RAPID COMMUNICATIONS

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

Magnetism in RbC_{60} studied by muon-spin rotation

W.A. MacFarlane, R.F. Kiefl, S. Dunsiger, and J.E. Sonier
Department of Physics and TRIUMF, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

J.E. Fischer
Materials Science Department and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 12 July 1995)

We report an investigation of the magnetic properties of orthorhombic RbC_{60} using muon-spin rotation (μSR). Measurements in zero applied field and high transverse field reveal a transition to a magnetic state below $T=60$ K. The μSR spectra at low temperatures indicate that the internal magnetic fields are quasistatic on the time scale of a few μs and have a Lorentzian-like distribution. These observations suggest that the magnetic structure is more disordered than a simple spin-density-wave state or an antiferromagnet.

There is considerable current interest in the recently discovered[1] stoichiometric intercalation compounds AC_{60} (A = K,Rb,Cs) since their electronic and magnetic properties may help elucidate the nature of superconductivity in the conductive A_3C_{60} phase. It is now generally accepted that the alkali-metal-intercalated fullerides are highly ionic compounds in which each alkali-metal cation donates an electron to a C_{60} molecule. The electronic properties are then determined by bands composed primarily of the molecular orbitals of C_{60}, in particular those formed from the triply degenerate lowest unoccupied molecular orbital (LUMO). However, the narrowness of these bands and the failure of band theory to explain the insulating behavior of A_4C_{60} suggest that strong electron correlation effects may be important in this class of compound[2] as in high-T_c copper oxide superconductors.

The recent synthesis of AC_{60} is particularly interesting since this material, like A_3C_{60}, has an odd number of electrons in the LUMO which should favor metallic behavior. RbC_{60} has two clearly distinguished crystalline phases; above about 350 K x-ray diffraction peaks can be indexed to an fcc structure in which the cations are located in the octahedral interstitial site.[3] At lower temperatures the stable phase denoted o-RbC_{60} has a (body-centered) orthorhombic unit cell with approximate dimensions: 9.1, 10.1, and 14.2 Å.[4] Although there is disagreement over the conductive properties of the high-temperature fcc phase, IR transmission,[5] NMR spin relaxation,[6] and conduction-electron spin resonance (CESR)[7] all confirm that o-RbC_{60} is indeed an electrical conductor between 60 and 350 K. Although it has been proposed to be a quasi-one-dimensional conducting polymer[8,4] the degree of one-dimensionality is questionable since the intrachain ball separation (~1.4 Å) is not much different than the smallest interchain ball separation (~1.6 Å). Furthermore, according to recent density-functional calculations,[9] the rehybridization of C orbitals at the C_{60}-C_{60} bond impedes conduction along the chains and leads to nearly isotropic electronic properties for the experimentally determined lattice constants. Below 50 K a sharp drop in the CESR susceptibility (χ_s) of o-RbC_{60} has been observed and interpreted[7] as evidence for a transition to a nonconductive spin-density-wave (SDW) state. On the other hand, band-structure calculations predict that the ground state has electronic moments coupled ferromagnetically within a chain and antiferromagnetically between chains.[9]

In this paper we report an investigation of the properties of o-RbC_{60} using muon-spin rotation. The positive muon is a sensitive site-based probe of the internal magnetic fields and thus is useful in determining the presence and type of magnetic order. At a temperature of about 60 K we observe a gradual transition to a magnetic ground state which is characterized by a Lorentzian-like distribution of weak internal magnetic fields which are quasistatic on the time scale of the muon lifetime (2.2 μs). The exponential decay of the muon polarization at early times and the absence of any oscillatory behavior in the zero-applied-field (ZF) μSR spectra suggest the magnetic structure is considerably more disordered than for a simple spin-density-wave or antiferromagnetic state.

