Triplet Superconductivity in an Organic Superconductor Probed by NMR Knight Shift

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(Received 7 August 2001; published 19 December 2001)

The nature of the superconducting state in quasi-one-dimensional organic conductors has remained controversial since its discovery. Here we present results of ^{77}Se NMR Knight shift (K_s) experiments in $(TMTSF)_2PF_6$ under 7 kbar of pressure with a magnetic field aligned along the most conducting a axis. We find no noticeable shift in K_s upon cooling through the superconducting transition. Since K_s directly probes the spin susceptibility χ_s, the fact that χ_s remains unchanged through the superconducting transition strongly suggests spin-triplet superconductivity.

DOI: 10.1103/PhysRevLett.88.017004 PACS numbers: 74.70.Kn, 74.60.Ec

Understanding the nature of superconductivity has been one of the major interests in condensed matter physics for the past century. Until recently, most superconducting materials discovered were conventional (BCS type) with spin-singlet electron pairing which has zero total spin ($S = 0$), isotropic symmetry of the orbital order parameters, and phonon-mediated attractive pairing interactions. Quasi-two-dimensional superconductors such as the high T_c copper oxides [1] and possibly BEDT-TTF salts [2] seem to be more exotic, with an anisotropic orbital symmetry (d wave), but still spin-singlet pairing. Spin-triplet superconductivity ($S = 1$) which requires p-wave or odd orbital symmetry, analogous to superfluid helium 3 [3], is quite rare. Evidence in favor of a triplet pairing state has been presented only in UPt_3 [4] and Sr_2RuO_4 [5]. The experimental temperature-pressure phase diagram of tetramethyltetraselenafulvalene hexaflurophosphate $(TMTSF)_2PF_6$ [6] has superconductivity in close proximity to a spin density wave (SDW) phase, similar to the theoretical phase diagram for an interacting one-dimensional electron gas [7], where SDW lies adjacent to triplet superconductivity. This led to early suggestions of a triplet state for $(TMTSF)_2PF_6$, but proof has remained elusive. A strong suppression of superconductivity with nonmagnetic impurities [8,9] was argued for p-wave symmetry [10]. An absence of a coherence peak [11] and power-law behavior in the temperature dependent proton spin-lattice relaxation rate ($1/T_1 \propto T^3$) were argued [12] for some nodal structure on the Fermi surface indicative of non-s-wave symmetry. On the contrary, thermal measurements such as specific heat [13] and thermal conductivity [14] indicated a finite gap, rather than nodes, on the Fermi surface. None of the above experiments directly probe spin parity and they yield an ambiguous conclusion on the orbital symmetry. Much more attention has been refocused on the issue by recent upper critical field studies [15,16] showing that superconductivity persists up to more than 4 times the Pauli limit [17] (a conventional limit for singlet superconductors), which strongly support a spin-triplet state [18]. Here with NMR Knight shift we directly probe the spin susceptibility in the superconducting state.

As shown in Fig. 1, a high quality single crystal (size $1.75 \times 1.3 \times 0.7$ mm^3) of $(TMTSF)_2PF_6$ with three pairs of electrical contacts was enclosed in a tightly wound single layer coil. The unit was mounted inside a miniature

