^{13}C NMR and static magnetic susceptibility in C_{60} superconductors: Possible influence of Kondo impurity

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The static spin susceptibility, χ_s^{SQ} and χ_s^{NMR}, in C_{60} superconductors K_3C_{60} and Rb_3C_{60} was studied using a dc superconducting quantum interference device magnetometer and ^{13}C NMR. We found that χ_s^{SQ} has a peculiar temperature (T) dependence behaving as $(1-CT^2)$ with a positive constant $C\sim(1\times10^{-6})\ \mathrm{deg}^{-2}$, contrary to the almost T independent χ_s^{NMR}. These observations indicate a possibility that there exist Kondo-like impurities, whose Kondo temperature is ~500 K and whose content is ~0.001 spins per carbon. On the basis of these studies, the lattice constant dependence of the intrinsic spin susceptibility was established to be $d\chi_s/da_0=(5.7\pm0.4)\times10^{-4}$ emu/mol C_{60}/Å in A_3C_{60} superconductors where A is an alkali metal.
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The static magnetic susceptibility in C_{60} superconductors, A_3C_{60} where A is an alkali metal, has been studied using a dc superconducting quantum interference device (SQUID) magnetometer,[1–3] ESR,[2,4–7] and ^{13}C NMR (Refs. 8–10) by several authors. These studies showed that both the superconducting transition temperature T_c and the spin susceptibility χ_s increase with increasing lattice constant a_0, consistent with the BCS formula for T_c, except for the case of ammoniated A_3C_{60}.[10] However, a more detailed inspection of the reported data on χ_s shows that there exists significant disagreement. Firstly, the T dependence of χ_s obtained from the dc SQUID, χ_s^{SQ}, decreases with increase of temperature, contrary to χ_s^{ESR} obtained from ESR measurement which shows an increasing function of temperature. Secondly, there is a wide variation in the estimate of lattice-constant dependence of χ_s, $d\chi_s/da_0$, obtained from dc SQUID, ESR, and NMR measurements. In this context, we performed a careful investigation of the static magnetic susceptibility of A_3C_{60} superconductors using a dc SQUID magnetometer and ^{13}C NMR, which is reported in the present paper.

The static susceptibility was measured with a commercial SQUID magnetometer (Quantum Design Ltd.; MPMS). The sample, which is unstable in air, was sealed in a quartz tube divided by a thin wall at the center. The susceptibility of the sample was obtained by subtraction between two measurements for the tube containing the sample and the ''empty'' tube itself. The diamagnetic signal from the glass wall in the SQUID response has a different center-of-mass position from those of the sample. Because this may lead to an error, a short paramagnetic platinum wire was wound around the tube to correct the difference. ^{13}C NMR was observed using conventional pulse and Fourier transform NMR apparatus at a magnetic field of 4 and 9.4 T.

Powder samples of K_3C_{60} and Rb_3C_{60} were prepared to measure both NMR and static magnetic susceptibility. Two K_3C_{60} samples were prepared by the conventional vapor reaction technique. In one of the K_3C_{60} samples, the ^{13}C isotope was enriched to $\sim20\%$ from 1.1% of the natural abundance and the starting C_{60} powder was purified by the sublimation method.[11] In the following, this enriched sample is called $K_3^*C_{60}$ and the other is referred to as K_3C_{60}. A sample of Rb_3C_{60} was prepared by the liquid-ammonia reaction method.[12] It was found to include $\sim8\%$ NH_3, i.e., $(NH_3)_{0.08}Rb_3C_{60}$, by measurement of ^1H and ^{13}C NMR intensity at the same frequency with different fields of 1 T for ^1H NMR and 4 T for ^{13}C NMR. Low-field magnetic-susceptibility measurements gave T_c of 19 K for $K_3^*C_{60}$, 19.5 K for K_3C_{60} and 28 K for $(NH_3)_{0.08}Rb_3C_{60}$. The shielding fraction was more than 60% in all the samples. However, $K_3^*C_{60}$ used for SQUID measurement included a significant amount of pure C_{60} phase ($\sim25\%$). In the other samples, C_{60} was undetectable or less than $\sim5\%$.

