RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 10 1 SEPTEMBER 1995-II

Static magnetic order in the one-dimensional conductor RbC_{60}

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(Received 5 July 1995)

Muon-spin-relaxation measurements have been performed in the orthorhombic phase of the quasi-one-dimensional conductor RbC_{60}. Evidence for static magnetic order was found at $T \leq 70$ K, followed by a change of the magnetic moment/structure below $T \sim 20$ K, inferred from a substantial increase of the static random local fields. These results are consistent with the formation of the spin-density-wave state, although the possibility of a random spin freezing cannot be ruled out.

Alkali-metal-doped fullerenes show various fascinating properties, including superconductivity in A_3C_{60}. Among them, A_1C_{60} was initially identified as a cubic phase,[1,2] while it was later found that AC_{60} has an orthorhombic structure at low temperatures ($T \leq 400$ K).[3] Subsequently, x-ray measurements on orthorhombic RbC_{60} (Ref. 3) revealed that the C_{60} molecules form chains along the a axis with a very short spacing of 9.1 Å. More recent reports further revealed that the adjacent C_{60} molecules along these chains form covalent bonds with each other.[4] The spin susceptibility of o-RbC_{60}, estimated from the ESR intensity,[3] exhibits Pauli-like behavior above $T \sim 50$ K, while Korringa behavior was found in the NMR relaxation rate above $T \sim 80$ K. These results indicate that o-RbC_{60} has metallic conductivity between $T \sim 80$ and ~ 300 K. The spin susceptibility (from ESR) shows a gradual reduction to zero at lower temperatures ($T \leq 50$ K), suggesting the formation of a ground state via a Peierls transition. Indeed, the strongly one-dimensional (1D) structural properties, metallic high-temperature behavior,[3–6] and a conduction band presumably formed with a single electron per C_{60} molecule, all support the conjecture[3] that this system is a one-dimensional organic metal which undergoes a Peierls instability.

On the other hand, the reduction of the spin susceptibility in one-dimensional systems has been observed in several different cases: i.e., (1) formation of spin density waves (SDW's) leading to a magnetic ground state, e.g., in $TMTSF_2$-AsF_6 (TMTSF stands for tetramethyltetraselenafulvalene);[7] (2) formation of charge density waves (CDW's) leading to a nonmagnetic ground state, e.g., in tetrathiofulvalinium tetracyanoquinodiminethanide (TTF-TCNQ);[8] and (3) formation of a spin-Peierls (SP) state via dimerization of molecules along the chains, leading to a singlet ground state, e.g., in $CuGeO_3$.[9] Therefore, definite identification of the ground state requires more direct study using a microscopic magnetic probe. While ^{87}Rb NMR measurements in o-RbC_{60} found an increase of the spin-lattice relaxation rate $1/T_1T$ below $T \sim 70$ K,[4] the results were inconclusive in distinguishing between the above mentioned possibilities.

We have performed muon-spin-relaxation (μSR) measurements in o-RbC_{60}. The μSR technique allows detection of the spontaneous magnetic field associated with the SDW formation, as was demonstrated in various $TMTSF_2$-X ($X = PF_6$, ClO_4, and NO_3) compounds.[10] In contrast, no magnetic field is expected for the case of CDW or SP transition; previous results in $CuGeO_3$ confirm this feature for the SP transition.[11] 630 mg of polycrystalline RbC_{60} was prepared by solid-state reaction of stoichiometric amounts of Rb metal and high-purity (>99.9%) C_{60} powder. X-ray measurements indicate a single-phase sample with orthorhombic structure, and ESR measurements on this batch have reproduced the published results.[3] The sample, a disc approximately 10 mm in diameter and 3 mm thick, was sealed with He exchange gas in an Al sample container with a thin kapton window, and mounted in a He gas flow cryostat. μSR measurements were performed in the zero-field (ZF) and longitudinal-field (LF) configurations at the M-13 beam channel of TRIUMF. For details of the μSR method, see Refs. 12 and 13.

