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Superconducting State of κ -(ET)₂Cu[N(CN)₂]Br Studied by ¹³C NMR: Evidence for Vortex-Core-Induced Nuclear Relaxation and Unconventional Pairing

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We present the first ¹³C NMR measurements carried out in the superconducting state of a two-dimensional organic superconducting single crystal. Spin lattice relaxation rate and Knight shift are reported for magnetic fields parallel and perpendicular to the conducting layers. For perpendicular fields, the relaxation is dominated by the electronic excitations in the vortex cores. From the field dependence of $(T_1)^{-1}$ we obtain the upper critical field [$H_{c2}(0) = 10$ T]. In parallel orientation, the absence of field dependence reveals the existence of a lock-in state, where only relaxation by superconducting excitations is expected. The $(T_1)^{-1}$ then exhibits a T^3 law suggesting an unconventional pairing with a very anisotropic gap.

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κ -(ET)₂Cu[N(CN)₂]Br is a quasi-2D organic superconductor with a critical temperature T_c of 11.6 K [1]. In such material, there is still no general consensus on the mechanisms of superconductivity. For example, the experimental results for the magnetic penetration depth are still controversial, leading to differing conclusions as to the superconducting gap symmetry: Both isotropic *s*-wave [2,3] and a more unconventional pairing [4,5] have been proposed. It is therefore of interest to better understand the electronic properties in this material. We have used ¹³C instead of ¹H, because it is particularly adapted to probe the electronic properties for this material, since the carbon atoms lie in the core of the conducting layers. In particular, note that we can exclude the relaxation due to flux line motions, responsible for the well known peak in ¹H relaxation [5,6], because this should lead to T_1 's 16 times greater for ¹³C than for ¹H. These T_1 's are too long compared to those observed here. In this Letter, we present measurements made for two orientations of the crystal: the field perpendicular ($H_0 \parallel b$) and parallel [H_0 in the (a-c) plane] to the conducting layers. We show that the pairing is spin singlet and that the gap presents zeros at the fermi level or at least a very large anisotropy. For perpendicular fields, the observations are dominated by the effects of normal electrons in the vortex cores. From the field dependence of the relaxation, we extract the upper critical field [$H_{c2}(0) = 10$ T]. Finally, we notice that the normal state may be described by a Korringa-like law, but we emphasize the persistence of spin fluctuations.

We have performed the measurements on a rhombic-shaped single crystal ($0.5 \times 1 \times 1$ mm³). The sample was 100% ¹³C, enriched on both central carbon sites of the ET molecule. The high crystallographic quality of the sample has been demonstrated by spectra presented here and elsewhere [7].

A detailed study of the NMR spectrum leading to the line assignment and the determination of shift tensors has been presented in Ref. [7]. For clarity, here we briefly

discuss line shapes observed for different orientations. The spectrum is a sum of contributions coming from all carbon pairs. A pair of nonequivalent and interacting spins gives four lines (*a*, *b*, *c*, *d*) at the shifts in frequency $\omega_a = \frac{1}{2}\sqrt{\delta^2 + J^2} + J$, $\omega_b = \frac{1}{2}\sqrt{\delta^2 + J^2} - J$, $\omega_c = -\frac{1}{2}\sqrt{\delta^2 + J^2} + J$, and $\omega_d = -\frac{1}{2}\sqrt{\delta^2 + J^2} - J$, where J is the dipolar coupling and δ is the difference of NMR frequencies of the two isolated carbon nuclei. The respective intensities are $I_a = I_c = I_0(1 + \sin 2\phi)$ and $I_b = I_d = I_0(1 - \sin 2\phi)$ with $\tan 2\phi = J/\delta$. In perpendicular field all molecules are equivalent, and we observe four lines as shown in Fig. 1(a). In parallel field there are, in general, two nonequivalent dimers in the crystal giving typically a spectrum such as the one in

