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^{13}C Nuclear Relaxation and Normal-State Properties of K_3C_{60} under Pressure.

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Abstract. – We report the pressure and temperature dependences of ^{13}C nuclear spin-lattice relaxation time T_1 in the normal state of K_3C_{60} . From the $1/T_1T$ temperature and pressure profiles, a Fermi-liquid theory is used to investigate the variation of the density of states and the amplitude of electron-electron interaction. Finally the results obtained are shown to support a pairing mechanism for superconductivity that would involve high-frequency modes.

The reaction of C_{60} with an alkali metal has recently led to the exciting discovery of a new class of superconducting materials A_3C_{60} with surprisingly high transition temperatures (19.6 K for $\text{A} = \text{K}$ and 29 K for $\text{A} = \text{Rb}$) [1-3]. The observed relation between T_c and the lattice constant, obtained through the study of a series of isostructural superconductors with composition $\text{A}_{3-x}\text{B}_x\text{C}_{60}$ (where A and B are K , Rb , Cs) [4], seems to indicate that variations in T_c can be accounted for by changes in the density of states at Fermi level. Therefore, the traditional BCS-like model based on the pairing of electrons to relatively low-frequency phonon modes [5] is one of the various theories suggested to account for the superconductivity in these compounds. However, the idea that high-frequency intramolecular vibrations of the C_{60} molecule are involved has also received consideration [6, 7]. From nuclear-relaxation measurements, Tycko *et al.* [8] conclude that the low-frequency phonons are the relevant ones for superconductivity with a consequently large value of the pair formation parameter ($\lambda \approx 0.6$). The strong-coupling limit is also supported by tunnelling experiments realized on Rb_3C_{60} [9]. On the other hand, Raman spectroscopy [10] and recent inelastic-

neutron-scattering study [11] clearly indicate that weak coupling to high-frequency intramolecular modes is rather involved.

Owing to the high compressibility of these materials, the density of states can be strongly influenced by hydrostatic pressures. For example, the superconducting transition temperature in K_3C_{60} is reduced by almost a factor of two when a 10 kbar hydrostatic pressure is applied [12, 13]. In this letter we show how ^{13}C nuclear spin-lattice relaxation measurements under pressure can be used as a tool to clarify the functional dependence between T_c and the density of states and, in turn, the nature of the exchanged phonon in the pairing mechanism.

All NMR data presented here have been obtained using an isotopically enriched sample (10% ^{13}C). The enriched clusters of C_{60} were previously prepared by using cored carbon rods packed with amorphous ^{13}C powder consumed in the electric-arc procedure described previously [14]. After extraction and purification of the resulting soot, intercalation of the C_{60} crystallites was conducted following the procedure described by McCauley *et al.* [15]. The C_{60} powder was first separated into two equal parts. One of these was treated with potassium vapour up to saturation, yielding the composition K_6C_{60} . This phase was identified by solid-state NMR, by reference to the work of Tycko *et al.* [16]. This sample was then mixed with the second half of the pure C_{60} powder and kept in a sealed glass tube. Finally the mixture was successively annealed at 240 K for few hours and at 340 K for few days. The composition of the final product has been checked by ^{13}C solid-state NMR with magic angle spinning of the sample, showing that the K_3C_{60} phase constitutes the main part of the system, with a small residue of pure C_{60} but no other phases present. Moreover, the superconducting transition temperature was checked by an a.c. susceptibility measurement which shows a well-defined transition at 19.6 K.

Temperature-dependent NMR measurements were performed with a Bruker MSL 400 spectrometer and for fields of 9.4 tesla (100 MHz) at $p = 1$ bar and 2.62 tesla (28 MHz) under pressure. The time dependence of the ^{13}C nuclear magnetization $M(t)$ was obtained using the saturation-recovery technique. The resulting curve was then fitted to a single exponential function in order to extract the spin-lattice relaxation time T_1 . In all these measurements no significant departure from this single exponential function has been observed. Measurements under pressure at 300 K and 80 K (the lowest temperature allowed with our system at the moment) have been performed with a home-made double-stage CuBe pressure cell using isopentane as a hydrostatic pressure medium.

