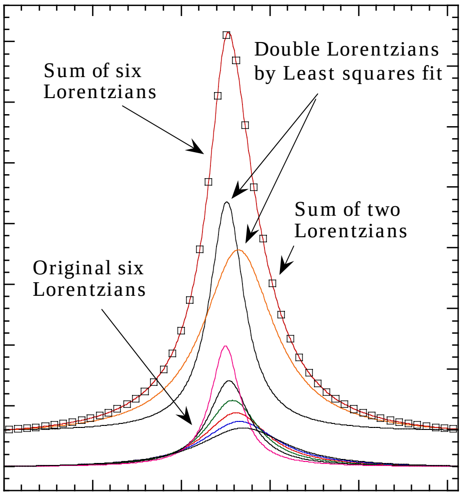

Fig. 5 Simulation of EPR spectra. The six Lorentzians with the linewidth distributed equi-interval between the minimum and the maximum ones are summed to get the top curve. Alternatively, such a curve can be reproduced with double Lorentzian represented by the middle two curves with the different linewidths; half of the maximum and 1.2 times of the minimum ones. This result suggests a possibility of spread of the linewidth, other than the possibility that there is two independent spin species for the double Lorentzian spectrum.

netic interactions. It is well known that in the vicinity of T_c, EPR linewidth shows a critical broadening arising from the critical fluctuation accompanying the AF phase transition.[22] In one-dimensional (1D) magnetic systems, it is also known that the resonance field shows anisotropic g-shift caused by 1D short-range order above T_c.[23] In the present powdered sample of Rb_1C_{60}, such anisotropic g-shift provides the line broadening proportional to the external magnetic field strength. The third candidate of the line broadening is a demagnetizing field that is proportional to the total magnetic susceptibility. It is, however, not a dominant contribution to the linewidth, since the magnetic susceptibility below 50 K reported by Janossy et al. [10] does not show such a large temperature dependence as the broad component does, as demonstrated in Fig. 4.

Therefore, the critical fluctuation and the SRO are the probable mechanism for the linewidth below 50 K. It is possible to discriminate these by investigating the frequency (magnetic field) dependence of the linewidth. A line broadening proportional to the magnetic field was actually observed. The temperature dependence of the slope, $\delta(\Delta H\mathrm{pp})/\delta f$, of such broadening is shown in Fig. 6. This is an evidence for a development of SRO below 40-50 K in Rb_1C_{60}. Since it is known that SRO develops above T_c, the increase of SRO down to 10 K as demonstrated in Fig. 6 is another evidence for the *spread* of the transition temperature, T_c below 50 K.

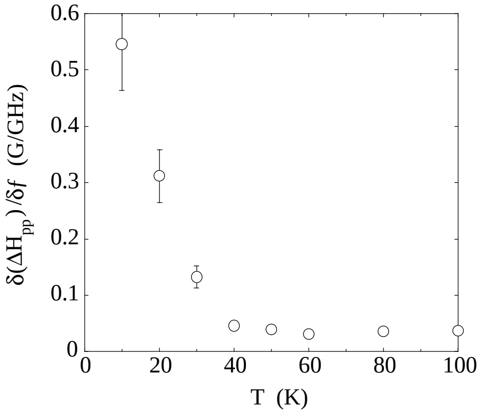

Fig. 6 The temperature dependence of the slope $\delta(\Delta H\mathrm{pp})/\delta f$ that comes from anisotropic g-shift in polycrystalline sample, which is an evidence of 1D SRO.

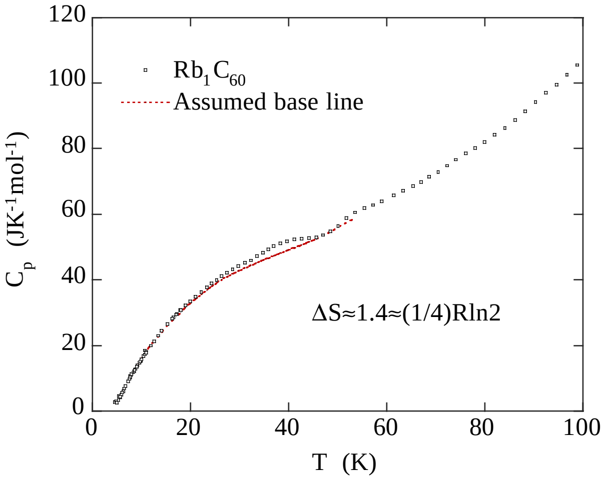

Fig. 7 The temperature dependence of the heat capacity. The dash is an assumed base line arising from a freedom of the lattice. Note that the estimated magnetic contribution amounts only one fourth of the expected entropy change of $R\ln 2$ for S=1/2 spins.

The heat capacity also supports the above conclusions. In addition to the heat capacity caused by the lattice degrees of freedom, a broad anomaly is found around 30-40 K as shown in Fig. 7. Since the AF state below 35 K has been suggested by the observation of ESR interpreted by AFMR,[10] magnetic heat capacity should be observed below the transition temperature, 50 K. Therefore, it is reasonable to interpret this anomaly as magnetic of origin. If all the spins with S=1/2 were transformed into the AF state from the paramagnetic state, this anomaly would correspond to the entropy change of $R\ln 2$. However, the entropy change estimated from the assumed base line shown by the dashed curve in Fig. 7 gives only one fourth of $R\ln 2$. This fact means that the remaining spins might be still in the paramagnetic state at 30 K and their entropy would be emitted in a more spread temperature range than that between 30 and 45 K. Thus, the heat capacity data is also consistent with the *spread* of SDW/AF transition temperature T_c.

In conclusion, the EPR linewidth and the heat capacity were measured and analyzed to conclude that the transition temperature T_c from the metallic state above 50 K to the CDW/AF ground state widely spreads from 40 K down to 10 K or less, accompanied by 1D SRO. Such a 1D nature of the magnetic interaction could be enhanced by a fact that AF-interaction between the nearest neighbor chains frustrates the intrachain AF-correlation, though a difference of the distances between intrachain balls and interchain balls is small. The most probable origin of a *spread* in the transition temperatures is a *spread* of the chain length caused by structural defects and disorder, which concerns with the nature of the polymer phase of A_1C_{60} that lies next to the multiple phases with metallic (monomer phase) and insulating (dimer phase) properties.

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