The measurements were performed on the M15 beamline at TRIUMF which provides a beam of ~100% spin-polarized positive muons. A sample[10] of RbC_{60} weighing 320 mg was sealed in an Al vessel with a thin Kapton window to allow entry of the low-energy (4 MeV) positive muons. An exchange gas of 10% He/90% Ar was used to ensure good thermal conductivity between the powdered sample and the target vessel. We estimate that about 80% of the muons stopped in the sample. Those that missed the sample were stopped in an annular disk of high-purity silver which has a very small temperature-independent muon-spin-relaxation rate. The temperature of the target vessel was controlled to within 0.2 K using either a cold-finger cryostat or a He gas flow cryostat. For zero-field measurements the ambient field at the sample was compensated by three orthogonal Helmholtz coils, effectively reducing the external field to <0.03 mT.

Conventional ZF-μSR spectra were taken at several temperatures between 2.6 and 250 K [see triangles in Figs. 1(a) and 1(b)]. Above 30 K excellent fits were obtained assuming the muon polarization had the following time dependence:

$$P_z(t)=A_0+A_1e^{-\lambda_{\mathrm{ZF}}t}, \tag{1}$$

0163-1829/95/52(10)/6995(4)/$06.00

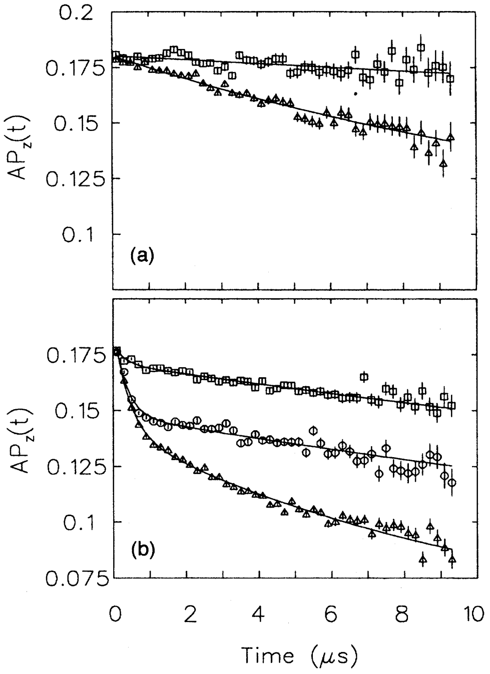

FIG. 1. Time dependence of the muon-spin polarization in o-RbC$_{60}$ in zero applied magnetic field and low longitudinal fields; (a) 75 K: triangles ZF, squares 3 mT; (b) 2.6 K: triangles ZF, circles 2 mT, squares 10 mT. The fit function shown here is the sum of one or two exponentials and a nonrelaxing term.

where the exponential term comes from the sample and the smaller constant term from the silver annulus around the sample. Above 60 K λ_{ZF} is small and weakly dependent on temperature (see Fig. 2). The static nature of the magnetic fields in this region is confirmed by the fact that the muon-spin relaxation can be quenched by application of a small external magnetic field [see squares in Fig. 1(a)]. We attribute the relaxation above 60 K to static nuclear dipolar fields from naturally occurring ^{13}C (1.1% abundance) and ^{85,87}Rb (100% abundance). Normally, muon-spin relaxation due to nuclear dipoles is best described by a Gaussian distribution of internal fields which leads to a Gaussian-like relaxation function (i.e., quadratic at early times). However, in materials such as RbC$_{60}$ where only a small fraction of the nuclei have moments, one expects a wider distribution of the nuclear dipolar fields and thus a more exponential-like form (linear at early times) as is evident in Fig. 1(a).

