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EPR in Rb_1C_{60} under Pressure

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Abstract. The orthorhombic one-dimensional polymer phase of Rb_1C_{60} is proposed to be a Mott-Hubbard insulator, having three-dimensional electronic states, on the border of the metal-insulator transition at ambient pressure. That is confirmed from the transition temperature T_N vs pressure phase diagram, which was obtained on the basis of the pressure dependence of T_N by electron paramagnetic resonance (EPR), together with the electrical resistivity data under pressure reported by Khazeni *et al.* [*Phys. Rev.* B**56**, 6627-6630 (1997)]. The EPR linewidth can be understood from the Elliott mechanism viewpoint.

INTRODUCTION

Intensive research has been done on the orthorhombic one-dimensional polymer phase of Rb_1C_{60} stabilized by the slow cooling from face centered cubic phase above 350 K [1, 2, 3]. EPR measurement showed a rapid decrease of its intensity around 50 K [4, 5] and antiferromagnetic resonance was observed at ambient pressure [6]. Along with the data indicating relatively high electrical conductivity [4], those results were considered to show that the ground state is insulating spin density wave (SDW) state that is characteristic of quasi-one-dimensional (Q1D) electronic states. Almost experimental results including NMR and μSR were mainly regarded as the evidence for the electronic states of *o*-Rb_1C_{60} to be 1D. In contrast to that, band calculations suggested that this material has 3D electronic structure and would be a Mott-Hubbard insulator with strong electronic correlation [7,8]. Therefore the electronic states of *o*-Rb_1C_{60} is still open question. Khazeni et al. reported the pressure dependence of the electrical resistivity on a single crystal [9]. They showed that the resistivity in Rb_1C_{60} 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 this study EPR intensity and linewidth were measured under several hydrostatic pressures to elucidate the electronic states of *o*-Rb_1C_{60}.

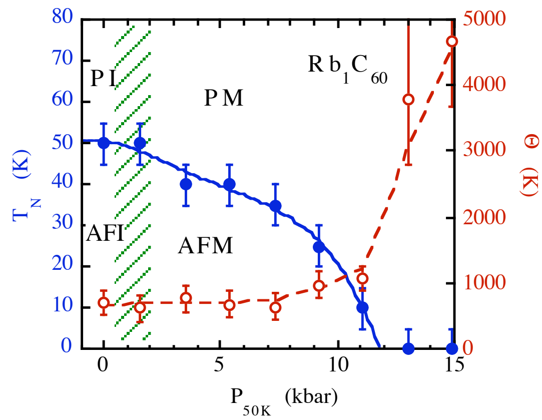
EXPERIMENTAL

EPR signals of Rb_1C_{60} powder sample were measured around 50 MHz under hydrostatic pressure using a clamp-type CuBe cell and Daphne 7373 oil as a pressurizing medium. The intensities were calibrated with *in-situ* ^{1}H NMR of the Daphne oil as reference. The linewidths were estimated by a least squares fit of the signals to Lorentzian functions. Pressure values at 50 K used in this report were corrected with the reported data [10] to account for the thermal contraction of the medium.

RESULTS AND DISCUSSION

The transition temperature T_N was estimated as the intensity peak temperature. The Curie-Weiss temperature Θ was also obtained from the temperature dependence of the intensity in the paramagnetic region above T_N [11]. Figure 1 shows T_N's and Θ's as functions of pressure. One can see that T_N approaches zero and Θ becomes large above 12 kbar, indicating that the pressure induced the transition from insulating to metallic state, which is consistent with the data of the electrical resistivity under pressure by Khazeni *et al*. mentioned above [9].