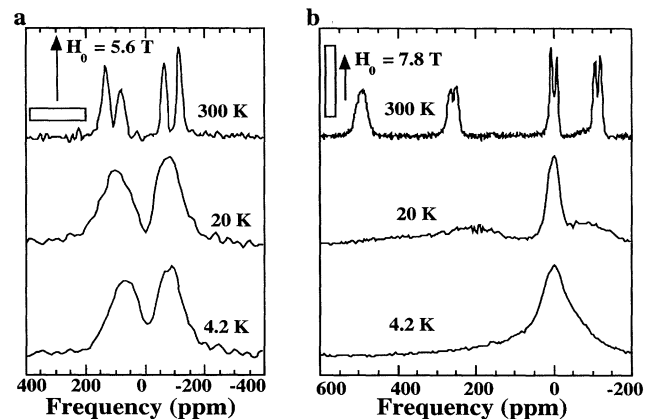


FIG. 1. ¹³C spectra (in ppm from neutral ET). (a) Perpendicular field of 5.6 T at 300, 20, and 4.2 K. At 300 K we measure $J = 1.5$ kHz (23 ppm) and $\delta = 190$ ppm (11.5 kHz). (b) Parallel field of 7.8 T at 300, 20, and 4.2 K. At 300 K the four lines on the right correspond to one of the two inequivalent molecules. We measure $J = 500$ Hz (6 ppm) and $\delta = 98$ ppm (8.4 kHz). As shown from the spectrum at 20 K, the inhomogeneous broadening is larger for the lines exhibiting a larger Knight shift.

Fig. 1(b). The large anisotropy of the shift tensors enables us to align the crystal in the field to within $\pm 0.25^\circ$.

In this Letter, we will use δ as a measure of the Knight shift. This choice supposes that both sites have nearly the same chemical shift which, according to results on neutral ET [8], is a fair assumption and further has the advantage of avoiding a possible demagnetizing effect. Unfortunately, the observation of an inhomogeneous line broadening below 190 K (proportional to the Knight shift) [7] makes it difficult to obtain an accurate value for δ . Also, the error on δ depends on the ratio J/δ . For example, when $J/\delta \gg 1$ the four-line spectrum is a doublet separated by $3J$, and when $\delta = J$ the two outer lines are separated by $3.4J$. Keeping these limitations in mind, we realize that we cannot determine δ when it is less than J . Consequently, we have measured δ only in the highest field (7.8 T), where J/δ is at its minimum for our field range. In this case we are able to obtain a good precision until δ becomes less than about 20 ppm. Finally, the extraction of a reliable set of T_1 's for the field and temperature dependence is not straightforward because of the dipolar coupling. The relaxation rates $(^lT_1)^{-1}$ and $(^rT_1)^{-1}$ measured for the left and right line of a double [Fig. 1(a)] are linear combinations of the rates of each carbon site [$(^1T_1)^{-1}$ and $(^2T_1)^{-1}$], with coefficients depending on J/δ [9] and therefore on the field and temperature. To suppress these parasitic dependencies we use an average rate defined as $2(T_1)^{-1} = (^lT_1)^{-1} + (^rT_1)^{-1} = (^1T_1)^{-1} + (^2T_1)^{-1}$ which does not depend on J/δ . We checked that this procedure always yields a field independent T_1 above T_c .

Let us consider first the results obtained in a field perpendicular to the conducting layers. These are presented in Fig. 2 (Knight shift) and Fig. 3 (T_1). As we will show, in high field (7.8 T), the majority of ^{13}C nuclear spins (80%) are inside vortex cores. In this case we have fitted the line shape with a unique value of δ which reflects the Knight shift due to normal electrons. The results (black circles in

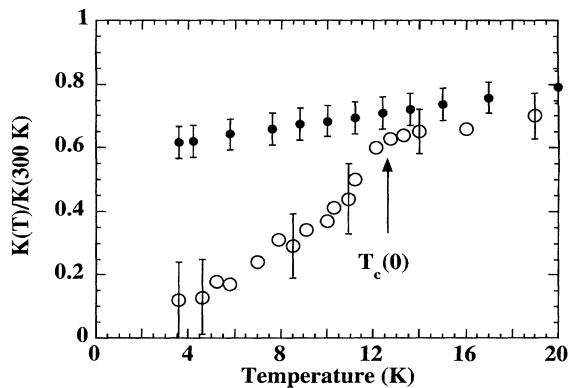


FIG. 2. Knight shift (δ) at 7.8 T in perpendicular field (black circles) and parallel field (open circles). It is normalized to unity at 300 K.

Fig. 2) show that there is no change at the superconducting transition and that the Knight shift decreases steadily from 50 K as we reported before [7]. From these data we have plotted the term $AK(T)^2$ (solid line in Fig. 3), where $A = 0.19\text{K}^{-1}\text{s}^{-1}$, and K is normalized to unity at 300 K. We remark that the Korringa relation $[(T_1T)^{-1} = AK^2]$ is obeyed above T_c (8 K at 7.8 T). From this observation we have assumed that this relation gives a good description of the electronic behavior in the vortex cores. Nevertheless, we must be careful about this Korringa-like behavior since it has already been reported [7,10] that $(T_1T)^{-1}$ is highly enhanced between 20 and 200 K, very likely due to spin fluctuations with a nonzero wave vector. Moreover, the amplitude of the Korringa coefficient A obtained at low temperatures is practically twice the value at room temperature ($A = 0.11\text{K}^{-1}\text{s}^{-1}$), indicating a persistence of these fluctuations.

