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Electronic states in Rb_1C_{60} studied by EPR under pressure: 3D Mott-Hubbard system

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Electron paramagnetic resonance (EPR) is applied to orthorhombic Rb_1C_{60} 1D polymer under hydrostatic pressure. The EPR linewidth is interpreted in terms of Elliott mechanism. EPR signal intensity provides us the antiferromagnetic transition temperature T_N where the intensity drops suddenly. Finally, a phase diagram of the electronic states in o-Rb_1C_{60} is constructed from T_N vs pressure diagram, along with the resistivity under pressure, reported by Khazeni *et al.* [Phys. Rev. B **56**, 6627 (1997)]. From this diagram we can definitely conclude that o-Rb_1C_{60} is not a SDW system typical for 1D electronic band, but a 3D Mott-Hubbard insulator near a border of the transition.

In the polymer phase of A_1C_{60} (A is K, Rb, Cs), one-dimensional polymer structure is formed by [2+2] cycloadditive mechanism.[1,2] So far, a lot of investigations on these materials have been reported because of its peculiar physical properties. K_1C_{60} shows a metallic temperature dependence of the electrical conductivity in the whole reported temperature range.[1,3] On the contrary, in Rb_1C_{60} and Cs_1C_{60}, the spin susceptibility by EPR shows a sudden decrease below ≈ 50 K.[3,4] These observations together with microwave and low frequency optical conductivities in Rb_1C_{60} were interpreted as a phase transition from a metallic state above 50 K to an insulating spin-density wave (SDW) ground state which is characteristic of electronic systems in quasi-one-dimension (Q1D).[3,4] Nevertheless, another possibility of spin glass (random spin freezing) was proposed based on μSR technique.[5–7] However, NMR in Cs_1C_{60} at ambient pressure,[8] and antiferromagnetic resonance (AFMR) (Ref. 9) in Rb_1C_{60} suggested an occurrence of antiferromagnetic long-range order in the 1D electronic state. Contrary to these experimental conclusions, from a theoretical aspect, 3D semimetallic electronic structure and 3D antiferromagnetic ordering in Rb_1C_{60} and Cs_1C_{60} with $I2/m$ symmetry has been concluded with first-principles electronic-structures method by Erwin, Krishna, and Mele (Ref. 10), which was supported by a pressure study in Rb_1C_{60} (Ref. 11).

Recently, single crystal studies were reported, which provides us fundamental information. The resistivity in single crystals has been reported by Khazeni and co-workers that K_1C_{60} is metallic with upturn around 50 K, but Rb_1C_{60} is insulating at ambient pressure.[12] By applying pressure Rb_1C_{60} also transforms to a metallic resistivity. On a structural aspect, Launois *et al.* reported x-ray analysis with single crystals that K_1C_{60} and Rb_1C_{60} have different symmetries, $Pmnn$ and $I2/m$, respectively,[13] which produces a difference of band structure from each other. Actually, Ogitsu *et al.* has concluded that K_1C_{60} with $Pmnn$ symmetry, that differs from $I2/m$ for the Rb_1C_{60}, is an anisotropic metal from a first-principles calculation.[14]

In this paper we describe a comprehensive study on Rb_1C_{60} with hydrostatic pressure to make clear the electronic states of this material. By applying pressure the interchain transfer energy could be mainly modified. A magnetic phase diagram was constructed from the temperature dependence of EPR signal intensity. Combining it with the resistivity data under pressure,[12] we can construct a phase diagram of the electronic states that tells us Rb_1C_{60} is on the border of Mott-Hubbard insulator-metal transition, but not SDW system with 1D metallic chains, which is fully consistent with the first-principles calculation of electronic structure.[10] This resolves a long-term controversy between the 3D electronic states predicted by the theory and the experimentally proposed 1D electronic structure, resulting in SDW ground state.

EPR intensity proportional to a spin susceptibility in a paramagnetic temperature range was calibrated with *in situ* measurement of ^{1}H NMR intensity in a reference material at around 50 MHz. EPR spectra were analyzed with a least squares fit to Lorentzian functions. For pressure experiment, a clamp-type cell made of CuBe alloy is used with Daphne 7373 oil as a pressurizing medium. Figures of pressure shown in this work are nominal values clamped at room temperature, shown by P_{rt}. Pressure loss caused by thermal contraction is corrected with the values reported by Murata.[15] The corresponding pressure below 50 K, $P_{50\,\mathrm{K}}$ is estimated by $P_{\mathrm{rt}} \times 1.096 - 2.215$.