In order to check the quality of the sample, we have measured the temperature dependence of the ^{13}C spin-lattice relaxation time T_1 under atmospheric pressure. The results obtained for $1/T_1T$ (fig. 1) coincide with those by Tycko *et al.* [8] and the present results obtained by Holczer *et al.* [17]. Thus the data confirm that $1/T_1T$ effectively decreases by 35% from 300 K to 50 K. For a nearly free-electron band model, this quantity is expected to be temperature-independent. Therefore, to explain this variation one can see if it can be simply related to an additional relaxation process. As, at room temperature, the spectrum of K_3C_{60} is narrowed by rapid reorientations of C_{60} molecules, we can ascribe this additional process to molecular motions. The resulting expression for the total relaxation rate would then read

$$\frac{1}{T_1} = \frac{1}{T_1^{\text{elec}}} + 2\gamma_N^2 \delta H_{r.m.s.}^2 \frac{\tau}{1 + \omega_N^2 \tau^2}, \quad (1)$$

where $1/T_1^{\text{elec}}$ stands for the electronic contribution to the relaxation rate. The second term is the well-known expression for the molecular-motion contribution [18-20]. Here, γ_N is the ^{13}C gyromagnetic ratio, τ is the correlation time for molecular reorientation, ω_N is the angular

Larmor frequency and $\delta H_{\text{r.m.s.}}$ is the amplitude of the fluctuating local field produced by molecular motions (here $\delta H_{\text{r.m.s.}} \propto \omega_N$). Using experimental data, we can now estimate this contribution. First of all, since no field dependence of T_1 has been detected between 3 T and 10 T, it is clear that molecular reorientations in K_3C_{60} are much slower than what is found in pure C_{60} [19,20]. This observation already implies that we are in the limit of long correlation times where $\omega_N \tau \gg 1$. Moreover, we also observe that a powder pattern line shape already develops at 250 K, which indicates that the product of the correlation time and the static linewidth must be of the order of unity ($\delta H_{\text{r.m.s.}} \tau \approx 1$). Using $\delta H_{\text{r.m.s.}}/\omega_N = 200$ p.p.m. given by the width of the spectrum at low temperature, we find $\tau \approx 70 \mu\text{S}$ which gives from eq. (1), $1/T_1 = 0.001 \text{ S}^{-1}$ for the non-electronic contribution. A value which is small compared to the relaxation rate obtained at 300 K ($1/T_1 = 3$). As we further reduce the temperature, this relaxation mechanism is expected to be even less efficient, therefore this mechanism can certainly not explain the observed temperature dependence.

The influence of thermal contraction of the lattice on the bandwidth has also been proposed to account for the temperature dependence of $1/T_1 T$ [8]. However, the observed variation seems too large to be attributed to non-interacting electrons alone. Therefore, we believe that electron-electron correlations could also play a significant role. As shown for example in the context of more anisotropic organic conductors like the Bechgaard salts which present similar temperature and pressure dependences in $1/T_1 T$, the effect of thermal dilatation is further enhanced by uniform spin correlations that are present in the high-temperature domain of these materials [21,22]. In order to clarify this point, we first observed here that the poor nesting properties inherent to the closed Fermi surface of a

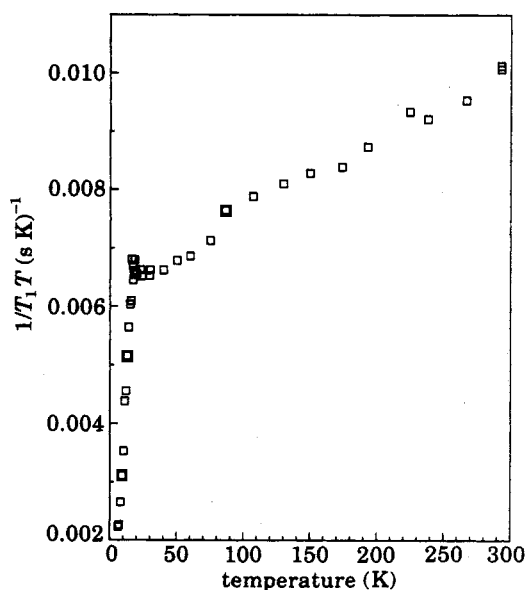


Fig. 1.