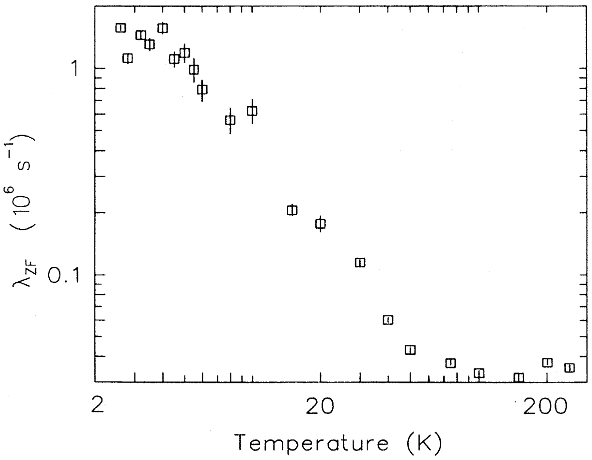

FIG. 2. The average muon-spin-relaxation rate in o-RbC$_{60}$ from single exponential fits to the first 2.5 μs below 15 K, and to the entire 10 μs above 15 K.

Figure 2 shows that the temperature dependence of λ_{ZF} obtained from fits of the data to Eq. (1). The increase below 60 K clearly establishes the transition to a magnetic state. For temperatures below 15 K the relaxation function becomes more complicated. Good fits over the entire time range could be obtained assuming 2/3 of the sample signal relaxes according to a two-component exponential and 1/3 is time independent. [See triangles in Fig. 1(b).][11] However, the parameter λ_{ZF} plotted in Fig. 2 is derived from fits to a single exponential over a restricted time interval (2.5 μs for runs taken below 15 K) where a single exponential gives a good fit. Note that in the case of multiexponential relaxation this procedure yields the average relaxation rate weighted by the amplitudes for the various components. A comparison of the spectra at 2.6 K in ZF and low longitudinal field is shown in Fig. 1(b). As in the case of the data at 75 K only small external magnetic fields (10 mT) are required to suppress λ_{ZF}. This establishes that most of the observed spin relaxation is due to small static internal magnetic fields as opposed to large rapidly fluctuating magnetic fields. Since λ_{ZF} in Fig. 2 is a measure of the static internal field λ_{ZF}^2 should scale approximately with the order parameter for the magnetic transition. Note that λ_{ZF} rises gradually below the transition and does not saturate until the temperature falls below about 5 K. This suggests there may be a very broad distribution of transition temperatures. Recently Uemura *et al.* have reported ZF-μSR results on a different sample of o-RbC$_{60}$. Although the ZF-μSR spectra look similar to those shown in Fig. 1 the temperature dependence appears to be different and suggests the presence of two transitions at 75 and 20 K in that sample.[12]

One can characterize the field distribution in the magnetic state more precisely by comparing the single exponential relaxation rate λ_{ZF} with that predicted for a Lorentzian distribution of internal fields seen in highly disordered systems such as dilute spin glasses.[13,14] For example, a Lorentzian distribution of internal magnetic field $p(B)=(w/\pi)\times[1/(w^2+B^2)]$ gives rise to a muon-relaxation function in ZF:

$$P_z(t)=\tfrac{1}{3}+\tfrac{2}{3}(1-\lambda t)e^{-\lambda t}, \qquad (2)$$

where $\lambda=2\pi\gamma_\mu w$ and $\gamma_\mu=0.1355$ MHz/T is the gyromagnetic ratio of the muon. This function looks exponential at early times with a relaxation rate $\lambda_{ZF}=4/3\lambda$. Substituting the λ_{ZF} observed in RbC$_{60}$ at 2.6 K one obtains an estimate for w of 1 mT. The actual field distribution is more complicated than a simple Lorentzian since Eq. (2) does not fit the low-temperature ZF spectra for times greater than a few μs. Nevertheless, there must be a substantial high-field tail as in the case of a Lorentzian distribution in order to explain the exponential-like relaxation at early times. The static nature of the internal fields along with the absence of any oscillatory behavior in the ZF spectra well below the transition temperatures implies that the peak in magnetic field distribution is close to zero field. This is unexpected for an ordinary antiferromagnet or simple spin-density wave where well below the transition temperature there exists a peak at finite field with a sharp cutoff. For example, in materials known to possess SDW ordering, such as the tetramethyltetraselenafulvalene (TMTSF) compound $(TMTSF)_2PF_6$ (Ref. 15), damped oscillatory behavior is normally observed at small reduced temperatures. Although in a few materials, such as $(TMTSF)_2ClO_4$, these oscillations are less obvious, the measurements in those cases were not taken at small reduced temperatures where narrowest line shapes are expected.[15] The signature for an antiferromagnet is even more distinctive since the entire spectral weight is centered at one or at most a few field values. The field distribution observed in o-RbC_{60} more closely resembles that seen in highly disordered magnetic materials such as spin glasses. One possible source of disorder is competition between polymerization and dimerization. Recently a completely dimerized state of KC_{60} has been observed in samples which are quenched rapidly through the fcc to orthorhombic transition at 350 K.[16]

