Evidence from ^{77}Se Knight shifts for triplet superconductivity in $(TMTSF)_2PF_6$

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We present ^{77}Se nuclear magnetic resonance (NMR) Knight shift (K) studies in pressurized $(TMTSF)_2PF_6$ with a magnetic field aligned along the b axis, perpendicular to the conducting chains but parallel to the conducting plane. On cooling deep into the superconducting state, no observable change in K from both spin echo and free induction decay signal was found. This strongly suggests triplet superconductivity in $(TMTSF)_2PF_6$.

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Following the discovery of superconductivity in the layered, quasi-one-dimensional charge transfer salt $(TMTSF)_2PF_6$ (Ref. 1), there was extensive discussion of the symmetry of the ground state. For example, triplet superconductivity and the spin-density wave (SDW) phase of the one-dimensional electron gas (as described by g-ology[2]) are adjacent to each other, analogous to the $(TMTSF)_2PF_6$ system where superconductivity is only observed after eliminating the SDW phase with applied pressure. Further, the suppression of superconductivity by defects produced by irradiation[3,4] and by chemical substitution[5,6] led to early suggestions of p-wave symmetry.[7] However, specific heat,[8] thermal conductivity,[9] and resistive upper critical field studies[10,11] had indicated conventional, BCS-like pairing. The issue was revived by recent measurements of the upper critical field H_{c2} with substantially improved accuracy in angular alignment and lower temperatures.[12,13] Superconductivity persists to more than four times the Pauli limit[14] H_p (limiting field for singlet superconductors), when the field is applied in the plane of the molecular layers. Even with a field-induced dimensional crossover, which greatly increases the orbital critical field,[15,16] an additional mechanism, such as the formation of the inhomogeneous LOFF state[17,18,19] or triplet superconductivity, is required to exceed H_p in the Bechgaard salts $(TMTSF)_2X$ ($X = PF_6$, ClO_4, AsF_6, etc.). The lack of evidence for a first order phase transition that occurs between a LOFF state and a uniform superconductor, the observed $H_{c2} > 4H_p$ and the recent theoretical analysis of the in-plane H_{c2} anisotropy argue strongly against the LOFF state.[13,20] Direct evidence of triplet superconductivity came from recent NMR Knight shift experiments where Lee *et al.*[21] found an absence of resonant frequency shift when the system passes through the superconducting state with the magnetic field aligned along the a axis, parallel to the conducting chains. The present NMR Knight shift study, which is done at a pressure of 6.4 GPa with a magnetic field aligned along the b axis perpendicular to the chains but parallel to the ab-conducting plane, is then additional strong evidence supporting triplet superconductivity.

In general, a singlet superconducting ground state leads to a vanishing of the spin contribution K_s in the total K as temperature decreases well below the critical temperature T_c. With magnetic field aligned along the b-axis, the expected average shift for the inequivalent ^{77}Se sites is approximately 310 ppm upon cooling from the normal state to a singlet superconducting phase. However, we conclude from our measured spectra that no change is observed within $\delta K_s = 0 \pm 20$ ppm uncertainty. To ensure that the pressurized sample was superconducting while acquiring the NMR data, we conducted transport measurements time synchronous with the application of the radiofrequency pulses. Details of the experimental setup can be seen in Ref. 21.

Our principal result is shown in Fig. 1. The lower set of spectra was collected as free induction decays (FID's), and

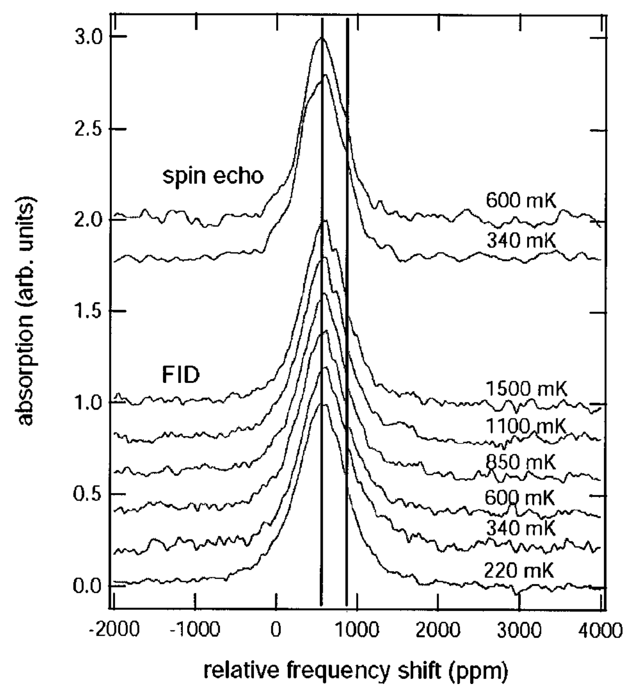

FIG. 1. ^{77}Se spectra collected at a pressure $P = 0.64$ GPa and various temperatures with the magnetic field $B = 2.38$ T oriented parallel to the molecular layers. The two solid lines mark the measured first moment, and the expected first moment for a singlet ground state.