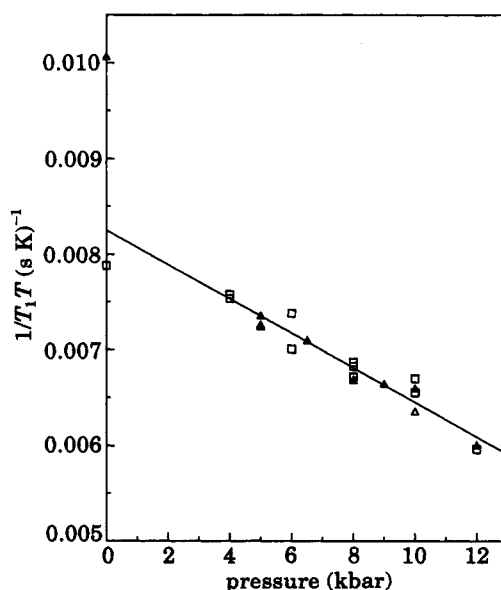


Fig. 2.

Fig. 1. - Temperature dependence of the ^{13}C spin-lattice relaxation time T_1 in K_3C_{60} plotted as $(T_1 T)^{-1}$ vs. T .

Fig. 2. - Pressure dependence of the ^{13}C spin-lattice relaxation time T_1 in K_3C_{60} plotted as $(T_1 T)^{-1}$ vs. P at 300 K (triangles) and at 80 K (squares). The continuous line is a linear regression fit of the data obtained at 80 K.

system like K_3C_{60} indicate indeed that only long-wavelength spin fluctuations (paramagnons), if any, matter. Therefore, deviations with respect to a Fermi-liquid behaviour in the normal state should be essentially absent. Thus, adopting a Fermi-liquid picture from which the expression for the imaginary part of the long-wavelength spin response function is given by [23]

$$\text{Im } \chi(\mathbf{q}, \omega \rightarrow 0) = \frac{\mu_B^2 \frac{\pi}{2} N(E_F) \frac{\omega}{v_F q}}{[1 + F_0^a + cq^2]^2}, \quad (2a)$$

in the collisionless (non-diffusive) limit and for vanishing frequency, one then easily gets the three-dimensional Fermi-liquid result for the electronic part of the relaxation rate:

$$\begin{aligned} \frac{1}{T_1 T} &= 8\pi |A|^2 \gamma_N^2 (g\mu_B)^{-2} \int_0^{q_c} \frac{\text{Im } \chi(\mathbf{q}, \omega \rightarrow 0)}{\omega} q^2 dq = \\ &= \pi |A|^2 \gamma_N^2 [N(E_F)]^2 (1 + F_0^a)^{-1} \left[1 + F_0^a \left(1 - \frac{2}{3\pi^2} \right) \right]^{-1}. \end{aligned} \quad (2b)$$

Here $C = (1/12) |F_0^a| k_F^{-2}$, and $F_0^a = N(E_F) f_0^a$ is the Fermi-liquid interaction parameter involved in the enhancement of the spin susceptibility $\chi_s = \mu_B^2 N(E_F) (1 + F_0^a)^{-1}$ with $N(E_F) = m^* k_F / \pi^2$ as the density of states for both spin orientations. In eq. (2b), $q_c (2/\pi^3)^{1/2} k_F$ is a momentum cut-off for spin fluctuations that allows only long-wavelength spin fluctuations to contribute to T_1^{-1} . Its precise value is chosen in order to recover the non-interacting Korringa result as $F_0^a \rightarrow 0$. Thus for a Fermi liquid that lies not too close to an instability, the enhancement of $1/T_1 T$ is nearly proportional to the one of χ_s^2 . Otherwise, for $F_0^a \approx -1$, one recovers the familiar linear relation $1/T_1 T \propto N(E_F) \chi_s$ which holds for a nearly ferromagnetic system [24, 25].

