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Determination of ^{13}C NMR isotropic Knight shift and deviation from BCS relation in A_3C$_{60}$ superconductors

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We determined the isotropic ^{13}C NMR hyperfine coupling constant as $a_{\text{iso}}/2\pi = 0.69 \pm 0.06$ MHz for the $\text{C}_{60}{}^{3-}$ ion near room temperature (RT). On this basis, the spin susceptibility at RT, χ_s(RT), was estimated in various alkali-metal doped C$_{60}$ compounds $A_3\text{C}_{60}$, which is approximately proportional to the lattice constant a_0; we found $d\chi_s/da_0 = (0.61 \pm 0.06) \times 10^{-3}$ (emu/mole C$_{60}$)/Å . The correlation between the superconducting transition temperature T_c and χ_s(RT) was determined. It was found that T_c of Na$_2$RbC$_{60}$, Na$_2$KC$_{60}$, Li$_2$CsC$_{60}$, and ammoniated $A_3\text{C}_{60}$ is significantly lower than that expected from the BCS relation based on χ_s(RT). [S0163-1829(96)52434-3]

In early works of alkali-doped C$_{60}$ superconductors, $A_3\text{C}_{60}$, the superconducting transition temperature T_c was believed to be a monotonic function of the lattice constant, a_0.[1] This relation has been well understood within a conventional BCS picture through the Fermi level density of states $N(E_F)$, which becomes large as a_0 increases.[1–3] More detailed studies have clarified that the T_c-a_0 relation of sodium-containing compounds with simple cubic (sc) structure, Na$_2A$C$_{60}$ (where A=K,Rb,Cs), is much steeper than that of $A_3\text{C}_{60}$ with face centered cubic (fcc) structure.[4,5] The origin was attributed to the difference in the $N(E_F)$-a_0 relation between sc and fcc structures[6] and also to other unknown parameters such as lattice imperfections or some disorders.[7] In the case of the former, the sc structure would lead to a T_c of higher than 40 K by a small lattice expansion of about 0.07 Å (0.5%) from Na$_2$CsC$_{60}$ of $T_c = 12$ K. In the case of Li$_2$CsC$_{60}$ and Li$_2$RbC$_{60}$ with fcc structure, superconductivity has not been observed down to 50 mK, while the empirical T_c-a_0 relation predicts T_c of a few kelvins.[8,9] More recently, ammoniated alkali-doped fulleride, $(\text{NH}_3)_xA_3\text{C}_{60}$ with $x \sim 1$, was prepared.[10–12] This family exhibits also different trends in the T_c-a_0 correlation. It is obvious that one of the most important issues at present is to clarify whether the deviation from the usual T_c-a_0 relation is due to the effect of the Fermi level density of states $N(E_F)$ in these "low-T_c materials." For this purpose, we employed ^{13}C NMR technique.

A systematic study of $N(E_F)$ in a series of $A_3\text{C}_{60}$ superconductors by ^{13}C NMR spin-lattice relation time T_1 has been reported in previous papers.[3,7,13] However, in some compounds which do not show metallic T_1T=const law and in which the T_1 is dominated by other mechanisms, $N(E_F)$ could not be determined. The detailed systematic analysis of the shift data also could give information on $N(E_F)$ and its variation with the compounds. However, it could not be performed. This is because the small Knight shift (order of several ppm) must be extracted from the ^{13}C NMR shift tensor, which has another important contribution from the chemical shift. In order to separate these two terms, additional information and precise determination of the shift are required. In the present work we determined an isotropic hyperfine coupling constant in $(\text{NH}_3)_{1.14}\text{K}_3\text{C}_{60}$ having a large temperature-dependent spin susceptibility[12] and narrow ^{13}C NMR spectra above $\sim$200 K. Based on this, we clarified the variation of Knight shift and spin susceptibility, χ_s, in several $A_3\text{C}_{60}$ compounds with different T_c's. We found that $N(E_F)$ falls on a universal $N(E_F)$-a_0 line for all the compounds studied here around room temperature (RT) and thus in the low-T_c materials the T_c deviates from that expected from the BCS relation based on χ_s at RT.