An inset to Fig. 1(b) shows a typical magnetization curve as a function of the magnetic field for $(NH_3)_{0.08}Rb_3C_{60}$ and K_3C_{60}. As in previous reports,[1–3] there is a ferromagnetic contribution, whose origin has not yet been clarified. There-

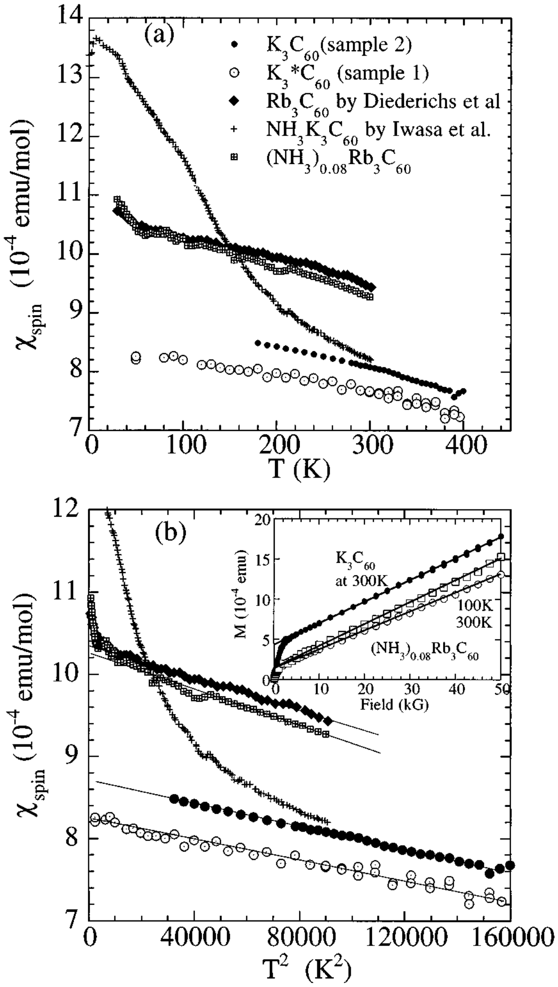

FIG. 1. T dependence of spin susceptibility, χ_s^{SQ}, obtained from SQUID magnetometer measurements in K_3C_{60}, Rb_3C_{60}, $(NH_3)K_3C_{60}$, and $(NH_3)_{0.08}Rb_3C_{60}$. (a) χ_s^{SQ} vs T, and (b) χ_s^{SQ} vs T^2. The inset to (b) shows examples of magnetization curve as a function of magnetic field. The straight lines are guide for the eye.

fore, we determined χ from the high-field region (~ 1 T) as usual. Diamagnetic contributions from C_{60} core, alkali cations, and NH_3 molecules were subtracted to obtain the spin susceptibility χ_s. The values used are -20, -13, -5, -14.4, and -262.8 ($\times 10^{-6}$ emu/mol) for Rb, K, Na, NH_3, and C_{60}, respectively. A possible diamagnetic conduction-electron contribution was ignored, as in Ramirez *et al.*,[1,2] because the effective mass in C_{60} superconductors is expected to be much larger than the free electron value.

The T dependence of χ_s is shown in Figs. 1(a) and 1(b) as a function of T and T^2, respectively. In all the samples, χ_s is found to have a weak temperature dependence, described by $(1-CT^2)$ where C is a positive constant and (7.6×10^{-7}) deg^{-2} for K_3C_{60} and (9.8×10^{-7}) deg^{-2} for $(NH_3)_{0.08}Rb_3C_{60}$. As shown in Fig. 1, the data for Rb_3C_{60} reported by Diederichs *et al.* also exhibit a T-square dependence,[3] while $(NH_3)K_3C_{60}$ data presented by Iwasa *et al.* show a quite different behavior.[13]

Such T-square dependence is not unusual even in conventional metals. When the Fermi surface is broadened by thermal energy $\sim k_BT$, the Pauli-spin susceptibility[14] is calculated, up to the order of T^2, to