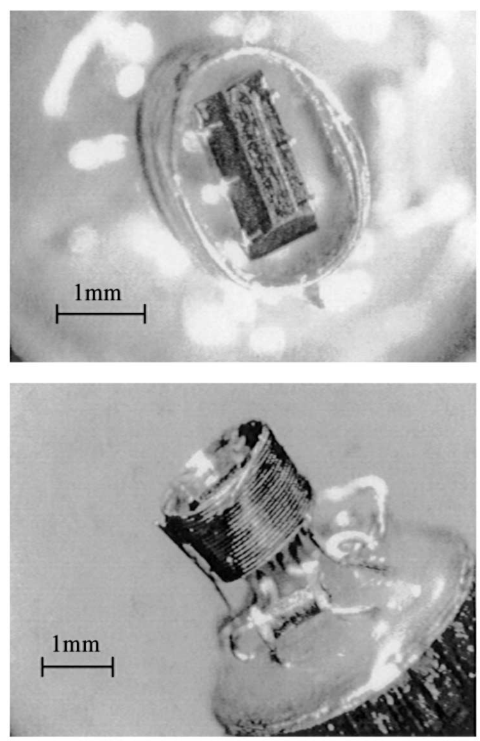

FIG. 1. Sample arrangement for the Knight shift. Upper panel: A top view shows an oval shaped NMR coil and three pairs of electrical contacts on the crystal. Lower panel: A side view also shows a sub-mm diameter pickup coil used to inductively measure T_c of Pb, and thus the pressure.

nonmagnetic BeCu pressure cell and loaded onto the bottom of the mixing chamber of a dilution refrigerator. We were thus able to conduct simultaneous electrical transport and NMR measurements under a pressure of 7 kbar at a base temperature of 0.09 K. Precise angular positioning of the sample with respect to the applied magnetic field $\mu_0 H = 1.43$ T was obtained by utilizing a split coil superconducting magnet with an external rotator (goniometer) on which the entire dilution refrigerator sits. The pressure was determined at low temperature from the measured difference in the superconducting transition temperatures (T_c) of two Pb samples, one located inside and one outside the pressure cell.

The NMR frequency shift (K) occurs from the magnetic coupling between nuclei and electrons, and the Knight shift (K_s), associated with electron spins, is directly proportional to spin susceptibility χ_s; that is, $K_s = \alpha\chi_s$. Since the spin susceptibility vanishes in a singlet superconductor at low enough temperature [χ_s(singlet super) = 0 as $T \rightarrow 0$], there will be a change in the resonant frequency on going from the normal state to the singlet superconducting state: $\delta K_{N\text{-}S} = K(\text{normal}) - K(\text{super}) = \alpha(\chi_s(\text{Pauli}) - \chi_s(\text{super})) = \alpha\chi_s(\text{Pauli})$. On the contrary, in an equal pairing triplet superconductor, $\chi_s(\text{super}) = \chi_s(\text{Pauli})$, $\delta K_{N\text{-}S} = 0$, and K remains unchanged on cooling into the superconducting state. The standard way of obtaining α is to construct a K versus χ_s plot as shown in Fig. 2. To evaluate α here, the y coordinates are obtained from the temperature dependence of the paramagnetic shift at 12 T, $\delta K = (\omega - \omega_d)/\omega$, where ω_d is the resonant frequency in a diamagnetic reference compound $Se(CH_3)_2$. The x coordinates are obtained from magnetic susceptibility studies by Miljak *et al.* [20] and electron spin resonance studies by Dumm *et al.* [21], and from pressure effects as reported by Forro *et al.* [19]. The δK and χ_s are therefore related by implicit functions of temperature. For the singlet case, the spin susceptibility in the superconducting state eventually vanishes (as $T \rightarrow 0$), and the δK is reduced to 840 ppm by extrapolation of χ_s to zero. On the other hand, for the equal spin pairing superconductor, δK and χ_s retain their normal state values $(\chi_s, \delta K) = (1.38 \times 10^{-4}$ emu/mol, 3450 ppm) as marked by the solid circle and triangle at 20 K in Fig. 2. As observed by Forro *et al.* [19], an applied pressure of 7 kbar causes a constant downward shift of χ_s by an amount 0.48×10^{-4} emu/mol for the entire temperature range. Thus the normal state χ_s as well as the δK is reduced to the values indicated by the diamond symbol in Fig. 2. The expected change in δK, i.e., $\delta K_{N\text{-}S}$, if we were to have a singlet superconductor, is therefore 1700 ppm, as marked by the double-ended arrow in Fig. 2.