$A_3\text{C}_{60}$ specimens were prepared by a technique using alkali-azide (some of them are the same specimens used in Ref. 14) and also a conventional direct reaction method with alkali metal and C$_{60}$ in a glass tube. Several ammoniated $A_3\text{C}_{60}$ specimens were prepared by the method described in previous papers.[10–12] Raman experiments showed no evidence for deviation from 3− for the valence of C$_{60}$. A conventional pulse NMR apparatus was operated at 40.6 MHz for ^{13}C NMR measurement. The NMR frequency shift from that of tetramethylsilane (TMS) as a reference substance is given by part per million (ppm).

In Fig. 1, examples of ^{13}C NMR spectra at room temperature are shown. The narrow linewidth of 10–20 ppm indicates that C$_{60}$ molecular rotation takes place in all these

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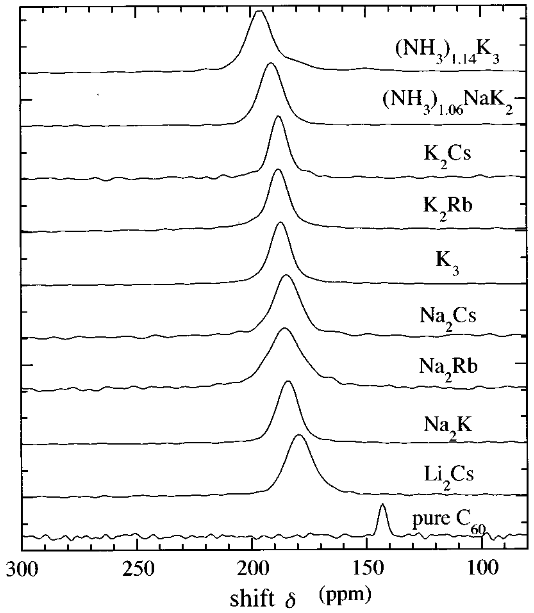

FIG. 1. Examples of ^{13}C NMR spectra at room temperature. These spectra were taken 2–5 times for each specimen and the averaged values for the peak shift are shown in Table I.

specimens at room temperature. (Below ~100 K, all these specimens show a linewidth broader than ~80 ppm due to the anisotropy of the ^{13}C NMR shift tensor.) In $(NH_3)_{1.14}K_3C_{60}$, we observed a temperature dependence of the resonance frequency; 5.7 ppm between 300 and 200 K. This should be attributed to the temperature-dependent susceptibility[12] reported for the same specimen as the present study. Combining the NMR shift δ with the susceptibility (χ) data measured by a superconducting quantum interference device (SQUID) magnetometer, we obtained the δ-χ plot in Fig. 2. The spin susceptibility measured by ESR technique for the same sample was also temperature dependent similar to that measured by the SQUID magnetometer,[12] implying that the temperature dependence is dominated by the spin part.

In general, the NMR isotropic shift δ is represented by $\delta = K_{\mathrm{iso}} + \delta_{\mathrm{chem}}$,[15] where K_{iso} and δ_{chem} are the isotropic Knight shift and isotropic chemical (orbital) shift, respectively, and a_{iso} is the isotropic hyperfine coupling constant. Here, we assume that δ_{chem} is temperature independent. On the other hand, K_{iso} should be proportional to electronic spin susceptibility χ_s; $K_{\mathrm{iso}} = (h\gamma_e\gamma_n/2\pi)^{-1} a_{\mathrm{iso}}\chi_s$, where γ_e and γ_n are the electronic and ^{13}C nuclear gyromagnetic ratio, respectively, and h is Planck's constant. Since the susceptibility measured by a method such as SQUID magnetometry is a sum of χ_s and other temperature-independent terms, only $dK_{\mathrm{iso}}/d\chi_s$ is deduced to be $(58 \pm 5) \times 10^3$ ppm/(emu/mole C_{60}), as shown in Fig. 2, giving $a_{\mathrm{iso}}/2\pi = 0.69 \pm 0.06$ MHz for the $C_{60}{}^{3-}$ ion.