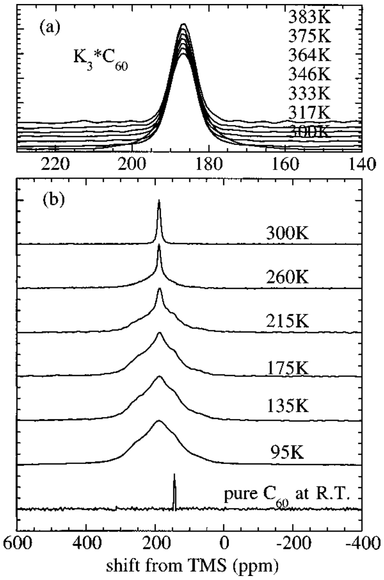

FIG. 2. (a) and (b) show examples of ^{13}C NMR spectra in $K_3^*C_{60}$ at various temperatures. In K_3C_{60}, the almost T-independent shift was also confirmed between 250 and 400 K.

$$\chi_s = \chi_{s0}\left[1+\left(\frac{\pi^2}{6}\right)(k_BT)^2 \frac{d^2 \ln N(E)}{dE^2}\bigg|_{E_F}\right], \tag{1}$$

where $\chi_{s0}=2\mu_B^2 N(E_F)$. Here, $N(E_F)$ is the electronic density of states at the Fermi level for one spin direction and μ_B's the Bohr magneton. Such behavior must be observed even by ESR, as well as by SQUID measurements. However, all ESR measurements of χ_s reported up to the present show the opposite temperature variation of the SQUID data, except for $(NH_3)K_3C_{60}$.[13] This discrepancy may suggest that there is a contribution from impurities or defects in SQUID measurement which cannot be detected by the ESR technique. ESR determination of χ_s, however, is difficult because of changes in cavity conditions and skin depth in the metallic samples with temperature. Alternatively, in the present work, we employed ^{13}C NMR to clarify χ_s and $N(E_F)$.

Figures 2(a) and 2(b) show examples of ^{13}C NMR spectra in $K_3^*C_{60}$ at different temperatures. Essentially the same spectra were observed in K_3C_{60}. Figure 3(a) shows the isotropic shift of the ^{13}C NMR spectra, δ, with reference to the resonance frequency of tetramethylsilane (TMS), along with χ_s^{SQ} of K_3C_{60} and $(NH_3)_{0.08}Rb_3C_{60}$.

The shift δ is a sum of the chemical shift δ_{chem} and the Knight shift K_s. The Knight shift is given by $K_s = (2\pi/h\gamma_e\gamma_n)a_{iso}\chi_s$, where a_{iso} is isotropic hyperfine coupling constant for C_{60}^{-3} and χ_s is spin susceptibility per molecule. In general, the shift is anisotropic and given by second rank tensors. However, in this paper we focus our attention on the isotropic part because a reliable estimate has been reported only for a_{iso} as $a_{iso}/2\pi = 0.69\pm 0.06$ MHz for C_{60}^{-3} molecule.[10] Further, it is naturally assumed that the chemical shift does not vary significantly within A_3C_{60} with the same valence C_{60}^{-3}. Using $\chi_s = 8.22\times 10^{-4}$ (emu/mol C_{60}) and $\delta = 195.9$ ppm at room temperature in $(NH_3)_{1.14}K_3C_{60}$,[10,13] we obtain $K_s = 47.9$ ppm for $(NH_3)_{1.14}K_3C_{60}$ and $\delta_{chem} = 148.4$ ppm from TMS, close to the value of 150 ppm