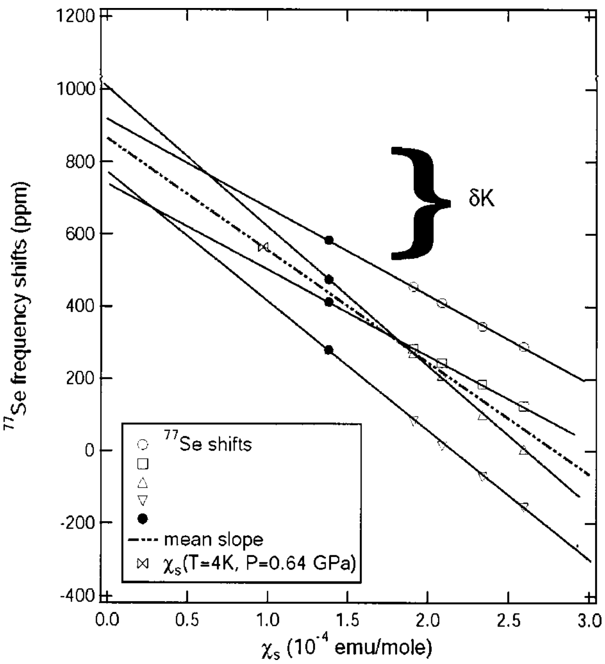

FIG. 2. NMR shifts K vs the spin susceptibility χ_s for magnetic fields applied along the b axis at ambient pressure. The symbols indicate the NMR shift from four inequivalent Se sites with the applied field. The filled circles are obtained at $T=4$ K. The dashed line is the mean slope of the four solid lines; it is used to estimate the spin contribution to the shift K_s at $P=0.64$ GPa from the known reduction of χ_s (to 0.97×10^{-4} emu, marked with a bowtie symbol) with the applied pressure.

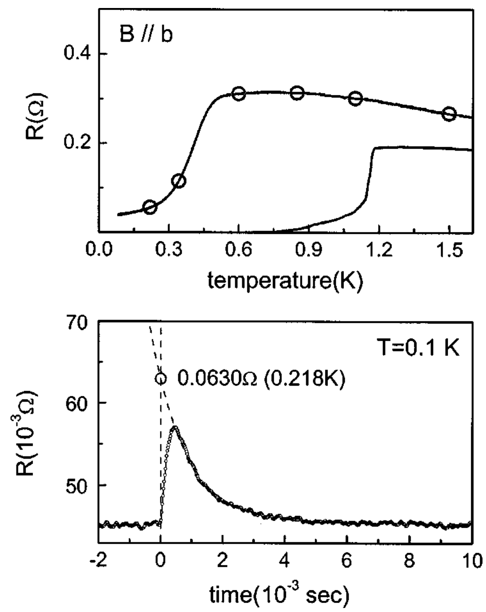

FIG. 3. (a) Interlayer resistance R vs temperature at zero applied magnetic field and at the ^{77}Se measuring field of $B=2.38$ T applied parallel to the b axis. (b) Time synchronous resistance measurements triggered and recorded simultaneous with the rf pulses for the NMR measurements. The bath (equilibrium) temperature was at $T=0.1$ K.

the upper as spin echoes. Spectra were recorded at various temperatures, for a magnetic field aligned parallel to the layers to within 0.1° and parallel to the b axis to within a couple of degrees. To within the experimental uncertainty, it is obvious that there is no change in the first moment. The two vertical lines mark the measured first moment and the expected position of the spectrum if the spin susceptibility had vanished. The lack of any observable difference between the spectra as the temperature is varied indicates that the system is not a singlet superconductor. Below, we establish the relationship between the spin susceptibility and the Knight shift, and define a critical temperature and spontaneous heating effects due to an applied rf pulse.

