RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 6 1 FEBRUARY 1995-II

Electronic localization in Rb_4C_{60} from bulk magnetic measurements

I. Lukyanchuk and N. Kirova
Groupe de Dynamique des Phases Condensées, Université Montpellier II, c.c. 026, F-34095, Montpellier, Cedex 05, France and L. D. Landau Institute for Theoretical Physics, 2, Kosygina Street, 177940, Moscow, Russia

F. Rachdi and C. Goze
Groupe de Dynamique des Phases Condensées, Université Montpellier II, c.c. 026, F-34095, Montpellier, Cedex 05, France

P. Molinie
Institut des Matériaux de Nantes, Laboratoire de Physique Cristalline, 2, rue de la Houssinière, 44072 Nantes, Cedex 03, France

M. Mehring
2, Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany

(Received 9 September 1994; revised manuscript received 7 November 1994)

The dc-magnetization measurements were performed between 50 G and 40 kG using a superconducting quantum interference device magnetometer on powder samples of Rb_4C_{60}. The magnetic susceptibility reveals thermally activated behavior with an activation energy of 1200±100 K and a diamagnetic temperature-independent part $\chi_d = -3\times10^{-4}$ emu/mol. By calculation of the related magnetic moments and by comparison with the NMR and EPR data we conclude that the additional electrons are localized on the C_{60} molecule and form a spin-singlet ground state. The temperature-dependent paramagnetism is due to thermally excited electrons. Strong electron correlations and lattice distortions (crystal field or/and Jahn-Teller effect) are discussed as a possible origin for the lowest unoccupied molecular orbital (LUMO) level splitting and for gap formation. The experimental results are in good agreement with the existence of Jahn-Teller or crystal-field distortions, providing the t_{1u} LUMO level degeneracy is lifted.

One of the most important questions in alkali-metal-doped fullerides concerns the nature of the ground state of carriers. A large body of experimental and theoretical work deals with the metallic properties of A_3C_{60} ($A=$K, Rb), where the collection of electrons behaves as a classical Fermi liquid. There is a superconducting phase transition at a critical temperature ($T_c\approx30$ K for Rb_3C_{60}) higher than was obtained in orgainic compounds. Fullerene-based compounds with different alkali-metal stoichiometries provide a good opportunity to investigate the effects of electron-electron correlations. These are expected to be more pronounced when the carrier density of states decreases.

At the moment, only the following compounds with a partially filled three-fold degenerate lowest-unoccupied-molecular-orbital (LUMO) level are known: AC_{60} (with one electron per C_{60}), A_3C_{60} (with one electron per C_{60}), and A_4C_{60} (with four electrons per C_{60}). The electronic properties of the AC_{60} and A_4C_{60} phases have been investigated to a much smaller extent than for A_3C_{60}.

In this paper we report bulk magnetization measurements on Rb_4C_{60}. The magnetic susceptibility reveals thermally activated behavior with an activation energy of 1200± 100 K. By calculation of the related magnetic moments and by comparison with NMR measurements we conclude that the localized electrons form a spin-singlet ground state. Temperature-dependent paramagnetism is provided by thermally excited electrons.

A powder sample of Rb_4C_{60} was prepared following the procedure reported in detail previously.[1] The powder of Rb_4C_{60} was synthesized by first preparing the compound Rb_6C_{60} using a vapor-transport method. Part of the Rb_6C_{60} was then used to prepare Rb_4C_{60} by direct reaction with additional stoichiometric amounts of pure C_{60}. Then (40±5) mg of the reaction product was sealed in a NMR Pyrex tube. The sample was characterized by high-resolution ^{13}C NMR spectroscopy. It contains $(20\pm2)\%$ of the phase Rb_3C_{60} and $(80\pm2)\%$ Rb_4C_{60}.