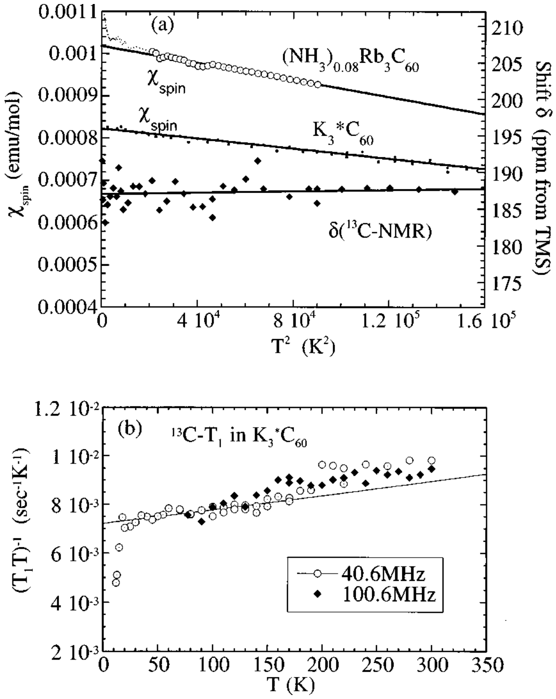

FIG. 3. (a) T dependence of ^{13}C NMR isotropic shift in $K_3^*C_{60}$, along with the spin susceptibility, χ_{spin}, of $K_3^*C_{60}$ and $(NH_3)_{0.08}Rb_3C_{60}$ obtained from SQUID measurements. The solid lines for χ_{spin} are fitting curves with Eq. (3). (b) T dependence of $^{13}C-1/T_1T$ in $K_3^*C_{60}$. The solid line indicates an expected variation from the lattice expansion with temperature.

given in a previous estimate from an interpolation between shift values for neutral C_{60} in pristine C_{60} and C_{60}^{-6} in A_6C_{60}; 143 and 156 ppm.[10,15] The reading from the left-hand scale for δ in Fig. 3(a) gives χ_s^{NMR}.

The ^{13}C NMR spectra in Rb_3C_{60} were also observed between 30 and 300 K. The isotropic shift is constant within ~10 ppm around 192 ppm. These observations in K_3C_{60} and Rb_3C_{60} were essentially consistent with previous reports.[8,16]

Therefore, Fig. 3(a) shows that the Knight shift (proportional to χ_s) is nearly T independent, contrary to χ_s^{SQ}, and that χ_s^{NMR} is smaller than χ_s^{SQ}. The difference suggests that there is a contribution from impurity spins.[17] In this case, the NMR signal around impurity spins is expected to be easily wiped out, as in ESR. Thus, the intrinsic susceptibility must be obtained from NMR measurements rather than from dc static susceptibility measurement.

^{13}C NMR T_1 also gives information on $N(E_F)$. The result for K_3C_{60} is shown in Fig. 3(b). Up to the order of T^2, $1/(T_1T)$ in metal is given by

$$\frac{1}{T_1T}=\left(\frac{1}{T_1T}\right)_0\left[1+\left(\frac{\pi^2}{3}\right)\frac{(k_BT)^2}{N(E)}\left.\frac{d^2N(E)}{dE^2}\right|_{E_F}\right], \qquad (2)$$

where $(1/T_1T)_0$ is the usual metallic T-independent term and proportional to $N^2(E_F)$.[18] The observed $1/(T_1T)$ in Fig. 3(b) is slightly T dependent and may be explained by a variation of $N(E_F)$ due to lattice contraction and/or the second term in Eq. (2). However, it is found that the lattice contraction is enough to explain the observed T dependence below

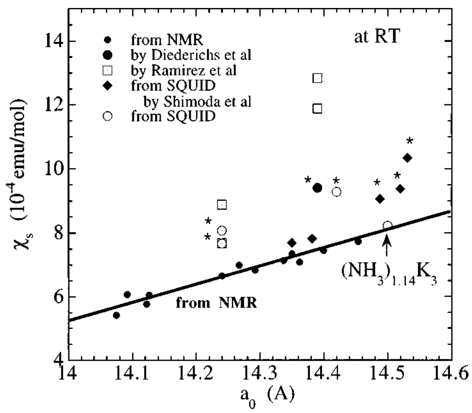

FIG. 4. Spin susceptibility, χ_s, obtained from the SQUID magnetometer and NMR as a function of the lattice constant. The stars show the samples in which the T-square-dependent susceptibility was observed.

~150 K in magnitude. In a previous paper, we estimated $d\chi_s/da_0$ from the ^{13}C Knight shift at high-T and ^{13}C-T_1 at low T as $(5.54–6.10)\times10^{-4}$ emu/mol C_{60}/Å.[10,19] Providing the enhancement factor in χ_s, the so-called Stoner enhancement, is T independent, the value for $d\chi_s/da_0$ and the lattice contraction can lead to the solid line in Fig. 3(b).

