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Magnetic susceptibility of the one-dimensional polymeric phase of RbC$_{60}$

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Detailed magnetic susceptibility measurements of the RbC$_{60}$ polymeric phase have been carried out. A decrease in the susceptibility on cooling below 50 K consistent with the temperature dependence of the electron spin resonance intensity hitherto reported has been observed. It has been shown that this temperature dependence can be interpreted in terms of the spin density wave scenario in a consistent manner and that the density of states at the Fermi level can be estimated as 11.9 states/(eV C$_{60}$). This value is in reasonable agreement with 8 states/(eV C$_{60}$) estimated by the tight-binding band structure calculation.

I. INTRODUCTION

Several kinds of alkali-metal-doped polymeric C$_{60}$ materials connected by covalent bonds without any additional linking groups have recently been considerably paid attention to.$^{1-3}$ In particular, AC$_{60}$ (A = K, Rb, and Cs), first reported as the electrically conducting alkali fulleride linear-chain polymer,$^4$ is currently of high interest. Stephens et al. have first reported a relatively simple crystal structure of polymeric AC$_{60}$ with parallel polymer chains consisting of covalently bonded C$_{60}$ molecules.$^1$ Recently, Launnois et al.$^5$ have found that the single crystal of the polymeric phase of RbC$_{60}$ is actually monoclinic, space group $I\bar{2}2m$ (without measurement of the monoclinic angle). Bendele et al.$^6$ have reached a similar conclusion with the monoclinic angle $\beta = 90.3^\circ$.

One of the most interesting aspects of these materials is their low-dimensional-like electronic properties, which are different among the AC$_{60}$ polymers with each kind of A. In the electron spin resonance (ESR) study, it was suggested that the polymeric RbC$_{60}$ and CsC$_{60}$ are quasi-one-dimensional (1D) conductors and that the phase transition at 50 K causes antiferromagnetic (AF) ordering of spin density waves$^4$ (SDW) under that temperature, while the KC$_{60}$ polymeric phase remains almost an isotropic metal.$^7$ Such a 3D metallic property of KC$_{60}$ has been confirmed by nuclear magnetic resonance (NMR).$^8$ On the other hand, the nature of the ground state of RbC$_{60}$ and CsC$_{60}$ is still under debate. Recently, Jánossy et al. have observed the AF magnetic resonance$^9$ (AFMR) in powder samples of RbC$_{60}$ and CsC$_{60}$ at high frequencies (75, 150, and 225 GHz) and their experimental data supported the above scenario of the quasi-1D SDW system. Bennati et al.$^{10}$ have reached similar conclusions from a high-field ESR investigation. However, they have added that all the features in the ESR results interpreted by AFMR scenario can also be well explained within the spin-glass model. Moreover, in polymeric CsC$_{60}$, it has been reported that detailed $^{13}$Cs-NMR investigations revealed the coexistence of a spin-Peierls (non-magnetic) state with 3D magnetic order below 13.8 K.$^{11}$

Meanwhile, a theoretical study on the RbC$_{60}$ polymeric phase$^{12}$ has led to different predictions from the experimental results concerning the dimensionality of the corresponding phase; the crystal orbital (CO) study on this compound on the basis of the tight-binding calculation including both $\sigma$ and $\pi$ electrons instead favors a dimensionality of three. Therefore, both the dimensionality of the electronic structure and nature of the low-temperature phase currently seem to remain open questions.

In general the ESR data do not correspond to the static magnetic susceptibility and, moreover, the former hardly allows us to discuss the magnetic behavior around the transition temperature of the magnetically ordered state in a quantitative manner.$^7$ In the present article, we present the measurement results of bulk magnetization of the polymeric phase of RbC$_{60}$ by a superconducting quantum interference device (SQUID) magnetometer and discussion of the above-mentioned problem by means of quantitative analysis of the data of temperature dependence of the static magnetic susceptibility.