Additional measurements were also taken in a large external magnetic field of 1.45 T applied transverse to the initial spin-polarization direction. In such a transverse field (TF) μSR experiment the muon spin precesses at a frequency which is the vector sum of the external field plus the internal field. The frequency spectra taken on RbC_{60} at low temperatures could be decomposed into two components: a broad line due to the signal from the sample plus a small-amplitude very narrow line from the silver annulus. Excellent fits to the μSR time spectra were obtained assuming an exponential relaxation of the precession signal from the sample. This is consistent with a Lorentzian-like internal field distribution seen with ZF-μSR. Comparing Figs. 2 and 3(a), it may be seen that the fitted TF-μSR relaxation rate (λ_{TF}) has the same temperature dependence as λ_{ZF}. The observed reduction in λ_{TF} compared to λ_{ZF} is expected since in TF only the $\hat{z}$ component of the internal field (i.e., along the direction of the applied field) contributes to the line broadening whereas in ZF the two components perpendicular to the initial muon polarization contribute. Figure 3(b) shows the average precession frequency in the sample as a function to temperature. The lack of any significant temperature dependence above the transition (in particular the absence of Curie behavior) is further evidence that above 60 K o-RbC_{60} is nonmagnetic. Below 60 K one observes a small upward frequency shift which closely follows the temperature dependence of λ_{TF} and λ_{ZF}. We may conclude from the TF data that there is a gradual transition to a magnetic state at 60 K upon cooling and that it is not significantly affected by the presence of an external field of 1.45 T.

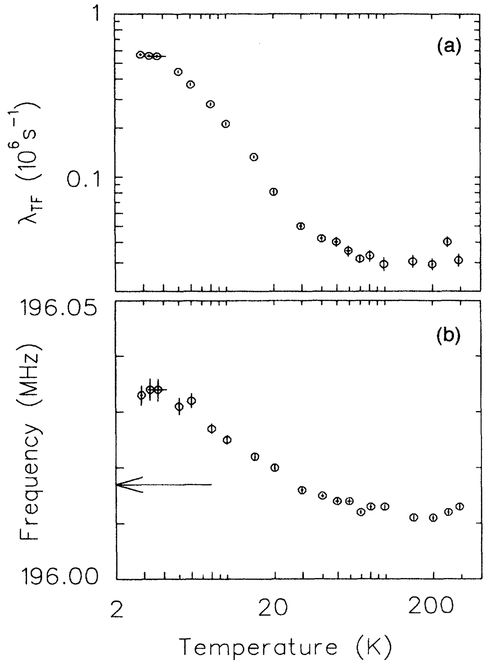

FIG. 3. Temperature dependence of the muon-spin-relaxation rate (a) and average precession frequency (b) in a transverse magnetic field of 1.45 T. At the same field a reference sample of high-purity silver gave a frequency of 196.035 MHz, which, accounting for the known muon Knight shift in silver (Ref. 18), yields the unshifted reference frequency 196.017 MHz indicated by the arrow.