Figure 1 shows the time evolution of the muon-spin-

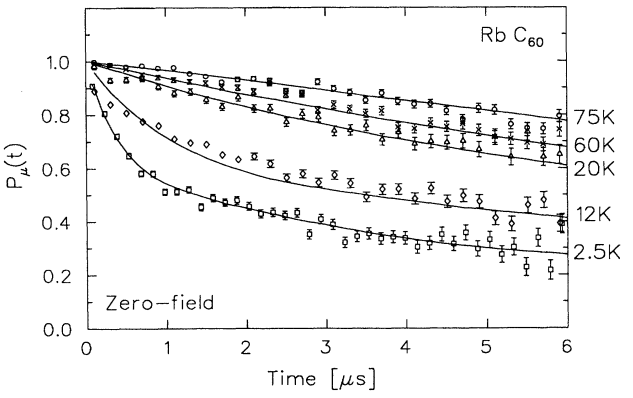

FIG. 1. Muon-spin-relaxation function $G(t)$ observed in orthorhombic RbC_{60} in zero external field. The solid line represents a fit with $G_m(t) \times G_{nd}(t)$, where $G_m(t)$ is given in Eq. (1).

polarization, i.e., the muon-spin-relaxation function $G(t)$, observed in zero field at various temperatures. The relaxation rate is almost independent of temperature between $T=125$ and 75 K, while it increases significantly below 75 K with decreasing temperature. We found a further rapid increase of the relaxation rate below $T\sim 20$ K, which saturates around $T=5$ K. We calibrated the total muon asymmetry by performing a transverse-field measurement. Figure 1 corresponds to a fit assuming ~90% of the initial asymmetry comes from the specimen, while the rest originates from the sample holder, the cryostat wall, or some other temperature-independent background. The data in Fig. 1 indicate that the majority of the sample volume undergoes a magnetic transition.

As shown by the $T=2.5$ K data in Fig. 1, the line shape of $G(t)$ observed at low temperatures exhibits a fast decay, followed by a slower relaxation, suggesting the existence of multiple groups of muons subject to internal fields of different magnitudes. A good fit to the observed results can be obtained by assuming the magnetic contribution $G_m(t)$ of the relaxation function

$$G_m(t)=\sum_{i=1}^{2} A_i[\tfrac{1}{3}+\tfrac{2}{3}(1-a_i t)\exp(-a_i t)]. \qquad (1)$$

The function within [ ] represents the static relaxation function for a Lorentzian distribution of random local fields.[13] To account for the relaxation above $T=75$ K, which is presumably due to nuclear dipolar field from Rb and ^{13}C nuclei, we multiplied a slowly decaying Gaussian function $G_{nd}(t)=\exp(-\Delta^2 t^2)$ with $\Delta=0.043$ μs^{-1} to $G_m(t)$, and fit the observed function as $G(t)=G_m(t)\times G_{nd}(t)$ assuming no temperature dependence of $G_{nd}(t)$. Since $G_{nd}(t)$ decays only very slowly, the existence of this term does not significantly affect the results below $T\sim 50$ K. This procedure, however, helps in identifying the transition at $T=75$ K, which involves only a small increase over the internal field from the nuclear dipolar fields.

Since the observed relaxation was rather slow at $T\geq 20$ K, we could observe only a very beginning part of the line shape $G_m(t)$ at high temperatures. Consequently, little information can be obtained above $T=20$ K concerning the division between the first and second terms of Eq. (1). In order to avoid possible trade-off effects between the asymmetry and relaxation parameters, we estimated $A_1=0.41$, $A_2=0.59$, and $a_2/a_1=0.125$ by fitting the results below $T=5$ K, and then fixed these parameters in fitting the results obtained at other temperatures. This procedure is equivalent to assuming the same line shape of $G_m(t)$ for all the observed temperatures. The solid lines of Fig. 1, which represent the fits obtained in this procedure, show a reasonable agreement with the observed data.

The temperature dependence of the magnitude of internal field parameter a_1, obtained with this fit for data taken in zero external field, is shown in Fig. 2. This parameter represents the larger of the two different magnitudes of the observed internal field; the other one, a_2, is eight times smaller. A small finite value of a_1 above $T=75$ K indicates that the