II. SAMPLE PREPARATION AND CHECK

The sample was prepared by solid-phase reaction of C$_{60}$ and Rb, the latter of which was directly generated by thermal decomposition from RbN$_3$ under continuous heating at 400°C for 4 days in vacuum. In order to estimate the composition of the reaction product, the x-ray photoelectron spectroscopy (XPS) measurement was performed using Mg K$\alpha$ radiation (ULVAC PHI Model 5500). The C 1s peak was observed at 285.4 eV and that Rb 3d$_{3/2}$ and 3d$_{5/2}$ peaks were observed at 110.9 and 112.3 eV, respectively. Since the N 1s peak was not observed at all, one could expect that RbN$_3$ had completely decomposed to Rb metal and N$_2$ during the reaction. The composition was estimated to be Rb$_{1.1}(C_{60})_{1.0}$ by the usual XPS procedure.

The structure of the RbC$_{60}$ powder sample thus prepared was examined by the x-ray diffraction (XRD) pattern recorded at a beam line X3B1 of the National Synchrotron Light Source at Brookhaven National Laboratory with a wavelength of 1.14902 Å. Formation of the polymeric phase was confirmed since the diffraction pattern was completely in accordance with our previous data of liquid-phase prepared RbC$_{60}$ with lattice parameters of approximately $a = 9.1$, $b = 10.1$, and $c = 14.2$ Å.$^{13}$

Prior to the static magnetic susceptibility measurement, the ESR data of the present sample was checked using JEOL

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JES TE-200 ESR spectrometer operated at the X band (9.4 GHz) with 100 kHz field modulation equipped with an Oxford liquid-He-flow cryostat covering the region from room temperature to 1.7 K. During a scanning for the ESR measurement at each fixed temperature, the deviation of the temperature was controlled within ±0.2 K. The ESR signals for selected temperatures are shown in Fig. 1. In the range 50–200 K, the intensity of the ESR signal was almost temperature independent, while the peak-to-peak linewidth ($\Delta H_{pp}$) became gradually smaller due to a decrease in temperature. Such Pauli paramagnetic behavior of the intensity and the motional narrowing of the ESR peak clearly indicate that the present sample is metallic above ~50 K. At 50 K, the onset of rapid broadening of the peak and the decrease of its intensity was observed and this quantity once became approximately zero around 15 K and then increased on cooling below 10 K, probably following the Curie law. These behaviors completely agree with what have been found in the aforementioned studies, and hence we are now in position for a further check of the static magnetic susceptibility of the RbC$_{60}$ sample.

### III. MAGNETIC SUSCEPTIBILITY MEASUREMENT

The magnetic susceptibility measurement was performed using a SQUID magnetometer (Quantum Design MPMS-SS) with the maximum magnetic field of 40 kG operating from 100.0 K to 4.5 K. The deviation of the temperature was controlled within ±0.5% of each fixed temperature. The core diamagnetic contribution was estimated to be 2.74 × 10$^{-4}$ emu/mol from the published Pascal constants of the rubidium ion, and the diamagnetic susceptibility of neutral C$_{60}$ (Ref. 15) and was corrected for all the data.

In Fig. 2 is shown the magnetic field dependence of the magnetization per mol ($M_{mol}$) for the RbC$_{60}$ sample at selected temperatures. The spin-flop transition suggested by the ESR study$^{9,10}$ could not be observed in the magnetic-field range $H=0$–40 kG. However, it is well known that anomaly or change in the gradient of the $M_{mol}$–$H$ curve characteristic of the spin-flop transition is extremely slight in powder sample compared with crystal.$^{16}$ The existence of a very small amount of the ferromagnetic impurity is seen in Fig. 2(b), the value of which ($M_s$) was estimated as 2.8 emu G/mol ($\approx 3 \times 10^{20} \mu_B$/mol, $\mu_B$ denoting the Bohr magneton). The ferromagnetic component obtained from usual Honda-Owen plot turned out to be almost temperature independent and was subtracted from all the data of the magnetic susceptibilities throughout the present article.