Figure 1 shows the temperature dependence of EPR linewidth under the various pressures. Below T_N the EPR linewidth could be reproduced by the sum of two Lorentzians; the narrow linewidth ≈ 2 Gauss, probably due to Curie spins arising from impurity sites and the broader one, ≈ 7 Gauss, intrinsic to Rb_1C_{60} influenced by the antiferromagnetic or-

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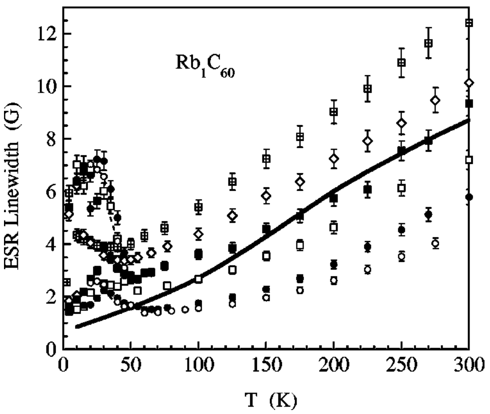

FIG. 1. Temperature dependence of the EPR peak-to-peak linewidth in Rb_1C_{60} measured around 50 MHz. From bottom to top, P_{rt} ($P_{50\,\mathrm{K}}$) is 0, 3.5 (1.6), 6.9 (5.4), 10.4 (9.2), 12.2 (11.2), and 15.6 (14.9) kbar. The solid line shows the resistivity (in arb. units) under 10.6 kbar and 8 kbar at 300 K and 10 K, respectively, reproduced from Ref. 12.

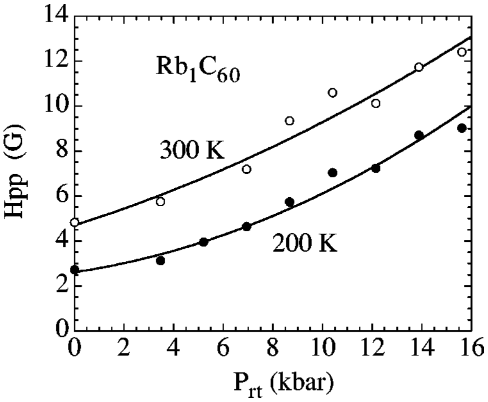

FIG. 2. Pressure dependence of the EPR linewidth both at 200 and 300 K. The solid curves are guide for the eyes.

dering developed below T_N.[16] The presence of broad signal below T_N suggests that the observed phase transition even under high pressure is magnetic in origin. Interestingly the EPR linewidth broadens below 10 K even under the highest pressure, where the spin susceptibility is paramagnetic. This suggests still a presence of antiferromagnetic correlation near the border between antiferro- and para-magnetic states.[11]

The EPR linewidth shows a monotonic increase in the paramagnetic temperature range, which has been interpreted by a spin-phonon scattering via spin-orbit interaction, Elliott mechanism. This mechanism could be a dominant origin for the EPR linewidth in the systems with free charge carriers, such as semiconductors and metals.[17–20] As a result, the EPR linewidth would be proportional to the electrical resistivity of the metals which is proportional to the phonon-scattering frequency of the free charge carriers. Actually, the temperature dependence of EPR linewidth reasonably agrees with that of the resistivity in the metallic phase at 10.6 kbar, as demonstrated by the solid curve taken from Ref. 12 in Fig. 1. A disagreement below 150 K would be attributed to the magnetic broadening of the linewidth and a larger residual resistivity in the present powder sample. In the case of the semiconductors, as the present system with a small energy gap of ≈ 0.02 eV at ambient pressure,[12] the EPR linewidth would also be reproduced as Elliott has done.[17] Of course, it should not be necessarily proportional to the electrical resistivity, because the resistivity is dominated not only by the phonon scattering as the Elliott mechanism, but also by the number of free charge carriers.

Next, let us discuss the monotonic increase of EPR linewidth with increasing pressure in Fig. 2. With the interpretation in terms of the Elliott broadening $\propto (\Delta g)^2 \tau_m^{-1}$, two parameters, τ_m^{-1} and Δg are expected to change with the pressure. Generally, the number of phonons would decrease with hardening of a spring constant of lattice by the pressure. Actually, the resistivity in the metallic range decreases with increasing pressure,[12] consistent with the expected variation of the number of phonons. Then, τ_m^{-1}, proportional to the number of phonons, could not be an origin for this monotonic increase. Therefore, $\Delta g = \lambda / \Delta E$ would be a probable origin of the observation in Fig. 2. The pressure could decrease the ΔE, the minimum energy difference between the bands of charge carriers and the Rb^+ cations, through broadening of both bands by the pressure.