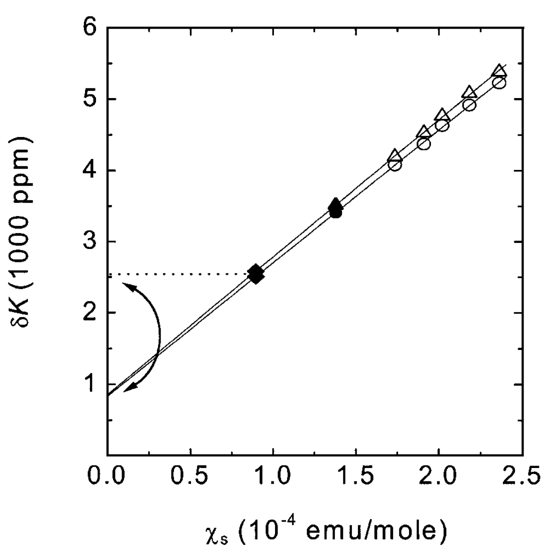

FIG. 2. Clogston-Jaccarino plot δK versus the spin susceptibility χ_s of $(TMTSF)_2PF_6$. The data in symbols (circles and triangle) are obtained at ambient pressure with $\mu_0 H(\parallel a) =$ 12 T and correspond to the absorption peaks from two nonequivalent Se sites. The solid diamond symbol is the result after an adjustment for the applied pressure according to Forro *et al.* (Ref. [19]).

An applied magnetic field $\mu_0 H = 1.43$ T is precisely aligned (much better than 0.1°) to the most conducting a axis where the hyperfine coupling, i.e., the expected shift, is large due to the anisotropic nature of the dipolar coupling to the electron spins at the nuclear site. Figure 3 shows ^{77}Se NMR spectra from small tilt angle free induction decays at various temperatures. Here the horizontal axis origin ($x = 0$) is taken as the averaged first moment $\langle\omega\rangle_{\text{normal}}$ in the normal state. The temperature dependence of the spin susceptibility through the superconducting transition was considered theoretically by Fulde and Maki (FM) [22] in the presence of an applied magnetic field for a singlet superconductor. From the K-χ_s plot and the measured $\langle\omega\rangle$ we can construct χ/χ_n as a function of temperature. The inset in Fig. 3 shows our measured χ/χ_n as compared to the FM calculation for $H/H_{c2} = 0.63$ (curve b) and near zero (curve a). Since our field of 1.43 T corresponds to $H/H_{c2}(0) \approx 0.4$–0.5, if we had a singlet superconductor, χ/χ_n should fall between these two calculated curves in the inset. The main result of this study is that there is no significant change in K_s on cooling deep into the superconducting state (as compared to the expectation from the FM calculation).

With the magnetic field precisely aligned along the a axis, we expect Josephson vortices in this highly anisotropic TMTSF system [23]. The normal cores of the vortices then remain between the superconducting sheet and the FM calculation is appropriate. However, if the vortex cores were to induce normal regions, then a simple "two-fluid" model would predict a normal fraction equal to H/H_{c2}. The resulting temperature dependence of the spin susceptibility is shown as curves c and d in the inset in Fig. 3. Two resonant absorptions in the NMR line shape, originating from Cooper pairs and normal electrons at vortex cores, would be resolved when the full width at half maximum (FWHM) of each spectrum is smaller than