The temperature dependence of the static susceptibility $\chi_{exp}$ thus obtained under selected magnetic fields is shown in Fig. 3. In this magnetic field range, the shapes of the susceptibility curves are almost the same although the subtle decrease of the susceptibility is seen for 40 kG, which would

![FIG. 1. ESR line shapes at selected temperatures.](image1)

![FIG. 2. (a) External magnetic field dependences of the magnetization at selected temperatures. (b) Detailed field dependence of magnetization at $T=4.5$ K.](image2)

![FIG. 3. Temperature dependences of the susceptibility measured under selected external field ($H=500$ G–40 kG).](image3)
be probably due to saturation of some magnetization component. It is striking that rapid decrease in \( \chi_{\text{exp}} \) under 50 K was not apparently observed, being different from the ESR data mentioned above. One of the possibilities to comprehend this discrepancy would invoke the Curie-type impurity concealing behavior of the susceptibility from conduction electrons. In order to quantitatively evaluate that susceptibility, the following strategy was employed. First, \( \chi_{\text{exp}} \) was decomposed into three kinds of terms as

\[
\chi_{\text{exp}} = \chi_{TD} + \chi_{\text{Curie}} + \chi_{TI},
\]

where \( \chi_{TD} \) and \( \chi_{TI} \) stand for the temperature-dependent term free from the Curie contribution and the temperature-independent one, respectively, and

\[
\chi_{\text{Curie}} = \frac{N_{\text{mol}} g^2 \mu_B^2 S(S+1)}{3k_B(T-\theta)}.
\]

In Eq. (2), \( N_{\text{mol}} \), \( g \), \( S \), \( k_B \), and \( \theta \) are spin concentration per mole, Landé \( g \) factor, spin quantum number, Boltzmann constant, and Weiss constant, respectively, as usual. Second, we assume that \( \chi_{TD} \) becomes approximately equal to zero below 14 K and, therefore, only \( \chi_{\text{Curie}} \) contributes to the temperature dependence of the susceptibility there. It is well known that the intensity of the 2 band ESR resonance of this compound becomes approximately equal to zero below \( \sim 20 \) K, and we have also obtained a similar ESR result as described above. Besides, as we mentioned in the Introduction, Jánossy et al. have recently reported the result of high-field ESR investigation where spin-flop-like behavior appeared at 20–15 K. Hence, we have inferred that we could safely choose to set \( \chi_{TD} \) to zero below 14 K, which is sufficiently low. Eq. (1), \( \chi_{TI} \) originates from Pauli paramagnetic term, and \( \chi_{TD} \) can be considered as the temperature-dependent part of the magnetic susceptibility intrinsic in the RbC\(_{60}\) polymeric phase.

In Fig. 4 is shown the fitting result of Eq. (1) to the data of \( H=1 \) kG. The difference of the experimental data \( \chi_{\text{exp}} \) and \( \chi_{\text{Curie}} + \chi_{TI} \) in Fig. 4(a) thus signifies the net of \( \chi_{TD} \), which is replotted in Fig. 4(b). This temperature dependence of \( \chi_{TD} \) is consistent with that of the ESR intensity mentioned above, i.e., the ESR intensity rapidly decreases below \( \sim 50 \) K. A similar temperature dependence was confirmed for all the data measured under other magnetic fields.

### IV. DISCUSSION

In the case for which (i) the electronic system of RbC\(_{60}\) polymeric phase is quasi-1D, and (ii) the SDW scenario defines the ground state of this substance, the susceptibility tensor of the system ought to be characterized by the two principal values, \( \chi_l \) and \( \chi_\perp \), \( \chi_l \) being the value for the direction parallel to the axis of easy magnetization and \( \chi_\perp \) for the directions perpendicular to that. With these principal values, the susceptibility for the powder RbC\(_{60}\) can be expressed by

\[
\frac{3}{2} \chi = \frac{3}{2} \left( \chi_{\text{exp}} - \chi_{\text{Curie}} \right) = \frac{\chi_l + 2 \chi_\perp}{3}.
\]

![Graph](image)

**FIG. 4.** (a) Temperature dependence of the susceptibility at \( H=1 \) kG. The solid curve represents \( \chi_{\text{Curie}} + \chi_{TI} \) (see text). (b) Temperature dependence of \( \chi_{TD} \) (see text). The solid curve is the calculated \( (2/9)\chi_l \) with Eq. (10) using \( \Delta/k_B=82.3 \) K.

The coefficient \((3/2)\) ahead of \( \chi \) was added in consideration of the Landau diamagnetic contribution. Here, \( \chi_\perp \) is expected to be almost temperature independent, similar to that in the usual antiferromagnetic system. According to Ref. 19, \( \chi_\perp \) is expressed with the Pauli paramagnetic susceptibility \( \chi_{Pauli} \) or the Fermi density of states (DOS) \( N(\varepsilon_F) \) in the 1D metallic state as given by

\[
\chi_\perp = \chi_{Pauli} = \mu_B^2 N(\varepsilon_F).
\]

From Eqs. (3) and (4), \( (2/3)\chi_\perp \) mostly corresponds to \( \chi_{TI} \).