There is an extensive literature related to NMR work on $(TMTSF)_2PF_6$, in both the ambient pressure spin-density wave phase[22] and the pressurized metallic phase.[23,24] For the most part, the previous work includes studies of the local magnetic environments of either the protons in the methyl groups or ^{13}C spin labeled on the various inequivalent sites. Another possibility is ^{77}Se. Its abundance is 8%, $I=\frac{1}{2}$, and $^{77}\gamma=8.129$ MHz/T. There are reports of ^{77}Se spin-lattice relaxation rate measurements in the metallic state for powdered samples[23] and single crystals,[24] but very little spectroscopy that we know of.[25] However, it is generally known from band structure calculations as well as EPR studies that the largest spin densities associated with the conduction band are closely linked with molecular orbitals originating with the selenium atoms.[26] For these reasons, the ^{77}Se nucleus was a clear choice for the Knight shift experiments.

Figure 2 shows the paramagnetic shifts in the normal state as a function of the spin susceptibility for $B\|b$. The dashed line is the mean slope. This type of plot $(K-\chi)$ is often used to separate shifts of orbital and chemical origin from shifts K_s originating from the hyperfine coupling, and therefore proportional to χ_s. The absolute value of χ_s was extracted from Miljak *et al.*,[27] who obtained a strong temperature dependence that probably results from a combination of lattice contraction and low-dimensional correlation effects. Thus, just as for the recent study identifying Sr_2RuO_4 as a triplet superconductor,[28] temperature is an implicit parameter relating K to χ_s. The shifts K are measured at an ambient pressure relative to the NMR line (at ν_0) of ^{77}Se in $Se(CH_2)_2$. That is, $K=(\nu-\nu_0)/\nu_0$. We are interested in comparing our measured results to the expected change δK from the normal state shift for a singlet superconductor where K_s vanishes.

To evaluate δK, we first corrected for the effect of the applied pressure by reducing χ_s by 30%,[29] from 1.38×10^{-4} emu to 0.97×10^{-4} emu (marked as a bowtie symbol for identification purposes). Since the hyperfine constant is not likely altered by the applied pressure, the sensitivity of the measurement is reduced by the same amount, 30%. The 310 ppm difference between $K(4\,\mathrm{K}, P=0.64\,\mathrm{GPa})$ and $K(\chi_s=0)$ is from the hyperfine coupling to the spin and is the expected change δK for a singlet superconducting ground state. It is indicated in Fig. 2 by the large bracket; the two vertical lines in Fig. 1 allow for comparison to the linewidth. As an aside, we note that the shifts are significantly greater with the field aligned along the a axis.

In Fig. 3(a), we show the interlayer resistance R vs temperature for $B=0$ T, and the ^{77}Se measuring field of $B=2.38$ T along the b axis. There is a sharp reduction at $T_c(B=0\ \mathrm{T})=1.18$ K, followed by a resistive tail (probably related to sample or pressure inhomogeneity) before resistance vanishes to zero at $T\sim0.8$ K.

In addition to confirming the superconducting state, *in situ* transport measurements along with NMR provide a crucial diagnostic tool at the lowest temperatures, since the sample itself can be used as an excellent thermometer in the middle of the superconducting transition. We found that the thermal time constant of the sample (plus surrounding fluids and NMR coils) was approximately 1 ms. The NMR spectra are acquired on a time scale of 100 μs. The duty cycle for the rf pulsing was kept very low, so that the average heating was negligible. A resistance measurement with short time constant made the heating by the rf pulses observable and therefore controllable. An example of the time-synchronous transport measurements, recorded under the same conditions as the data which give the spectra in Fig. 1, is shown in Fig. 3(b). The resistance is measured using a standard four probe lock-in technique at a frequency of 3.14 kHz. We verified that the electronic time constant was about 0.3 ms. The pulses used for the FID experiments were of duration 1 μs using power levels less than 10 mW. At a recycle time of 1 sec, the time-averaged power is somewhat less 10 nW. Immediately after the pulse, the sample resistance (temperature) begins to rise, reaching a maximum at about 600 μs later. Afterward, an exponential decay is observed with the time constant of 1 msec. The shape of the heating curve suggests that the NMR coil, not the sample, is the source of the heating. Since the Knight shift measurement is completed in less than 100 μs, it is possible that the sample experiences no heating in this time. The high limiting value of the sample heating is obtained by extrapolating the exponential part of the heating curve back to the time of the pulse. The resistance and temperature at this time are an upper bound to the heating effects. These upper bounds are the temperatures that we quote in the rest of the paper. They are indicated as the open circles in Fig. 3(a) and are those labeling the spectra in Fig. 1. The main objective here is to make sure that our NMR K_s measurements were done in both the normal and well inside the superconducting state.