Figure 3 shows the temperature dependence of the EPR intensity under various hydrostatic pressures. In the paramagnetic region it is proportional to the spin susceptibility, but it rapidly disappears below antiferromagnetic transition temperature T_N and instead antiferromagnetic resonance (AFMR) develops with different resonance conditions from that for EPR.[9] Actual disappearance below T_N is, however, rather slow because of distribution of T_N caused by a probable chain length distribution.[16] Then, we defined T_N as a

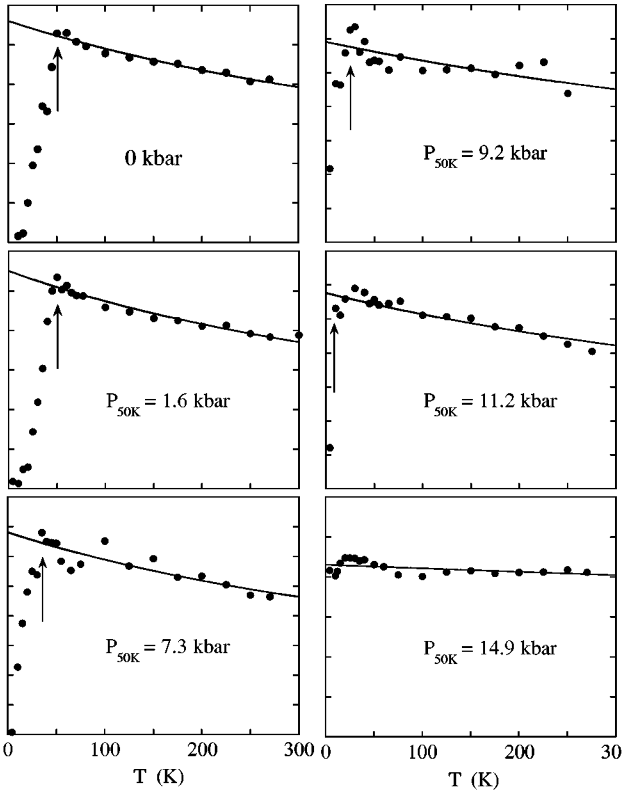

FIG. 3. Temperature dependence of the EPR signal intensity (arb. units) in Rb_1C_{60} under the various pressures. The solid curves indicate the Curie-Weiss fitting to the data. The vertical arrows indicate the estimated T_N's.

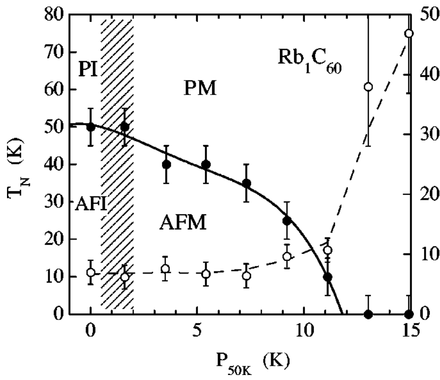

FIG. 4. Temperature-pressure phase diagram of Rb_1C_{60}, deduced from the pressure dependences of T_N (the closed circles) and resistivity (Ref. 12). PI: paramagnetic insulator, AFI: antiferromagnetic insulator, PM: paramagnetic metal, and AFM: antiferromagnetic metal. These phases are consistent with the Mott-Hubbard metal-insulator transition. The solid and dashed curves are guides for the eyes. The hatched area shows a border region between insulator and metal, based on Ref. 12. The Curie-Weiss temperature, Θ (right-hand scale) is also shown by the open circles.

peak temperature, indicated by the vertical arrows in Fig. 3. With increasing pressure, T_N decreases from 50 K down to less than the minimum temperature of 2 K studied. The curves in Fig. 3 indicate a Curie-Weiss fitting to the data in the paramagnetic temperature range, demonstrating that the Curie-Weiss temperature Θ increases with the pressure, almost Pauli-like above 10 kbar, as shown in Fig. 4. Here, it should be noted that the estimated Weiss temperature is the lower bound at each pressure, because the EPR intensity at low temperatures would be enhanced by the corresponding quantity to the reduction of pressure, caused by thermal contraction. Then, the above feature of Fig. 3 suggests that above T_N the pressure could induce a transition of the electronic states in Rb_1C_{60} from localized to itinerant, which agrees well with the pressure dependence of the resistivity in single crystal (Ref. 12). At ambient pressure, the ground state of Rb_1C_{60} has been confirmed to be an antiferromagnetic insulator,[9,12] but not under the pressure. However, it is reasonably assumed to be antiferromagnetic even under the pressure below 10 kbar because of the following reasons; (1) the transition temperature varies smoothly with increasing pressure and (2) the EPR linewidth remarkably broadens below the transition even under the pressure, suggesting a magnetic ordering, such as antiferromagnetism, but not ferromagnetism because of the observed reduction of signal intensity, instead of sizable signal enhancement characteristic of ferromagnetic resonance (FMR).