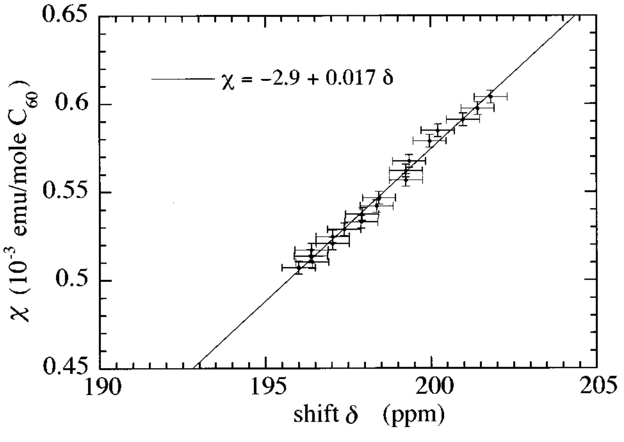

FIG. 2. δ-χ plot in $(NH_3)_{1.14}K_3C_{60}$.

TABLE I. ^{13}C NMR isotropic shift δ from TMS in A_3C_{60} compounds. All these compounds show the narrow spectra with linewidths of 10–20 ppm due to C_{60} molecular rotation. The Knight shift K_{iso} and spin susceptibility χ_s are given by $K_{\mathrm{iso}} = \delta - 150$ ppm and $\chi_s = 1.73 \times 10^{-5} K_{\mathrm{iso}}$ emu/mole C_{60}, respectively. For independent electrons, we have $N(E_F) = 1.55 \times 10^4 \chi_s = 0.27 K_{\mathrm{iso}}$ (states/eV C_{60} spin).

Substance	Shift δ around RT (ppm)	Shift δ at 500 K (ppm)
Li_2CsC_{60}	179.5	
Na_2KC_{60}	184.1 (fcc), 181.6 (sc)	
Na_2RbC_{60}	185.8 (fcc), 182.3 (sc)	
Na_2CsC_{60}	185.7 (fcc), 182.2 (sc)	
K_3C_{60}	186.7	
K_2RbC_{60}	188.6	189.5
K_2CsC_{60}	187.8	189.2
Rb_3C_{60}		193
$(NH_3)_{1.06}NaK_2C_{60}$	191.3	
$(NH_3)_{0.67}NaK_2C_{60}$	190.8	
$(NH_3)_{1.14}K_3C_{60}$	195.9	

For instance, the value for $a_{\mathrm{iso}}/2\pi$ can be compared with 2.0 MHz reported for Rb_3C_{60},[16] having an error within 50%. On account of the difficulty of the precise determination of the shift from the broad spectra and/or a small temperature dependence of χ in Rb_3C_{60}, we believe that the difference between these two should not be taken seriously. However, we emphasize that in the present study the value for $a_{\mathrm{iso}}/2\pi$ was determined at high temperature, where the large amplitude C_{60} molecular rotation is taking place.

Next, we take 150 ppm as the origin of the Knight shift, following a previous paper.[16] This was empirically determined by using the shift for insulating substances, i.e., 143 ppm for pure C_{60}, and 156 ppm and 157 ppm for $C_{60}{}^{6-}$ in K_6C_{60} and in Rb_6C_{60}, respectively. This means that one additional electron to C_{60} leads to a chemical shift of ~2.3 ppm. Then we have $K_{\mathrm{iso}} = 46$ ppm for $(NH_3)_{1.14}K_3C_{60}$ at 300 K, which corresponds to $\chi_s = 0.78 \times 10^{-3}$ emu/mole C_{60} at 300 K. Similarly, we can estimate χ_s from the isotropic shift δ in Table I in other compounds, using the relations $K_{\mathrm{iso}} = \delta - 150$ ppm and $\chi_s = 1.73 \times 10^{-5} K_{\mathrm{iso}}$ emu/mole C_{60}. For free electrons, the spin susceptibility is given by $\chi_s = 2\mu_B^2 N(E_F)$, where μ_B is the Bohr magneton and $N(E_F)$ is the density of states at the Fermi level for one spin direction. Then we have $N(E_F) = 1.55 \times 10^4 \chi_s = 0.27 K_{\mathrm{iso}}$ (states/eV C_{60} spin), where the units of χ_s and K_{iso} are (emu/mole C_{60}) and (ppm), respectively. For example, 186 ppm of