These NMR results clearly indicate that the peculiar T dependence of χ_s^{SQ} is due to impurities. The susceptibility due to impurity spin varies as $(1-CT^2)$ instead of the usual Curie-Weiss law, $\sim(T-\Theta)^{-1}$. Therefore, in this case we suggest a possibility that the impurity spins must couple with conduction electrons, and show the so-called Kondo effect.[20,21] The spin susceptibility of Kondo impurity, χ_I, is known to be described by

$$\begin{aligned}&\chi_I\sim(T-\Theta_A)^{-1} \quad \text{for } T>T_K,\\ &\chi_I\sim1-(T/\Theta_B)^2 \quad \text{for } T<T_K, \qquad (3)\\ &\chi_I\sim(g\mu_B)^2/k_B\Theta_C \quad \text{for } T=0,\end{aligned}$$

where Θ_A, Θ_B, and Θ_C are roughly the Kondo temperature, T_K.[22,23]

In the sd model, $T_K=T_F\exp[1/JN(E_F)]$, where T_F is the Fermi temperature, J is a sd-interaction coupling constant. (The interaction Hamiltonian is given by $\mathcal{H}_{sd}=-J\vec{s}\cdot\vec{S}$, where $\vec{s}$ and $\vec{S}$ are conduction and impurity electron spins, respectively.) In A_3C_{60}, if T_K is higher than the measuring T range, 400 K, the susceptibility of the impurity spins should follow the second formula of Eq. (3).

Figure 4 shows χ_s^{SQ} vs the cubic lattice constant a_0 for various A_3C_{60}'s at RT. The solid lines with a slope of 5.7 $\times10^{-4}$ emu/mol C_{60}/Å shows χ_s estimated from the ^{13}C Knight shift K_s at high-T in the previous paper[10] where the origin of the K_s was changed to 148.4 ppm from 150 ppm, as discussed above. We find that overall agreement between SQUID data and NMR Knight-shift measurements is roughly established, except the data for Rb_3C_{60} by Ramirez *et al.*[1] The present result on χ_s^{SQ} of $(NH_3)_{0.08}Rb_3C_{60}$ is close to that of Diederichs *et al.*[3] rather than that of Ramirez *et al.* The reason for this disagreement is not clear at the present.

However, because χ_s^{SQ} includes the impurity-spin contribution, it must deviate from χ_s^{NMR}. This is actually seen in Fig. 4. Assuming the intrinsic spin susceptibility is given by χ_s^{NMR} and T independent, $\chi_s^{\mathrm{SQ}}=\chi_s^{\mathrm{NMR}}+\chi_I$, we can deduce the Kondo temperature, T_K, and spin contents from the experimental data in Fig. 3(a) using Eq. (3): $T_K \sim 500$ K and 0.0008 spins/carbon for K_3C_{60} and $T_K \sim 500$ K and 0.0014 spins/carbon for $(NH_3)_{0.08}Rb_3C_{60}$. Using $T_F \sim 2000$ K and $N(E_F) \sim 7$ states/eV/C_{60}/spin$=0.12$ states/eV/spin/carbon, we have $J=-0.15$ eV per C_{60} or $J=-9.1$ eV per carbon.

In some Kondo alloys, the NMR signal of host elements around Kondo impurities has been observed as satellite lines or line broadening.[24–26] While a similar study in the present system would be possible, we could not obtain any decisive conclusion so far. This is because of a low sensitivity of ^{13}C NMR and the broad linewidth at low T which varies with temperature due to C_{60} molecular rotation.