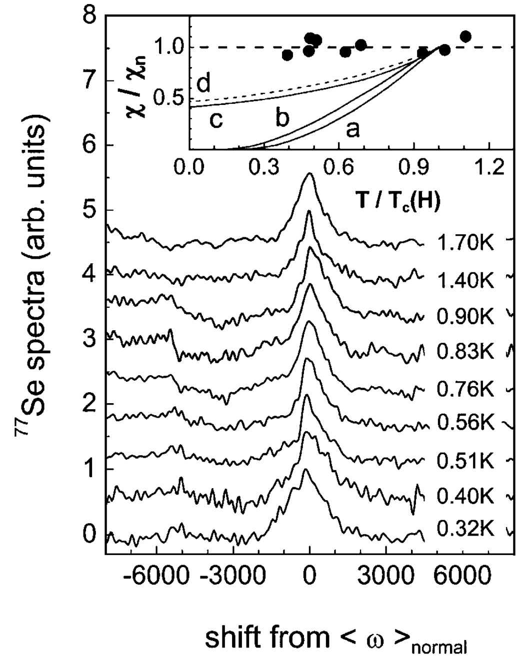

FIG. 3. ^{77}Se NMR spectra collected above and below T_c (0.81 K at 1.43 T). Each trace is normalized and offset for clarity. The temperatures shown in parentheses are the measured equilibrium temperatures before the pulse. In the inset, the spin susceptibility normalized by the normal state χ/χ_n from measured first moments are compared with Fulde and Maki's calculation for $H/H_{c2}(0) \sim 0$ (curve a) and 0.63 (curve b). Curves c and d are obtained from the ratio of applied field (1.43 T) to the measured upper critical field $H_{c2}(T)$ at which the superconducting criteria "onset" and "50% transition" have been used, respectively, to determine $H_{c2}(T)$.

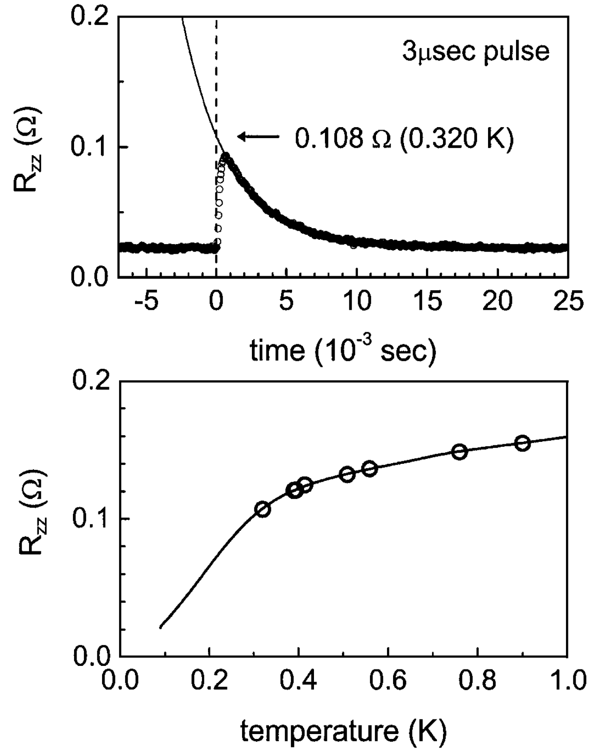

FIG. 4. Top: Time synchronous interlayer resistance measurements, triggered simultaneously with the NMR rf-pulse sequence. Bottom: Interlayer resistance R_{zz} versus temperature at the ^{77}Se field of $\mu_0 H = 1.43$ T which was applied 6° away from the a axis.

the separation. Considering the FWHM and the expected separation, obtained as 1100 and 1700 ppm for singlet (or 0 ppm for triplet), respectively, the absence of a double resonant absorption at the base temperature suggests either spin-triplet superconductivity or an absorption line shape dominated by normal electrons at vortex cores. It is clear that the latter is highly unlikely with our field configuration where the normal core contribution is expected to be minimal.