The magnetic susceptibility χ of the Rb_4C_{60} sample was obtained from dc magnetization measurements between 50 G and 40 kG using a quantum design superconducting quantum interference device (SQUID) magnetometer. The onset of a superconducting phase transition in the fraction of Rb_3C_{60} at $T_c\approx30$ K restricts the low-temperature magnetization measurements below T_c. The bare data of the temperature dependence of the magnetization of Rb_4C_{60} in a Pyrex sample holder at $H=5$ and 40 kG and of the magnetization of the empty sample holder at $H=5$ kG are shown in Fig. 1. The accuracy of the measurements consists of $\sim5\times10^{-7}$ G. We have found that between 5 and 40 kG the magnetization M_{glas} of the empty holder is proportional to the applied field H: $M_{\text{glas}}=\chi_{\text{glas}}H$, whereas the magnetization of the sample in the glass holder, M_{tot}, has the field- and temperature-independent constant contribution $m=(3\pm0.5)\times10^{-5}$ G ($M_{\text{tot}}=m+\chi_{\text{tot}}H$) from the ferromagnetic impurities which are always present in the sample.[3] To avoid this contribution we have found the total magnetic susceptibility of the sample and the sample holder as $\chi_{\text{tot}}=[M(40\text{ kG})-M(5\text{ kG})]/35$ kG. After this the correction on the sample holder was made. As it follows from Fig. 1(a), the susceptibilities of the glass

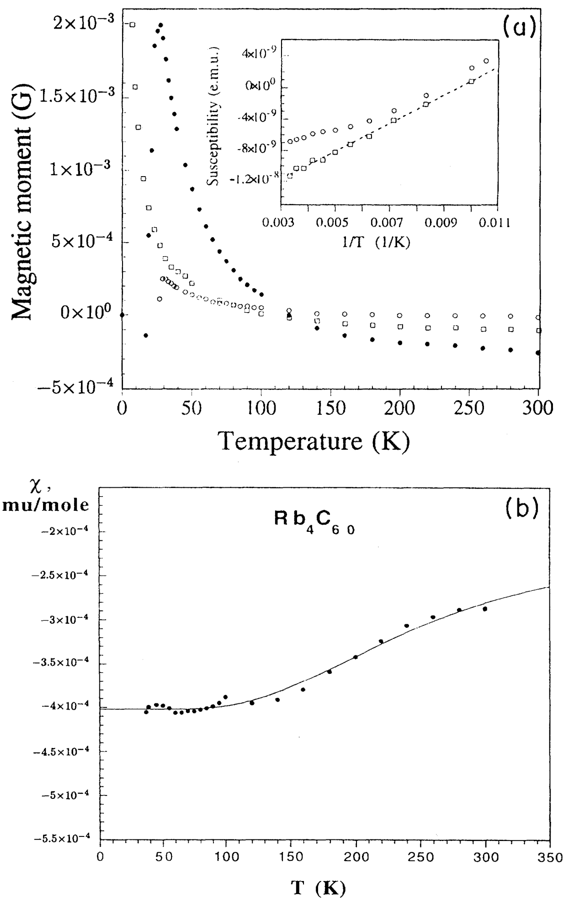

FIG. 1. (a) Temperature dependence of the magnetic moment of Rb_4C_{60} obtained using a SQUID magnetometer. The inset shows the susceptibility. (b) Temperature dependence of the magnetic susceptibility of Rb_4C_{60} obtained using a SQUID magnetometer. The line is the fit of data points by expression (1).

holder with and without the sample have a dominant Curie contribution. We have attributed it mainly to the sample holder since the EPR data[4] shows that the paramagnetic impurities from the Rb_4C_{60} sample itself weakly contribute to the resulting susceptibility. We were not able to deduce the sample susceptibility directly by subtracting the χ_{glas} from χ_{tot} because the sample holder used for the measurements of χ_{glas} has a slightly lower mass than the one used for the meausrements of χ_{tot}. To correct this difference we have scaled χ_{glas} according to the ratio of the Curie constants for $\chi_{\text{tot}}(T)$ and $\chi_{\text{glas}}(T)$. The temperature behavior of $\chi_{\text{tot}}(T)$ and of the rescaled sample holder susceptibility as a function of $1/T$ with 100 K$\leq T \leq$300 K is shown in the inset of Fig. 1. Below 100 K the contribution from the sample holder dominates (more than 90%) in the total susceptibility; while above 100 K it consists of about 70%. The sample holder corrections are assumed to be the main source of the errors bars of the Rb_4C_{60} susceptibility as indicated below. To obtain the final value of $\chi_{Rb_4C_{60}}$ we have also corrected the result on the 20% of the phase Rb_3C_{60}, assuming $\chi_{Rb_3C_{60}}=9.7\times10^{-4}$ emu/mol.[2]