We can construct the phase diagram of electronic states in Rb_1C_{60} with the pressure dependence of T_N together with the pressure dependence of the resistivity,[12] as shown in Fig. 4. They reported that a slope of the resistivity versus T transforms from semiconducting to metallic in between 5 and 8 kbar at 300 K and that at low temperatures probably below 50 K, where the thermal contraction ceases, it does in between 0.5 and 1.4 kbar, as schematically described by the hatched area in Fig. 4. The substantial difference of transition pressure results from a first-order resistive transition around 180 K.[12] Following this diagram, the electronic states of Rb_1C_{60} at ambient pressure changes from the paramagnetic insulator (PI) with pseudo-gap (Ref. 12) to the antiferromagnetic insulator (AFI) with decreasing temperature. Above 2 kbar it changes to the metallic state at least enough below 200 K,[12] where, with cooling, it does from the paramagnetic metal (PM) to the antiferromagnetic metal (AFM). These are the remarkable experimental facts that the both phases of PI and AFM contradict to the supposition of the phase transition of spin density wave (SDW) in 1D metals, which is stabilized by a symmetry change accompanied with an opening of the energy gap at the Fermi energy, giving rise to an insulating state. It should be noted, on the contrary, Fig. 4 is a typical phase diagram for a Mott-Hubbard system,[21,22] which is rather natural, if one takes account of the fact that Rb_1C_{60} has a half-filled three-dimensional (3D) electronic band[10] with the $I2/m$ lattice symmetry.[13] This phase diagram suggests the on-site Coulomb energy U is comparable to the transfer energy t at ambient pressure. AFM phase is known to be characteristic of the magnetically frustrated systems,[22] as in the present system;[10] comparable magnitude of the intrachain transfer energy t_{intra} to the interchain transfer energy t_{inter}, sizably enhanced by the pressure. Although we have no structural data under the pressure yet, the pressure in the present range would mainly affect the interchain distances by virtue of the van der Waals coupling between the chains, but not within the chain, having strong covalent bondings. This fact along with the insulating ground state suggests that t_{intra} at ambient pressure is not large enough to make the electronic states of a chain metallic. Under the pressure, t_{inter} is highly enhanced to construct a three-dimensional network of all the C_{60} balls via eight nearest interchain neighbors. Then, we conclude that at ambient pressure the electronic states of Rb_1C_{60} having a half-filled band, is nearly on the border of the Mott-Hubbard insulator-metal transition, but is not in the SDW instability of 1D metal. This is consistent with the band calculation by Erwin and co-workers.[10]

Usually, it is discussed that the narrower EPR linewidth of ≈ 5 G in the present system than the superconducting compounds, Rb_3C_{60} with the width of ≈ 450 G is due to the one dimensionality of the electronic states in Rb_1C_{60}. However, this difference between the two compounds could be interpreted simply with the difference of Δg's;[16] 0.0011 for Rb_1C_{60} and 0.0137 for Rb_3C_{60}, which predicts more than 100 times narrower linewidth for the present system with the Elliott broadening mechanism $\propto(\Delta g)^2\tau_m^{-1}$. Transport of the charge carriers with spins studied by the frequency dependence of EPR linewidth also suggested a less 1D character,[16] consistent with the present conclusion. Therefore, the difference of the EPR linewidth does not reflect that of the dimensionality, but do that of the electronic band structures in these systems.

The one-dimensional SDW ground state in Cs_1C_{60} has also been concluded from NMR result of $(T_1T)^{-1}=1.7+1430T^{-0.95}$, nearly T-independent T_1^{-1}, for ^{13}C and ^{133}Cs.[8] However, this kind of relation is general in the 3D antiferromagnet not only for the localized spin systems,[23] but also for the itinerant electron systems.[24] Actually, we tried successfully to reproduce the reported data as a 3D antiferromagnetic system.[23,24] Then, the NMR data do not contradict with the present conclusion, but are consistent with the 3D electronic state.

In conclusion, we demonstrated that 1D polymer phase of o-Rb$_1$C$_{60}$ is a 3D Mott-Hubbard insulator at ambient pressure, instead of 1D SDW system proposed by a lot of experimental investigations. In a very similar system even in the lattice parameters, Cs$_1$C$_{60}$ with $T_N \approx 40$ K, it is suggested to be also a Mott-Hubbard insulator in more left side position of Fig. 4, from the smaller Curie-Weiss temperature than that in the present system. Such a study under the pressure is in progress. On the contrary, K$_1$C$_{60}$ with $Pmnn$ structural symmetry has a different electronic state from the Rb and Cs compounds with $I2/m$ symmetry.[13]

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