An important experimental issue that deserves close scrutiny is a possible spontaneous heating effect of the conduction electrons due to the NMR rf-pulse sequence. This very important issue is addressed in Fig. 4, where we used the sample itself as a local thermometer. The temperature dependence of the interlayer (c axis) resistance is shown in the bottom of Fig. 4. Since the sample remained at zero resistance during the NMR pulses at the ^{77}Se field ($\mu_0 H \parallel a = 1.43$ T), the pulse response measurements were done with a tilted angle, 6° away from the a axis, to obtain some measurable resistance at low temperature. The spontaneous sample response to the NMR pulse is shown in the upper panel of Fig. 4. A sharp rise in the resistance (and thus the sample temperature) followed the application of an rf pulse of 3 μsec duration with a power of 20 mW at $T = 0.09$ K. A subsequent slow decay of temperature with a time constant of 3 msec was observed. The crossing point at ($t = 0$ s, $R = 0.108\ \Omega$) between the trigger position and an extrapolation of the thermal relaxation was taken as the highest possible electron temperature at the time of the NMR data acquisition. All of the temperatures reported in our figures (shown as open circles in the bottom panel of Fig. 4) are extrapolated effective temperatures at the time of data acquisition for the K and are therefore upper limits to the actual sample temperatures.

From two different types of measurements, obtained simultaneously, the superconducting transition was identified consistently as shown in Fig. 5. As shown in the upper panel, a small enhancement of $1/T_1$ was found near T_c. Its identification as the Hebel-Slichter (HS) (or coherence) peak [11] awaits further experimentation in light of the absence of such a peak in previously reported zero-field proton $1/T_1$ measurements in TMTSF salts [12,24]. Moreover, if it is a HS peak, the present measurements do not distinguish clearly the nodal character of the order parameter, as the data lie between the calculated zero-field results of Hasegawa *et al.* [25] for triplet with line nodes or fully gapped triplet [26].

In summary, we have found that the spin susceptibility, measured via NMR Knight shifts, remains unchanged

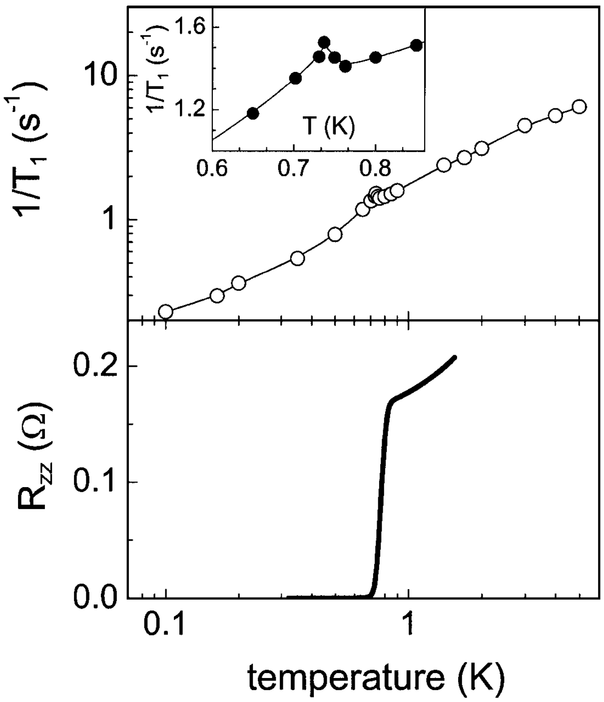

FIG. 5. ^{77}Se spin-lattice relaxation rate versus temperature with $\mu_0 H = 1.43$ T aligned along the a axis and simultaneously recorded interlayer resistance are shown in upper and lower panels, respectively. Notice from the metallic temperature dependence of resistance that the applied pressure of 7 kbar completely suppresses the spin density wave phase.

upon cooling through the superconducting state in $(TMTSF)_2PF_6$. This observation is inconsistent with any scenario involving singlet superconductivity (with or without normal vortices) and strongly supports spin-triplet pairing.

We gratefully acknowledge K. Maki, A. G. Lebed, and C. Sa de Melo for useful discussions. The work was supported by the U.S. National Science Foundation under Grants No. DMR-9971530 (S. E. B.), No. DMR-0072554 (W. G. C.), No. DMR-0076331 (M. J. N.), No. DMR-9808595 (W. K.), No. DMR-9976576 (P. M. C.), and No. DMR-9809483 (I. J. L.).

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