The resulting temperature dependence of the magnetic susceptibility of Rb_4C_{60} is shown in Fig. 1(b). We estimated the error bar of the temperature-independent contributions as $\pm5\times10^{-5}$ emu/mol and for the temperature-dependent part above 100 K as $\pm2\times10^{-5}$ emu/mol. Two important conclusions are reached: (i) χ increases with temperature; (ii) the characteristic scale of $\chi(T)$ is much smaller than the susceptibility of the conducting Rb_3C_{60}. Hence in Rb_4C_{60} the additional electrons at LUMO level form a localized rather than a paramagnetic metallic state. The preliminary EPR experiments show the same temperature dependence of the EPR susceptibility.[4] This confirms the spin paramagnetic origin of the temperature-dependent part of $\chi(T)$.

Our magnetization measurements agree with the NMR properties of A_4C_{60} which are also quite different from those for the Pauli paramagnetic metallic phase A_3C_{60}. Actually, the NMR shifts for A_4C_{60} (38 ppm with respect to C_{60} for both K_4C_{60} and Rb_4C_{60} at 300 K) are smaller than those for A_3C_{60} (44 ppm for K_3C_{60} and 52 ppm for Rb_3C_{60}).[1] The NMR shift of K_4C_{60}, which seems to be provided by contact hyperfine coupling of ^{13}C with spins of additional electrons, weakly decreases with temperature[5] in the same fashion as $\chi(T)$. The spin-lattice relaxation time T_1[0.11 s for K_4C_{60} and 0.08 s Rb_4C_{60} at 300 K (Ref. 1)] is substantially shorter than the Korringa value T_1 for metallic phases [0.35 s for K_3C_{60} and 0.22 s Rb_3C_{60} at 300 K (Ref. 1)]. The value of $1/T_1T$ increases exponentially with temperature[5,6] with the activation gap of 100 meV.

The principal question which could possibly be answered from the magnetic measurements is the spatial extent of the localization: whether it is of Anderson type (caused by disorder or intermolecular spin and/or charge density wave) or the four additional electrons are localized *on site* on the C_{60} molecule (Mott-Hubbard or phonon assistant localization). We think that the second possibility is more likely since in the high-resolution ^{13}C NMR no intersite inhomogeneity of the magnetization was observed at room temperature when the *on-site* (intramolecular) magnetism is motionally narrowed.[1] The activation character of the magnetic properties of Rb_4C_{60} indicates that the four *on-site* localized additional electrons form the spin singlet ground state. The temperature-dependent paramagnetic contribution is provided by the thermally activated electrons. The three-fold degenerate t_{1u} LUMO level with x,y,z type orbitals is known to admit up to six additional electrons. The spin singlet ground state of four additional electrons is formed as a result of the splitting of the three-fold degenerate t_{1u} LUMO level. This splitting can be provided by the following mechanisms.

(i) The body-centered-tetragonal (bct) ionic A^- crystal field of A_4C_{60} lifts the three-fold degeneracy of LUMO level into two-fold degenerate $x\pm iy$ and nondegenerate z levels. If the $x\pm iy$ state has a lower energy it becomes occupied by the four electrons forming a singlet ground state. (See Fig. 2).

(ii) The dominance of electron-phonon interaction[7–9] results in the Jahn-Teller instability which lowers the C_{60} icosahedral symmetry with splitting of three-fold degenerate t_{1u} LUMO level in the same way as the bct crystal field. The $x\pm iy$ state in this case always has a lower energy which leads to a spin-singlet ground state.

FIG. 2. The figure illustrates the lifting of the three-fold degeneracy of LUMO level into two-fold degenerate $x \pm iy$ and nondegenerate z level.

(iii) The dominance of electron-electron Coulomb interaction was shown[10,11] also to give rise to a spin singlet $(L=0, S=0)$ ground state formation.