On the other hand, \( \chi_l \) asymptotically approaches zero at \( T=0 \), and \( (1/3)\chi_l \) should correspond to \( \chi_{TD} \). \( \chi_l \) could be derived from the energy dispersion relations as follows: The conventional linear dispersion relationship appropriate for the metallic state described by

\[
\varepsilon_k - \varepsilon_F = \hbar v_F(k-k_F),
\]

where \( k_F \) and \( v_F \) correspond to the Fermi wave vector and Fermi velocity, respectively [see Fig. 5(a)]. When an energy gap is generated around the Fermi level in the SDW state, the dispersion relation should instead be given by

\[
E_k - \varepsilon_F = \text{sgn}(k-k_F) \left( \hbar^2 v_F^2 (k-k_F)^2 + \frac{\Delta^2}{2} \right)^{1/2},
\]

where \( \Delta \) corresponds to the energy gap as illustrated in Fig. 5(b). The Fermi DOS is obtained from the condition

\[
N_{SDW}(E,\Delta)dE = N(\varepsilon_F)d\varepsilon_F.
\]

where \( N_{SDW}(E,\Delta) \) is the DOS in the SDW state. With Eqs. (5)–(7) one obtains,
The energy gap can be obtained to be \( |\Delta| = 0 \) above the transition temperature, while for \( T < T_{SDW} \),

\[
|\Delta(T)| = \left( \frac{a_1}{2b} \right)^{1/2} (T_{SDW} - T)^{1/2},
\]

where \( a_1 \) and \( b \) are constant parameters and \( T_{SDW} \) the mean-field SDW transition temperature. From Eq. (11), the calculated \( |\Delta(T)|/k_B \) for \( T_{SDW} = 48 \) K, \( (a_1/2b)^{1/2} = 23.0k_B \) is shown by the solid curve in Fig. 6, and the value of \( \Delta(0)/k_B \) could be estimated from the intercept to be \( \Delta(0)/k_B = 160 \) K.

Another expression of the relation between \( \Delta(0) \) and \( T_{SDW} \) is given by

\[
\Delta(0) = 3.52k_B T_{SDW},
\]

FIG. 6. Temperature dependence of \( \Delta(T)/k_B \) derived from the data of \( \chi_{TD} \) at \( T = 20–60 \) K and Eq. (10). The solid curve represents the calculated \( |\Delta(T)|/k_B \) for \( T_{SDW} = 48 \) K, \( (a_1/2b)^{1/2} = 23.0k_B \) from Eq. (11) (see text).

A fit of the Eq. (10) to the data above 45 K is shown as the solid curve in Fig. 4(b), affording \( N(\varepsilon_F) = 11.9 \) states/(eV C\(_{60}\)) and \( \Delta/k_B = 82.3 \) K. Incidentally, it should be mentioned that the DOS of the normal state of the well-known superconductor K\(_3\)C\(_{60}\) has been estimated from the static susceptibility to be \( 31 \pm 6 \) states/(eV C\(_{60}\))\(^{1/2}\), which is about three times as much as the present result for RbC\(_{60}\).

As shown in Fig. 4(b), \( \chi_{TD} \) becomes smaller compared with the fitting curve as the temperature decreases, and this problem could be solved by introducing temperature-dependent value of energy gap \( \Delta(T) \) into Eq. (10).\(^{21}\) Based on the \( \chi_{TD} \) data for the temperature range \( T = 20–60 \) K and Eq. (10), \( \Delta(T)/k_B \) was plotted in Fig. 6. This increase of \( \Delta(T) \) on cooling could correspond to the gradual opening of the pseudo-energy-gap.