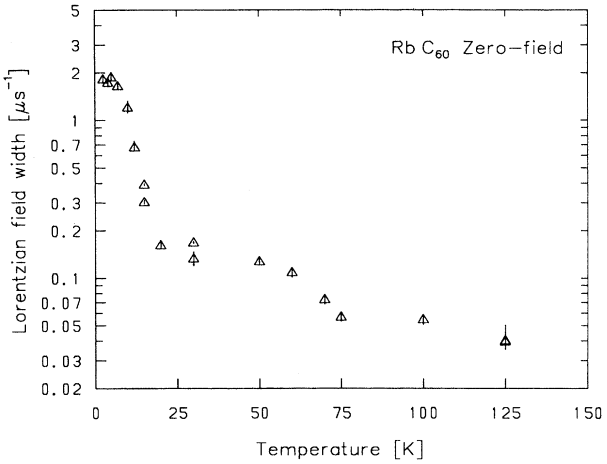

FIG. 2. Temperature dependence of the magnitude a_1 of the static internal magnetic field in RbC_{60} determined by zero-field μSR. Two transitions are seen at $T=75$ K and $T=20$ K.

line shape of $G(t)$ at high temperatures is slightly different from the Gaussian shape of $G_{nd}(t)$. The origin of this is unclear; it could be due to some small background signal and/or to endohedral muonium. Below $T=75$ K, we see a clear increase of the internal field. The observed relaxation in zero field at $T=50$ K is due to a static internal magnetic field, since a small longitudinal field LF=101 G completely eliminates the relaxation, as shown in Fig. 3(a).

Another clear increase of the internal field is found below $T=20$ K. Figure 3(b) shows the dependence of $G(t)$ at $T=2.5$ K on applied longitudinal field. The solid line represents the relaxation functions calculated for the same distribution of static random local fields which produced Eq. (1) for the case of zero field. The good agreement confirms that

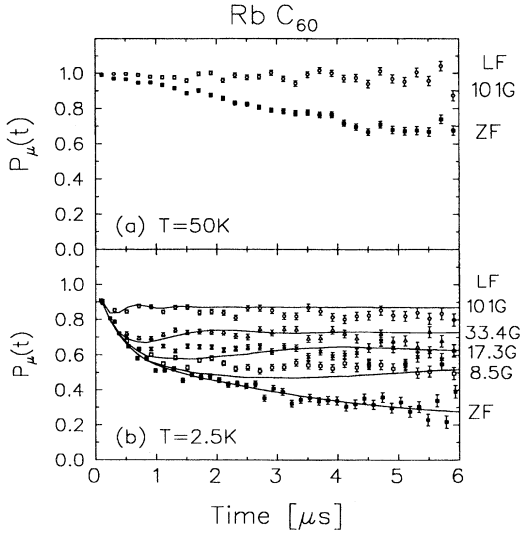

FIG. 3. (a) Comparison of the muon-spin-relaxation function $G(t)$ at $T=50$ K in zero field and a longitudinal field LF=101 G. (b) Dependence of $G(t)$ at $T=2.5$ K on applied longitudinal fields. Solid lines represent relaxation functions for static random local field distribution determined in zero field using Eq. (1).

the observed relaxation is completely due to a static spontaneous magnetic field. The essential features of our μSR results, described above, are consistent with the independent set of μSR data recently obtained by MacFarlane *et al.*[14] This confirms that the present results are reproducible in studies using separate specimens made at different laboratories.

Our results demonstrate the appearance of a spontaneous static magnetic field below $T_N \sim 75$ K. This ordering temperature is slightly higher than $T \sim 50$ K where the spin susceptibility in ESR starts to decrease.[3] However, $T_N = 75$ K agrees rather well with the reduction of the microwave absorption in RbC_{60} (Ref. 15) which starts around 70 K. Furthermore, NMR measurements[4] also found a change of T_1 near $T \sim 75$ K. The discrepancy between the ESR and μSR, NMR temperature scales may be due to the fact that μSR and NMR are more sensitive to internal fields while ESR detects the internal field only via the loss of intensity of the electrons resonating at the free-electron value.

Both microwave absorption and ESR spin susceptibility show a rather gradual reduction from metallic nature above the transition temperature. This gradual change may suggest that the transition occurs at different temperatures for different parts of the sample, i.e., a small part of the sample starts ordering at 75 K, followed by the remaining portion ordering at lower temperatures. Since the observed muon relaxation between $20 \leq T \leq 75$ K is so small, the present μSR results cannot distinguish between such a "gradual transition" from the possibility that the entire volume orders magnetically at $T = 75$ K. For the change at $T \sim 20$ K, our results clearly show that the entire volume of the sample is eventually involved.