Recently, the susceptibility measurements have been made in ammoniated A_3C_{60}, $(NH_3)_xNaA_2C_{60}$ with $A=$Rb or K by Shimoda *et al.* using a dc SQUID magnetometer.[27] The results for χ_s^{SQ} at 300 K are also shown in Fig. 4. In the case of $A=$Rb, their data show a T^2 dependence as reported in the present study. Therefore, up to now, the T-square dependence has been observed in K_3C_{60}, Rb_3C_{60}, and $(NH_3)_xNaRb_2C_{60}$, shown by * in Fig. 4, and not observed in $(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xK_3C_{60}$ at present. It should be emphasized that only the samples showing the T-square dependence are deviated from χ_s^{NMR} in Fig. 4. This also confirms that the T-square dependence in χ_s^{SQ} is due to impurity spins. However, the origin of the impurity spins has not yet been clarified. Oxygen contamination and/or collapsed C_{60} may be candidates.

In summary, we found a peculiar T dependence of spin susceptibility in A_3C_{60} superconductors as $(1-CT^2)$. This suggests the presence of Kondo-like impurities in the materials. The lattice constant dependence of the intrinsic spin susceptibility was established in A_3C_{60} superconductors from both NMR and SQUID measurements. The present finding invokes reconsideration of the previous reports based on the SQUID data to study the detailed electronic states and superconducting mechanisms in C_{60} superconductors. Further detailed studies, especially on the origin of the impurity spin, should be required. We also need to examine other possibilities for the T-squared dependence, such as the spin-clustering effect.

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[1] A. P. Ramirez *et al.*, Phys. Rev. Lett. **69**, 1687 (1992).
[2] W. H. Wong *et al.*, Europhys. Lett. **18**, 79 (1992).
[3] J. Diederichs *et al.*, Phys. Rev. B **54**, R9662 (1996).
[4] A. Janossy *et al.*, Phys. Rev. Lett. **71**, 1091 (1993).
[5] K. Tanigaiki *et al.*, Chem. Phys. Lett. **240**, 627 (1995).
[6] P. Petit and J. Robert, Appl. Magn. Reson. **11**, 183 (1996).
[7] K. Tanigaki *et al.*, J. Mater. Chem. **10**, 222 (1995).
[8] R. Tycko *et al.*, Phys. Rev. Lett. **68**, 1912 (1992).
[9] Y. Maniwa *et al.*, J. Phys. Soc. Jpn. **63**, 1139 (1994).
[10] Y. Maniwa *et al.*, Phys. Rev. B **54**, R6861 (1996).
[11] Y. Maniwa *et al.*, Jpn. J. Appl. Phys., Part 2 **33**, L173 (1994).
[12] X. Chen *et al.*, Chem. Mater. **10**, 503 (1998). The sample used in the present study, $(NH_3)_{0.08}Rb_3C_{60}$, is the same as in this study.
[13] Y. Iwasa *et al.*, Phys. Rev. B **53**, R8836 (1996).
[14] For example, see C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1996).
[15] G. Zimmer *et al.*, Europhys. Lett. **24**, 59 (1993).
[16] V. A. Stenger *et al.*, Phys. Rev. B **48**, 9942 (1993).
[17] Another possibility is temperature-dependent orbital susceptibility. However, recent analysis of ^{13}C NMR spectrum of K_3C_{60} in the superconducting state suggested that the orbital shift corresponding to the orbital susceptibility at 4.2 K is the same as that at room temperature.
[18] K. Mizuno (private communication); T. Saito, M.S. thesis, Tokyo Metropolitan University, 1985.
[19] Y. Maniwa *et al.*, in *Electrochemical Society Proceedings*, edited by K. M. Kadish and R. S. Ruoff (The Electrochemical Society, Inc., New Jersey, 1997), Vol. **97-14**, p. 1191.
[20] J. Kondo, Prog. Theor. Phys. **32**, 37 (1964).
[21] A. J. Heeger, Solid State Phys. **23**, 283 (1969).
[22] K. Yamada, Prog. Theor. Phys. **55**, 1345 (1976).
[23] K. Kume and K. Mizoguchi, J. Phys. F **7**, 1555 (1977).
[24] J. B. Boyce and C. P. Slichter, Phys. Rev. B **13**, 379 (1976).
[25] H. Alloul *et al.*, J. Phys. F **4**, 2050 (1974).
[26] K. Mizuno, J. Phys. Soc. Jpn. **30**, 742 (1971).
[27] H. Shimoda *et al.* (unpublished).