In general, the behavior of electronic properties near the SDW transition temperature can be discussed using the Landau theory of phase transitions. From Ref. 19, the temperature-dependent order parameter \( \Delta \) corresponding to the energy average of \( N(\varepsilon_F) \) at temperature \( T \) is

\[
\frac{N_{SDW}(E, \Delta)}{N(\varepsilon_F)} = \begin{cases} 
0 & \text{if } |E| < \frac{\Delta}{2} \\
\frac{|E|}{\{E^2 - (\Delta/2)^2\}^{1/2}} & \text{if } |E| > \frac{\Delta}{2}.
\end{cases}
\]

Thus \( \chi_{Pauli} \) becomes \( \mu_B^2 \langle N_{SDW}(\Delta) \rangle_T \), where \( \langle N_{SDW}(\Delta) \rangle_T \) is the thermal average of \( N_{SDW}(E, \Delta) \) at temperature \( T \),\(^{19,20}\) and hence

\[
\chi_{Pauli} = \int_{-\infty}^{\infty} \frac{|E|}{\{E^2 - (\Delta/2)^2\}^{1/2}} \frac{\partial f}{\partial E} dE = 2 \int_{0}^{\Delta/2} \frac{|E|}{\{E^2 - (\Delta/2)^2\}^{1/2}} \frac{\partial f}{\partial E} dE,
\]

where \( f \) is the Fermi-Dirac distribution function. For \( \Delta/(2k_B T) > 1/2 \), Eq. (9) becomes

\[
\chi_{Pauli} \approx \mu_B^2 N(\varepsilon_F) \sqrt{\frac{\pi \Delta}{k_B T}} \exp \left( -\frac{\Delta}{2k_B T} \right).
\]

The amplitudes of the energy-dispersion relation and the density of states near the Fermi wave vectors \( \pm k_F \) (a) in the metallic and (b) in the SDW states.

FIG. 5. The energy-dispersion relation and the energy dependence of the DOS near the Fermi wave vectors \( \pm k_F \).
which has the same form as that of the well-known Bardeen-Cooper-Schrieffer (BCS) relationship between the zero-temperature gap and the transition temperature. With Eq. (12) and the value of \( \Delta(0)/k_B \approx 160 \) K, the mean-field SDW transition temperature could be derived to be \( T_{SDW} \approx 45.5 \) K, which seems to be approximately self-consistent.

The above-discussed SDW scenario is realized on the indispensible assumption that the electronic system of RbC\(_{60}\) polymeric phase is quasi-1D. However, the theoretical investigations on this compound has, so far, led to conflicting predictions so that the electronic and magnetic properties of this compound remain strongly 3D-like. Recently, we have carried out the investigation about change in electronic structure of RbC\(_{60}\) polymeric phase crystal (\( A_{2/m} \)) with various chain orientations based on the tight-binding CO calculation including both \( \sigma \) and \( \pi \) electrons. It was found that the band structure of this compound is of quasi-1D for a certain limited range of chain-orientation angle, i.e., in the range \( \mu = 0^\circ - 5^\circ \), where \( \mu \) is the chain-orientational angle defined in Ref. 4, and there appears sufficient nesting property of the Fermi surface as shown in Fig. 7. The Fermi DOS has been estimated to be \( 8 \) states/(eV C\(_{60}\)) from this band calculation as shown in Fig. 8 to be compared with the present experimental value of DOS \( 11.9 \) states/(eV C\(_{60}\)). Note that further introduction of the relatively weak on-ball Coulomb repulsion \( U \) into the above tight-binding calculation would generally increase susceptibility proportional to the Fermi DOS.

V. CONCLUSION

We have performed a static magnetic susceptibility measurement for the RbC\(_{60}\) polymeric phase. The spin-flop transition suggested by the previous ESR study was unobserved, probably associated with the well-known fact that the anomaly in the \( \text{M-H} \) curve characteristic for the spin-flop transition is extremely slight in powder sample compared with that in crystal sample. Subtraction of the Curie paramagnetic term from the raw data gave a decrease in the susceptibility on cooling below 50 K, consistent with the temperature dependence of the ESR intensity. It was further discussed that this temperature dependence of the static susceptibility can be interpreted in terms of the SDW scenario self-consistently. The estimated Fermi DOS in metallic state is \( N(e_F) = 11.9 \) states/(eV C\(_{60}\)), being about one-third of that in K\(_3\)C\(_{60}\). The development of a more complete crystal of RbC\(_{60}\) will be of obvious importance along with further experimental investigations such as introducing partial profile relaxation and maximum-entropy methods into the XRD analysis.

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6P. W. Stephens (private communication) (see also Ref. 13).