Below T_c , $(T_1T)^{-1}$ presents a strong field dependence and tends to saturate at low temperatures (Fig. 3). This effect is a signature of a relaxation due to "normal" electrons in the vortex cores. This type of relaxation has been observed by Silbernagel, Weger, and Wernick [11] in a conventional type-II superconductor, V_3Si . More recently, such field effects have been studied in high-temperature superconductors HTS's [12,13]. In $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ the phenomenon is particularly important because of the small H_{c2} value.

To interpret the curves of Fig. 3, we will consider a simple model with only two sources of relaxation. The first (nT_1) comes from normal electrons in the vortex cores, and the second (sT_1) involves pair excitations across the superconducting gap. Considering that all carbon nuclei belong to the same spin bath, we measure the total rate defined as

$$\frac{1}{T_1} = \frac{H_0}{H_{c2}} \frac{1}{^nT_1} + 1 - \left(\frac{H_0}{H_{c2}}\right) \frac{1}{^sT_1}, \quad (1)$$

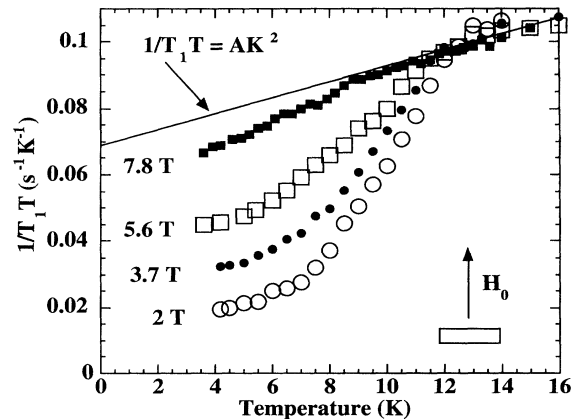


FIG. 3. $(T_1T)^{-1}$ in perpendicular field. We note the absence of Hebel-Slichter peak. The saturation and the linear field dependence at low temperature is the signature of electrons in the vortex cores.

where H_0 is the applied field and $H_0 H_{c2}^{-1} = 2\pi \xi_{ac}^2 H_0 \Phi_0^{-1}$ is the total cross-section fraction of the vortex cores. The assumption that all nuclei are equally coupled is supported by the observation of single exponential decays and is usually attributed to a rapid spin diffusion. We can estimate the characteristic spin diffusion time τ on the vortex lattice length scale a to be $\tau = T_2 a^2 d^{-2}$, where T_2 is the spin-spin relaxation time and d the mean distance of two carbon nuclei. With $(T_2)^{-1} \approx 1$ kHz (line width at 300 K), $a \approx 450$ Å (estimated in a field of about 1 T) and $d \approx 4$ Å, we obtain $\tau \approx 10$ s which is too long to justify a relaxation averaging. The second mechanism is a rapid diffusion of vortex cores also invoked by Martindale *et al.* [13]. In κ -(ET)₂Cu[N(CN)₂]Br, the irreversibility line occurs at 4.2 K in a field of 1 T [3,5]; and, therefore, all our measurements were performed in the liquid state, permitting a rapid diffusion of vortex cores. Hence, the assumption of good contact between a given nucleus and both relaxation sources seems to be fully justified.

At $T \ll T_c$ the relaxation is dominated by the effects of normal electrons (${}^nT_1 \ll {}^sT_1$). Therefore, if we assume that the normal state follows a Korringa law, we should observe

$$\frac{1}{T_1 T} = \frac{H_0}{H_{c2}} \frac{1}{{}^nT_1 T} = AK(T)^2 \frac{H_0}{H_{c2}}. \quad (2)$$

In Fig. 4, an analysis of the field dependence is presented. First, we have plotted $(T_1 T)^{-1}$ at 4.2 K versus the field (black squares). Taking for $({}^nT_1 T)^{-1}$ the value at 12 K (dotted line), we derive a crude estimate of H_{c2} . To refine this estimate we have extrapolated the data to zero temperature using the T -dependent relation (2), with the first estimate for H_{c2} . The zero temperature extrapolations are plotted as open circles and the normal state value as the dashed line. In this way we estimate $H_{c2} = 10$ T and $\xi_{ac} = 60$ Å. This value of ξ_{ac} is somewhat large compared to those already published

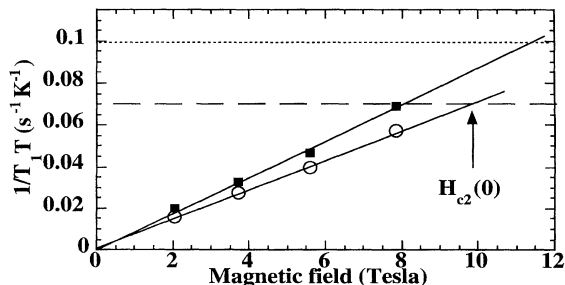


FIG. 4. $(T_1 T)^{-1}$ at 4.2 K (black squares) versus magnetic field. The dotted line corresponds to the 12 K value. Open circles correspond to the zero temperature extrapolated value with a Korringa relation (see text). The dashed line is the zero temperature extrapolation of the normal state.

