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ESR under pressure on polymer phase A_1C_{60} (A=Rb, Cs)

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Abstract

Electron spin resonance (ESR) studies under hydrostatic pressure were performed to investigate the electronic structure of orthorhombic linear polymer phase A_1C_{60} (A=Rb, Cs). Pressure dependence of the antiferromagnetic transition temperature and the Curie-Weiss temperature was investigated by the ESR intensity. On the basis of these data, together with the electrical resistivity on a single crystal under pressure (Phys. Rev. B56, 6627 (1997)), a Mott-Hubbard phase diagram is proposed for Rb_1C_{60}. At ambient pressure this material is suggested to be on the border of the metal-insulator transition.

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

1. Introduction

Since the discovery of linear polymer phase of A_1C_{60} [1], a lot of researches have been done to clarify the electronic structure of these materials. The structure of Rb_1C_{60} and Cs_1C_{60} has orthorhombic symmetry with $I_{2/m}$ space group [2,3]. The ESR studies on these two materials revealed that the intensity rapidly decreases below 50K [4,5]. These results, along with the microwave and optical conductivites [4], were attributed to the transition from metallic state to insulating spin density wave (SDW) ground state which is characteristic of quasi-one-dimensional (Q1D) electronic states. This transition was confirmed by an observation of antiferromagnetic resonance at ambient pressure [6]. Many other experiments including NMR and μSR were performed so far, and the electronic states of the polymer phase are regarded as the 1D. Khazeni et al. reported the pressure dependence of the resistivity on a single crystal [7]. They showed that in Rb_1C_{60} the resistivity is semiconducting at ambient pressure and below 200K the transition occurred from semiconductor to metal in the range of 0.5kbar and 1.4kbar.

In contrast to the experimental conclusions, theoretical studies favored three-dimensional (3D) electronic structure. Erwin et al. suggested 3D semimetallic electronic states from the first principle band calculation and the magnetic fluctuation giving rise to 3D antiferromagnetic ordering [8]. Ogitsu et al. predicted independently that Rb_1C_{60} has a half filled anisotropic band and would be a Mott-Hubbard insulator with strong correlation [9]. Thus the nature of the ground state and the dimensionality of the electronic states are still controversial.

In this report, we measured ESR intensity on polymer phase Rb_1C_{60} and Cs_1C_{60} as a function of temperature under various hydrostatic pressures to resolve the above-mentioned controversy. On the basis of the obtained results we propose a phase diagram for Rb_1C_{60} to be a Mott-Hubbard insulator near the border of the metal-insulator transition.

2. Experimental

ESR intensity was observed around 50MHz and calibrated with *in-situ* ^{1}H NMR of reference material. A clamp-type cell of CuBe alloy was used to apply pressure with Daphne 7373 oil as a pressurizing medium. Because pressure decreases with decreasing temperature due to thermal contraction of the medium, the pressure was indicated as P_{50K} corrected at 50K using the reported data [10], below which the pressure is nearly temperature independent.

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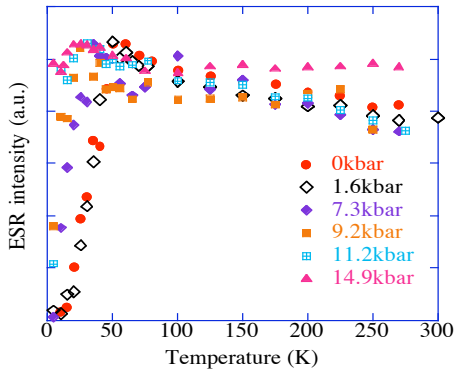

Fig. 1. The temperature dependence of ESR intensity in Rb_1C_{60} under several hydrostatic pressures.

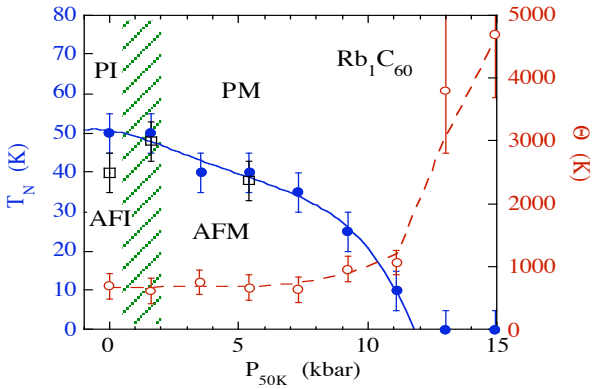

Fig. 2. The phase diagram of Rb_1C_{60}. PI: paramagnetic insulator, PM: paramagnetic metal, AFI: antiferromagnetic insulator, AFM: antiferromagnetic metal. closed circle: T_N in Rb_1C_{60}, open circle: Θ in Rb_1C_{60}, open square: T_N in Cs_1C_{60}.

3. Results and discussion

Figure 1 shows the temperature dependence of ESR intensity in Rb_1C_{60} under the pressure between 0kbar and 14.9kbar. The transition temperature (T_N) was defined as the peak temperature. In the paramagnetic region above T_N, the intensity is proportional to the paramagnetic spin susceptibility and below T_N the intensity rapidly decreases as the antiferromagetic resonance develops with different resonant condition. One can see that T_N and the slopes above T_N reduces with increasing pressure. At 14.9kbar the intensity becomes almost constant just like Pauli susceptibility. By a fitting these data to Curie-Weiss law the Curie-Weiss temperature (Θ) was estimated. The pressure dependence of T_N and Θ are shown in Fig. 2. Above 12kbar the transition disappears in the studied temperature range and Θ's become very high, suggesting the transition from localized to itinerant under pressure. From this result and the pressure dependence of resistivity [7], the nature of each phase was determined as shown in Fig. 2, which is a typical phase diagram of a Mott-Hubbard system.

The insulator phase at ambient pressure may suggest that the intrachain and interchain transfer energy would not be large enough to make the electronic states metallic within the chain as well as between the chains. The intermolecular distance along the chain, i.e. the intrachain transfer energy, would be hardly reduced under the present pressure range because of the strong covalent bond. On the other hand, the interchain distance dominated by van der Waals interaction could be easily reduced even under the present pressure range. Therefore the interchain transfer energy could be enhanced enough to make the interchain electronic states metallic. Thus the three dimensional network is developed under pressure through the paths between eight nearest interchain neighbors. Since C_{60} molecules form a triangle lattice they become a magnetically frustrated system. It is known that the antiferrromagnetic metal phase is characteristic of the frustrated systems [11].

The present results are consistent with the band calculation that predicted Rb_1C_{60} has a half filled three-dimensional conduction band. In contrast to that, the presence of the paramagnetic insulator phase and the antiferromagnetic metal phase is in contradiction to the spin density wave stabilized by an opening of an energy gap on the one-dimensional Fermi surface.

ESR intensity study in Cs_1C_{60} is also under way and preliminary data are indicated by the open squares in Fig. 2. More data are needed to construct a phase diagram and compare the two materials.

4. Conclusion

The phase diagram of Rb_1C_{60} is presented from the analysis of the ESR and the resistivity [7] data, suggesting that Rb_1C_{60} is the Mott-Hubbard insulator on the border of the metal-insulator transition at ambient pressure.

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