Hence the magnetic properties of A_4C_{60} can be described by the two level model, in which the ground state corresponds to the spin singlet state and the excited state is paramagnetic. The static magnetic susceptibility can be expressed as

$$\chi(T)=\chi_d+\chi_{\mathrm{VV}}+\frac{C}{T}\,n(T). \tag{1}$$

Here χ_d is the orbital diamagnetic part, χ_{VV} is the contribution from the Van Vleck spin paramagnetism. The last term describes the contribution of the excited paramagnetic states. The number of the excitations $n(T)$ is defined by the Boltzmann statistics:

$$n(T)=\frac{\nu_{\mathrm{ex}}e^{-\Delta/2kT}}{\nu_0+\nu_{\mathrm{ex}}e^{-\Delta/2kT}}, \tag{2}$$

where ν_0 and ν_{ex} are the filling numbers of the ground and the excited states correspondingly and Δ is the excitation energy. The molar Curie constant C is given by

$$C=ZN_A(g\mu_B)^2S(S+1)/k; \tag{3}$$

here Z is the number of the spins S per C_{60} molecule and N_A is Avogadro's number.

In order to perform the numerical fitting of the experimental data we assume that either the crystal field or Jahn-Teller distortions are relevant to the formation of the spin singlet ground state. For this case we have $\nu_0=4$ and $\nu_{\mathrm{ex}}=2$ (see Fig. 2). The effective number of spins per C_{60} molecule $Z=2$ (one spin $S=\frac{1}{2}$ originating from the excited electron whereas the second spin $S+\frac{1}{2}$ reflects the three residual electrons of the ground state).

From the curve $\chi(T)$ (Fig. 1) we have estimated a Curie constant of $C=0.8$ emu K/mol (for $g=2$), the activiation energy as $\Delta=1200\pm100$ K and a temperature-independent diamagnetic contribution of $\chi_d=-3\times10^{-4}$ emu/mol. From (3) we obtain $nS(S+1)=1.6\pm0.2$. This value is in good agreement with $S=\frac{1}{2}$, $n=2$. Since the EPR susceptibility has no temperature-independent part,[4] we conclude that the Van Vleck contribution χ_{VV} in (1) is negligible. Therefore all the temperature-independent part of the static susceptibility is due to the orbital diamagnetic effects. Correcting the diamagnetic contribution by the core susceptibility of the neutral C_{60} molecule, -2.5×10^{-4} emu/mol,[12] and four ions of $\mathrm{Rb}^+[\chi_{\mathrm{Rb}^+}=-0.22\times10^{-4}$ emu/mol (Ref. 13)] we obtain that the diamagnetic contribution due to four additional electrons is vanishingly small in the frame of the experimental error bars.

In conclusion, the parameters we have obtained from the bulk magnetization measurements reveal the qualitatively new electronic properties of the phase $\mathrm{Rb_4C_{60}}$ with respect to other alkali-metal-doped fullerides. We found that $\mathrm{Rb_4C_{60}}$ is an insulator in which the four *on-site* localized electrons form a spin singlet ground state. The observed paramagnetic properties are due to the thermally activated electrons. The experimental results are in good agreement with the existence of Jahn-Teller or crystal field distortions, providing the lifting of the t_{1u} LUMO level degeneracy. The excitation energy between the ground and the excited spin paramagnetic state is found to be about 1200 K. Similar conclusions were obtained also from NMR experiments.[5]

I. L. is grateful to A. Alexandrov for helpful discussions.

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[1] J. Reichenbach, F. Rachdi, I. Luk'yanchuk, M. Ribet, G. Zimmer, and M. Mehring, J. Chem. Phys. **101**, 4585 (1994).

[2] A. Jánossy *et al.*, Phys. Rev. Lett. **71**, 1091 (1993).

[3] A. D. Ramirez, M. J. Rosseinsky, D. W. Murphy, and R. C. Haddon, Phys. Rev. Lett. **69**, 1687 (1992).

[4] F. Rachdi *et al.* (unpublished).

[5] G. Zimmer, M. Helmle, M. Mehring, and F. Rachdi, Europhys. Lett. **27**, 543 (1994).

[6] R. Tycko, J. Phys. Chem. Solids **54**, 1713 (1993).

[7] C. M. Varma, J. Zaanen, and K. Raghavachari, Science **254**, 989 (1991).

[8] M. Schulter *et al.*, Phys. Rev. Lett. **68**, 526 (1992).

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

[10] S. Chakravarty, M. P. Gelfand, and S. Kivelson, Science **254**, 970 (1991).

[11] G. Baskaran and E. Tossatti, Curr. Sci. **61**, 33 (1991).

[12] R. S. Ruoff *et al.*, J. Phys. Chem. **95**, 3457 (1991).

[13] N. W. Ashkroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).