To obtain an independent and bulk measure of the superconducting transition, we recorded the spin-lattice relaxation rates $1/T_1$ for ^{77}Se that are shown in Fig. 4. Plotted in this way, the results look generally similar to what is expected for the normal state of pressurized $(\mathrm{TMTSF})_2\mathrm{PF}_6$ (Refs. 23, 24). A distinct peak that we associate with the onset of superconductivity is evident in $(T_1T)^{-1}$ near $T=0.7$ K (see upper inset). Unlike previously reported a-axis relaxation measurements,[21] a small enhancement of relaxation rate near T_c was not detected. However, considering that a large applied field destroys such an enhancement effect (Hebel-Slichter[30] peak), it is not too surprising that we have not observed the effect here at $B=2.38$ T. We note that there is a discrepancy in critical temperature determined from the electrical transport ($T_c=0.5$ K) and the relaxation ($T_c=0.7$ K). We cannot rule out a possibility that some other causes (such as pressure inhomogeneity having twin crystal

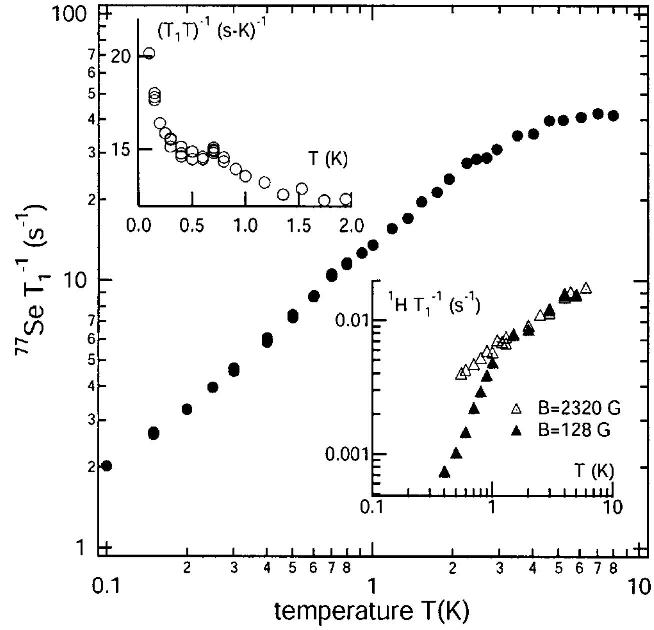

FIG. 4. ^{77}Se T_1^{-1} vs temperature for $B=2.38$ T$\|b$ axis. In the lower inset are shown the results of field-cycled ^{1}H T_1^{-1} measurements; at the top, the detailed temperature dependence of $(T_1T)^{-1}$ near the superconducting transition ($T=0.7$ K) is depicted.

and small cracks, etc., which could result the resistance tail at a zero field) may influence the electrical transport under the applied magnetic field. We also note that dynamic processes related to flux motion (when the sample is cooled in a magnetic field) could influence both resistance and T_1 measurements. A related issue is the general tendency for the relaxation rate to approach the normal state value. Well below $T_c(H)$ in a strong type-II superconductor, $1/T_1\sim(H/H_{C2})T$ because of the normal fraction in the pinned vortex cores and the Korringa relation.[31] In fact, $1/T_1$ for $(\mathrm{TMTSF})_2\mathrm{PF}_6$ appears to be extraordinarily sensitive to magnetic field, which we demonstrate by way of field-cycling experiments using the methyl group protons as a probe. Shown in the lower inset to Fig. 4 are experiments on another sample with slightly higher pressure (0.7 GPa) at $B=12.8$ mT and $B=232$ mT. The behavior at the lower field is similar to that observed by Takigawa *et al.*,[32] for field-cycled ^{1}H relaxation in superconducting $(\mathrm{TMTSF})_2\mathrm{ClO}_4$. At the resonance field of 232 mT, the fast drop of $1/T_1$ is nearly absent, although there is a distinct change in slope at $T=1$ K. Remarkably, the applied field $B=232$ mT at $T=0.5$ K is far below characteristic values for H_{c2} observed by Lee *et al.*[13] or in earlier studies. There are two aspects of the spin-lattice relaxation that we would like to emphasize. First, from the ^{77}Se relaxation rates and electrical transport, we have observed a clear onset for superconductivity at temperatures well above those where our NMR Knight shift measurements were performed. Second, even though the spin-lattice relaxation rates are high in the superconducting state, they are not simply related to the volume fraction of normal cores.

In conclusion, our present study, b-axis Knight shift experiments, provides an additional proof for the triplet pairing in this quasi-one-dimensional system and, along with the previous result of *a*-axis NMR Knight shift experiments,[21] further constrains the number of possibilities of order parameter. Those results suggest that the spin susceptibilities of both the *a* and *b* axes remain the same as in the normal state.

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