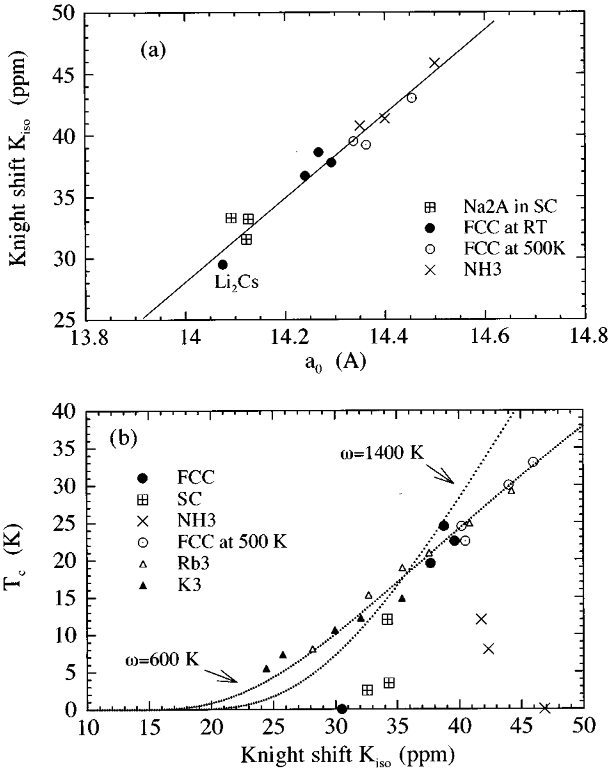

FIG. 3. (a) The correlation between shift δ and lattice constant a_0. In $(NH_3)_{1.14}K_3C_{60}$, an equivalent lattice constant for fcc is shown. (b) The relation between T_c and Knight shift K_{iso}. Close and open triangles were obtained from $T_c(a_0)$ dependence in Ref. 20 for K_3C_{60} and Rb_3C_{60} under pressure, respectively (see text). The dotted lines are calculated T_c using the McMillan equation with $\langle\omega\rangle=600$ and 1400 K for $\mu^*=0.2$. Without the Stoner enhancement factor (see text), an appropriate fitting for $\langle\omega\rangle=1400$ K cannot be obtained.

K_3C_{60} gives $\chi_s=0.62\times10^{-3}$ emu/mole C_{60}, and $N(E_F)=9.7$ (states/eV C_{60} spin). This value is compared with 0.6×10^{-3} emu/mole C_{60} in Ref. 17 and 0.6–0.9 $\times10^{-3}$ emu/mole C_{60} in Ref. 18, estimated from the static magnetic susceptibility measurements. This value is also consistent with ESR measurements, i.e., $N(E_F)=10$–15 (states/eV C_{60} spin) reported in Ref. 19. The agreement is fairly good and justifies the above assumption on the origin of the Knight shift.

The correlation between the shift and the lattice constant is shown in Fig. 3(a). The lattice constant at 500 K was estimated from those of room temperature by assuming $da_0/dT\sim3.5\times10^{-4}$ Å /K, i.e., a lattice expansion of 0.07 Å between 300 and 500 K.[19] Those for Na_2AC_{60} (where $A=$K,Rb,Cs) were shown in sc phase. We find that the correlation between the shift and the lattice constant is well established, giving $dK_{iso}/da_0=35\pm4$ ppm/Å or $d\chi_s/da_0=0.61\times10^{-3}$ (emu/mole C_{60})/Å on the assumption of the linear dependence. That is, the density of states $N(E_F)$ ($\propto\chi_s$) lies on the same universal line in A_3C_{60}, including fcc, sc, and ammoniated compounds, *suggesting that the electronic states of all A_3C_{60} compounds studied here are quite similar at least around RT where the molecular motion is significant.* This result rules out a possibility that the sc and fcc A_3C_{60} have a different $N(E_F)$-a_0 relation.[6]

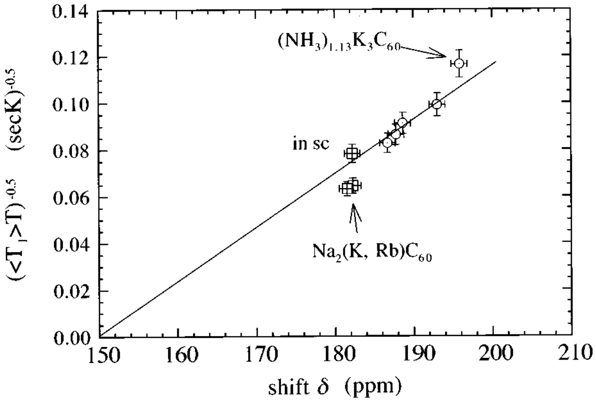

FIG. 4. The correlation between shift δ at RT and $\langle T_1T\rangle^{-0.5}$ at low temperature in Refs. 7 and 12. Both are expected to be proportional to $N(E_F)$. $\langle T_1T\rangle^{-0.5}$ for $(NH_3)_xNaK_2C_{60}$ has not yet been reported.