Finally we note that the amplitude of the precession signal observed in TF is similar to that in the superconducting Rb_3C_{60}, i.e., about 12% of the injected muons do not contribute to the precession signal. This suggests that as in other fullerides[17] a small fraction of the muons form the endohedral paramagnetic complex Mu@C_{60}, where Mu is muonium. In metallic A_3C_{60}, Mu@C_{60} can be identified as a small amplitude relaxing signal in a high longitudinal magnetic field. However, no such signal was seen in RbC_{60} between 40 and 100 K.

In conclusion a combination of ZF-μSR and high TF-μSR data on o-RbC_{60} reveal a gradual transition from a nonmagnetic state above 60 K to a magnetic state at lower temperatures. The internal magnetic field distribution well below the transition is more disordered than one expects from either a spin-density-wave state suggested by CESR or an antiferromagnetic state predicted in theory.

This work was supported by the Canadian NRC and NSERC. We are grateful to Curtis Ballard and Mel Good for technical assistance, and we thank K. Kojima, Y. J. Uemura, and G. M. Luke for sending us their results prior to publication. Work at Pennsylvania was supported by the National Science Foundation MRL Program under Grant No. DMR91-20668. We thank P. W. Stephens for the x-ray measurement and C. L. Lin for the SQUID measurement.

[1] J. Winter and H. Kuzmany, Solid State Commun. **84**, 935 (1992); O. Zhou *et al.*, in *Novel Forms of Carbon*, edited by C.L. Renscher *et al.*, MRS Symposia Proceedings No. **270**, (Materials Research Society, Pittsburgh, 1992); Q. Zhu *et al.*, Phys. Rev. B **47**, 13 948 (1993); D.M. Poirier and J.H. Weaver, *ibid.* **47**, 10 959 (1993).

[2] M.P. Gelfand, Supercond. Rev. **1**, 103 (1994), and references therein.

[3] Q. Zhu *et al.*, Phys. Rev. B **47**, 13 948 (1993).

[4] P.W. Stephens *et al.*, Nature (London) **370**, 636 (1994).

[5] M.C. Martin *et al.*, Phys. Rev. B **49**, 10 818 (1994).

[6] R. Tycko *et al.*, Phys. Rev. B **48**, 9097 (1993).

[7] O. Chauvet *et al.*, Phys. Rev. Lett. **72**, 2721 (1994).

[8] S. Pekker *et al.*, Science **265**, 1077 (1994).

[9] S.C. Erwin, G.V. Krishna, and E.J. Mele, Phys. Rev. B **51**, 7345 (1995).

[10] Prepared by annealing preweighed Rb and C_{60}. High resolution x-ray diffraction and SQUID magnetometry reveal ~ 2% Rb_3C_{60} as an impurity phase.

[11] The presence of a 1/3 nonrelaxing component in a ZF-μSR spectrum is a geometric effect arising from the projection of any randomly oriented static internal magnetic field along the initial muon-polarization direction. See for example R.S. Hayano *et al.*, Phys. Rev. B **20**, 850 (1979).

[12] Y.J. Uemura, K. Kojima, G.M. Luke, W.D. Wu, G. Oszlanyi, O. Chauvet, and L. Forro, preceding paper, Phys. Rev. B **52**, 6991 (1995).

[13] R.E. Walstedt and L.R. Walker, Phys. Rev. B **9**, 4857 (1974).

[14] Y.J. Uemura *et al.*, Phys. Rev. B **31**, 546 (1985).

[15] L.P. Le *et al.*, Phys. Rev. B **48**, 7284 (1993).

[16] Q. Zhu, D.E. Cox, and J.E. Fischer (unpublished); P. Petit, J. Robert, and J.E. Fischer (unpublished).

[17] R.F. Kiefl *et al.*, Phys. Rev. Lett. **68**, 1347 (1992); R.F. Kiefl *et al.*, *ibid.* **69**, 2005 (1992); R.F. Kiefl *et al.*, *ibid.* **71**, (1993).

[18] A. Schenck, *Muon Spin Rotation Spectroscopy* (Adam Hilger, Bristol, 1985).