In order to estimate the amplitude of correlations in these systems, we now look at the pressure dependence of $1/T_1 T$ obtained at 80 K and 300 K for K_3C_{60} up to 12 kbar. From fig. 2, two remarkable features are visible. Firstly, at room temperature $1/T_1 T$ decreases rapidly between ambient pressure and 5 kbar; secondly, above this pressure, the two data sets overlap perfectly indicating that $1/T_1 T$ is essentially temperature independent in this range. From the ambient temperature X-ray data of Zhou *et al.* [26], the lattice parameter of K_3C_{60} decreases by 1.2% under 10 kbar which, according to extended Huckel band structure calculations of Fleming *et al.* [4], corresponds to a reduction of 11% or so in the electronic density of states. If the interaction term F_0^a is neglected in (2b), this in turn leads to 22% reduction in $1/T_1 T$, a value smaller than the observed 35% pressure variation at 300 K (see fig. 2). To account for the enhanced variation of $1/T_1 T$, F_0^a must be approximately equal to -0.37 at 1 bar and 300 K. Therefore, if the band calculations are meaningful, we have to conclude that correlation effects play a significant role at room temperature. This conclusion is also supported by recent specific-heat and magnetic-susceptibility measurements realized by Ramirez *et al.* [27]. Moreover, their estimation of the interaction parameter ($F_0^a \approx -0.46$) is consistent with the value obtained independently here. As for the temperature variation of $1/T_1 T$, we know from the measurement realized by Tanigaki *et al.* [28] that the change in the lattice constant is 0.7% between 11 K and 300 K, which is equivalent to the variation produced by a pressure of 6 kbar for K_3C_{60} [26]. Therefore, within this picture, the observed temperature variation of the $1/T_1 T$ at 1 bar can be entirely understood in terms of the thermal contraction effects on the density of states, these effects being enhanced by correlations. The fact that $1/T_1 T$ is practically constant below the Debye temperature

($\theta_{\text{Debye}} = 70 \text{ K}$ [27]) also supports this picture. Then when we apply the pressure, we believe that the correlations are slightly depressed, while the thermal dilatation effects are known to be strongly reduced in organic conductors [22]. This would then explain why the temperature variation of $1/T_1 T$ at 10 kbar is strongly reduced. A similar situation which exists in the context of Bechgaard salts [22] has already been analysed in great details. However, in contrast to quasi-1D organic conductors for which a clear scaling relation between the observed enhancements in T_1^{-1} and $T\chi_s^2(T)$ has been clearly established, no clear temperature-dependent enhancement of the magnetic susceptibility [17,27,29] or Knight shift [8] for K_3C_{60} has been reported so far. For the Knight shift, its exact value is still unknown but it is probably around 43 p.p.m. [8], therefore a variation of only 10% becomes difficult to measure.

We can now use the pressure dependence of $1/T_1 T$ in order to estimate which pairing mechanism is involved for superconductivity in A_3C_{60} compounds. For that, we will assume that superconductivity in K_3C_{60} can be described by the weak-coupling result $T_c \propto \Omega \cdot \exp[-1/N(E_F)V]$, where Ω is the energy of the phonon and V is the electron-phonon coupling strength. If V is unaffected by pressure, we can write for the frequency of the exchange boson

$$\Omega = T_c(10 \text{ kbar}) \exp \left[\frac{\ln T_c(5 \text{ kbar}) - \ln T_c(10 \text{ kbar})}{\delta N/N} \right], \quad (3)$$

where

$$\frac{\delta N(E_F)}{N(E_F)} = \frac{1}{2} \frac{\delta(T_1 T)^{-1}}{(T_1 T)^{-1}} [1 + F_0^a].$$

From fig. 2, we get 11% variation on $1/T_1 T$ between 5 kbar and 10 kbar where there is no temperature variation. Using the values $T_c(5 \text{ kbar}) = 15.5 \text{ K}$, $T_c(10 \text{ kbar}) = 12 \text{ K}$ [12, 13] and in the absence of interactions, one finds $\Omega \approx 1250 \text{ K}$ for $\delta N/N \approx 5.5\%$. If we include the effect of interactions, $\delta N/N$ will decrease, which implies that ω increases further. Thus, within this simple weak-coupling picture, our results show that low-frequency (acoustic) phonons are very unlikely to be involved in superconductivity. This is consistent with Raman spectroscopy [10] and inelastic-neutron-scattering [11] studies, which indicate that phonons around 1500 K are effectively coupled to electronic states.

In conclusion, we believe that the results presented here have illustrated two main points. First of all, the possibility that electron-electron interactions play an important role on the properties of these compounds is indicated by the temperature dependence of $1/T_1 T$ at 1 bar along with its strong reduction under pressure of 5 kbar or so. Finally, within a BCS framework for the expression of T_c , the reduction of the electronic density under pressure is found to favour a pairing mechanism that would involve high-frequency intramolecular vibrations of the C_{60} molecules.

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