The observed line shape of $G(t)$ [Eq. (1)] is different from a typical μSR line shape observed for incommensurate SDW's in $TMTSF_2$-PF_6,[10] which is characterized by a rapid exponential decay followed by a few damped oscillations. However, we have found that the damped oscillation part becomes less pronounced for systems having a greater structural disorder and/or wider spatial spread of the muon site (e.g., $TMTSF_2$-ClO_4), leading to a line shape of $G(t)$ rather close to that observed in the present study. Moreover, if there are several crystallographically inequivalent muon sites with different magnitudes of local fields in the unit cell, such an oscillation could be easily smeared out. The involvement of some randomness, such as a spatial spread of the SDW amplitude, would also smear out the oscillation. Therefore, the absence of oscillations does not preclude the possibility that RbC_{60} undergoes an SDW transition.

The line shape of Eq. (1), with a single component ($i = 1$), is often seen in dilute alloy spin glasses.[13] The observed two-component signal (A_1 and A_2) with two different amplitudes (a_1 and a_2) of static fields, however, demonstrates that the distribution of random local fields at the muon site is more complicated than the Lorentzian distribution expected for a random freezing of dilute moments. The μSR data alone cannot clearly distinguish between the SDW and spin-glass states, since μ^+ is a pointlike real-space probe.

In the following, we consider the likelihood of these two possibilities combining the available experimental information from other techniques with the present results. The change of microwave absorption (proportional to conductivity), from metallic behavior above $T \sim 70$ K to insulating behavior below this temperature, suggests that the transition is associated with a metal-insulator transition, unlike simple spin-glass freezing. Regular antiferromagnetic order generally results in clear muon precession below T_N, which is different from the present observation.

In a spin-Peierls (SP) transition of perfect 1D chains, the ground state is singlet, and thus nonmagnetic. The present results in RbC_{60} clearly rule out this possibility. For imperfect 1D chains with finite chain lengths, one would expect a complicated phase diagram (as a function of the degree of chain-cutting) as observed in the Zn doped $CuGeO_3$.[9] There, it is possible that the SP transition opens a gap for charge conduction, followed by a spin-glass-like freezing of chain-end spins at a lower temperature. The sharpness of the x-ray Bragg peak in RbC_{60}, corresponding to the chain length of more than 2000 Å,[16] disfavors the possibility of such a "finite-chain SP transition" in RbC_{60}. The most direct confirmation, however, requires a search for satellite peaks in x-ray diffraction using a high-quality single crystal, which is currently unavailable.

Finally, we argue that the present results clearly rule out the possibility of a charge-density-wave formation, which would have lead to a nonmagnetic ground state. These considerations suggest that the transition observed at $T = 75$ K is likely due to the formation of an SDW state.

We can give a crude estimate of the SDW amplitude from the μSR results, for the case of the SDW ground state. The internal field at $T = 50$ K corresponds to about 5–10 % of that observed by μSR in $TMTSF_2$-PF_6,[10] where the SDW amplitude of $\sim 0.1 \mu_B$ was estimated from an NMR study.[17] This implies that the amplitude at $T = 2.5$ K in RbC_{60} is comparable to that in $TMTSF_2$-PF_6. A more precise estimate of the amplitude requires knowledge about muon sites and hyperfine coupling constants in RbC_{60}, which is currently missing. The origin of the apparent second transition at $T \sim 20$ K is not clear at the moment. It might suggest a change of magnetic structure, while it is also possible that the first transition at $T = 75$ K occurs for a partial volume fraction of the specimen while the remainder of the volume orders magnetically at temperatures even as low as $T \sim 20$ K. Further experimental studies are required to clarify this aspect.

In conclusion, we have presented evidence that RbC_{60} exhibits static magnetic order below $T \sim 75$ K. The combination of the present results with those currently available from other techniques suggests SDW formation as the likely origin of this magnetic freezing. The direct confirmation of spatial correlations of the frozen moments, however, requires further experimental results using a reciprocal-space probe, such as neutron scattering.

The authors would like to thank G. Grüner, L. Mihaly, and P.W. Stephens for helpful discussions; R.F. Kiefl and W.A. MacFarlane for communicating their unpublished μSR results on RbC_{60} and exchanging information with us; and the David and Lucile Packard Foundation, Yamada Science Foundation, and Swiss National Science Foundation for financial support.

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