Combining the present and the resistivity [9] results, we constructed the temperature-pressure phase diagram as shown in Fig. 2. It should be noted that this diagram is typical of a Mott-Hubbard system. Both of interchain and intrachain transfer energy are so weak that the elctronic structure is semiconducting at ambient pressure. The pressure could enhance the interchain transfer energy enough to make the interchain electonic states metallic since the interchain coupling is dominated by weak van der Waals interaction, but not covalent-bonds as within the chain. As a result, the three dimensional network is developed through C_{60} molecules in the nearest chains under pressure. This conclusion well agrees with the theoretical prediction that Rb_1C_{60} has a half filled 3D band. Contrary to that, SDW ground state with the energy gap at the Fermi energy of 1D metal is in contradiction to the paramagnetic insulator phase above T_N and the antiferromagnetic metal phase below T_N. It is noteworthy that the antiferromagnetic metal phase is characteristic of magnetically frustrated system such as the present one forming a triangle lattice [12]. Thus Rb_1C_{60} is concluded to be



a **FIGURE 1.** The T_N vs pressure phase diagram of Rb_1C_{60}. Closed circles: transition temperatureT_N, Open circles: Curie-Weiss temperature Q, PI: paramagnetic insulator, PM: paramagnetic metal, AFI: antiferromagnetic insulator, AFM: antiferromagnetic metal. Pressure is the estimated values at 50 K. The solid and dashed curves are guides for the eyes.

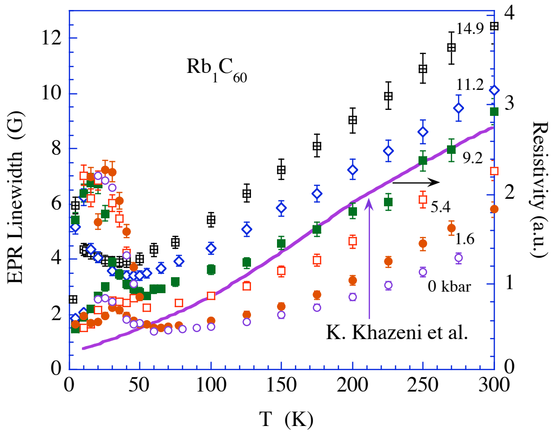


FIGURE 2. The temperature dependence of EPR linewidth. The pressures estimated at 50 K are indicated near each plot. The solid curve is the electrical resistivity (in arbitrary unit) at 10.6 kbar at 300K from Ref.9.

Mott-Hubbard system on the border of metal-insulator transition at ambient pressure.

The temperature dependence of EPR linewidths under various pressures is shown in Fig. 2. We discuss the linewidths in the paramagnetic range above T_N, where they increase with increasing temperature. The solid curve in Fig. 2 indicates the electrical resistivity at 10.6 kbar at 300 K reproduced from Ref. 9. The agreement of the temperature variations of the linewidth and the resistivity around this pressure, where the electronic state is metallic, implies that the linewidth is governed by Elliott mechanism, applicable to the free charge carriers bearing spins with spin-phonon scattering via spin-orbit interaction [13]. Then linewidth in metallic sample is proportional to the inverse of a momentum relaxation time, i.e., the electrical resistivity. Even in the semiconducting phase, however, the linewidth could increase with temperature as observed at the low pressure data in Fig. 2, since there exist thermally excited electrons in the conduction band, as Elliott discussed originally [13]. The resistivity, however, decreases with temperature since the number of free charge carriers rises as temperature goes up.

The linewidth of ≈ 5 G at 300K at ambient pressure is about 100 times narrower than that of 3D superconducting Rb_3C_{60}, ≈ 450G. This was regarded, so far, as an evidence that the electronic structure of Rb_1C_{60} is 1D, because Elliott mechanism is suppressed in the 1D systems [13]. On the contrary, this difference in the linewidths can be understood as the difference of the g-shifts Δg in these materials, $\Delta g \approx 0.0011$ for Rb_1C_{60} and $\Delta g \approx 0.0137$ for Rb_3C_{60} [14], which dominates the Elliott linewidth proportionally to $(\Delta g)^2$. Thus it could be considered that the linewidth is dominated by Elliott mechanism even in RbC_{60}.

CONCLUSION

EPR measurements under pressure were performed to reveal the electronic structure of 1D polymer phase of o-Rb_1C_{60}. From the pressure dependences of the transition temperature obtained from the temperature variation of EPR intensity and the electrical resistivity from Ref. 9, we constructed the phase diagram, which shows that this material is a 3D Mott-Hubbard system near the metal-insulator transition at ambient pressure. The origin of the EPR linewidth is the spin-phonon scattering via spin-orbit interaction.

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