On the contrary, the K_{iso}-T_c correlation does not have the universal curve, as shown in Fig. 3(b). There, we also show those for K_3C_{60} and Rb_3C_{60} obtained from the T_c-a_0 correlation under pressure,[20] where we used the present K_{iso}-a_0 correlation to obtain the K_{iso}-T_c. The T_c, except ‘‘the low-T_c materials,’’ is found to be well described by a conventional McMillan equation, if we use relevant phonon energy $\langle\omega\rangle$ of ~600 K, the effective Coulomb potential μ^* of 0.2–0.4, and the electron-phonon coupling constant λ given by $\lambda=0.0255\,K_{iso}$ for $\mu^*=0.2$ and $0.046\,K_{iso}$ for $\mu^*=0.4$. These values are roughly consistent with those in earlier reports[3,7] on ^{13}C-T_1. Taking the Stoner enhancement of K_{iso} into account [$K_{iso}\propto\chi_s\propto N(E_F)/(1-\alpha)$ with $N(E_F)\propto\alpha<\sim0.44$ for K_3C_{60} estimated in Ref. 3], we find $\langle\omega\rangle$ up to ~1400 K. On the other hand, the T_c's of Li_2CsC_{60} and Na_2AC_{60} ($A=$Rb or K) and ammoniated A_3C_{60} are much lower than those expected from the line for other fcc A_3C_{60}. This suggests that *the T_c variation in A_3C_{60} superconductors is not simply described by the change in $N(E_F)$ within BCS theory and/or the low-temperature electronic states are quite different from those at high temperature in these low-T_c materials.* To examine the latter possibility, we plotted a relation between shift δ at RT and $\langle T_1T\rangle^{-0.5}$ at low temperature (below ~120 K) using T_1 data,[7,12] where both should be proportional to $N(E_F)$. The results are shown in Fig. 4. We notice that those for the low-T_c materials [Na_2KC_{60}, Na_2RbC_{60}, and $(NH_3)_{1.14}K_3C_{60}$] deviate from a straight line. In the case of $(NH_3)_{1.14}K_3C_{60}$ it is consistent with the fact that the low-temperature spin susceptibility is larger than the high-temperature values, probably due to an electron correlation effect. Similarly Fig. 3(b) indicates that $N(E_F)$ of Na_2KC_{60} and Na_2RbC_{60} decreases with lowering temperature. Except for the low-T_c compounds, the linear dependence in Fig. 4 agrees with the assumption that the orbital contribution to the NMR shift does not strongly vary from sample to sample.

Such change can be due to phase transitions driven by Fermi surface instability or by ordering of the intercalated molecules. If the alkali metals are located at off center in the C_{60} interstitial sites, which was actually suggested in Li_2CsC_{60} (Ref. 9) and $(NH_3)_{\sim1}A_3C_{60}$,[11] the latter should be taken into account. This leads to a change of the crystal field at the C_{60} molecular site. Another possibility is related to disordered potentials induced by crystal imperfections (distortion) and/or site disorder of intercalated molecules, as well as C_{60} orientational disorder. These would significantly affect the electronic and superconducting properties in particular because of the narrow bandwidth of ~ 0.5 eV in this system. Such problems may be closely related to why fullerides, including higher fullerenes, doped with alkali metal or other elements are not usually good conductors, except A_3C_{60}.

In summary, we determined the spin susceptibility in various A_3C_{60} compounds at high temperature where the large amplitude molecular motions exist. The high-temperature electronic states are found to be quite similar in all A_3C_{60} compounds studied here, implying that the low T_c cannot be understood simply by $N(E_F)$ at high temperature within BCS theory. While the low-temperature electronic states were suggested to be significantly different from those of high temperature in some A_3C_{60} compounds, the issue whether or how the T_c suppression is explained within the BCS framework still remains to be solved. The possibility of Fermi surface instability and the effect of freezing of the molecular motion on the electronic states and superconducting properties should be investigated in the future.

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