[14]. However, all these determinations were based on an estimate of H_{c2} from the slope dH_{c2}/dT at low field near T_c . We think that our determination is perhaps more reliable because it is based on low temperature and high field measurements.

We now turn to the measurements performed in parallel field and presented in Fig. 2 (Knight shift) and Fig. 5 (T_1). The first striking observation is the absence of any field dependence of the relaxation. This provides strong evidence for the absence of vortex pancakes in this orientation (lock-in state), and that the field penetrates into the insulating layers and is screened by Josephson currents [15]. The lock-in state has been observed in such materials by ¹H NMR [6] and by ac susceptibility [16]. In these studies the authors emphasized the “angular sharpness” of this state. Here this observation is confirmed by the measurements carried out for a misalignment of about 2° (black squares), and we remark that the relaxation is highly enhanced due to the presence of pancake vortices.

Consequently, when the sample is well oriented with the field, the Knight shift gives the spin susceptibility in the superconducting state. We can see in Fig. 3 (open circles) that the Knight shift decreases more quickly below T_c and tends towards zero at low temperature. We think that this is evidence that the spin pairing is singlet. Indeed, it has been shown that in the case of a triplet state, there should be no difference between the normal and superconducting spin susceptibility [17]. On the other hand, with a singlet state, the Knight shift should follow the Yosida function [18] which tends to zero at low temperatures.

When the relaxation is not enhanced by normal electron excitations, we are able to probe the effect of superconducting pair excitations. We can see in Fig. 5 that

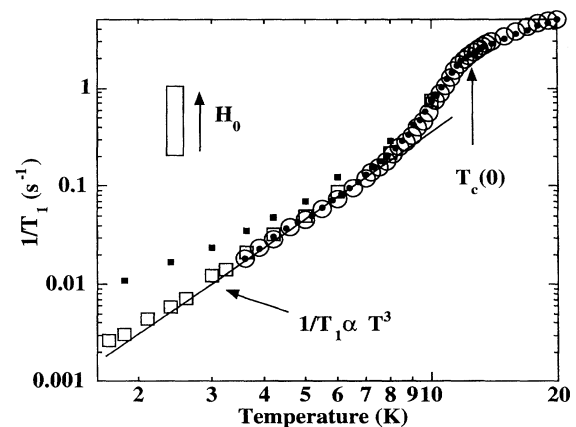


FIG. 5. $(T_1)^{-1}$ in parallel field: 5.6 T (open circles), 7.8 T (black circles), and 7 T (open squares). There is no Hebel-Slichter peak, and the relaxation rate exhibits a T^3 law at low temperature. Black squares correspond to a field of 7 T with a slight misalignment (about 2°).

$(T_1)^{-1}$ exhibits a T^3 law over a wide range of temperature and is not enhanced just below T_c (i.e., no Hebel-Slichter peak). Such a relaxation was first observed by Takigawa, Yasuoka, and Saito [19], in the context of a quasi-1D organic superconductor, $(\text{TMTSF})_2\text{ClO}_4$. Hasegawa and Fukuyama [20] have proposed a theoretical model based on an anisotropic gap with lines of zeros at the fermi surface. This model showed that, in this case, the Hebel-Slichter peak is removed and that the relaxation rate should follow a T^3 law at low temperature because of the linear density of states at low energy. This model was of interest because it opened the door to new types of pairing. In HTS's, the T^3 behavior has been observed several times [13,21]. This has often been interpreted as a signature of d -wave pairing. Indeed, theoretical calculations involving d -wave pairing are, in general, in good agreement with the experimental results [22]. Nevertheless, as Martindale *et al.* [13] have pointed out, it is experimentally difficult to distinguish a T^3 law due to a gap with nodes at the fermi level, from that of an $\exp(-\Delta/k_B T)$ behavior with varying Δ 's for an anisotropic nodeless gap. In the last case, we have estimated, in our particular problem $\Delta/k_B T_c = 0.3$ at the lowest temperatures and $\Delta/k_B T_c = 3.2$ near 10 K. These estimates would mean that if the gap is nodeless its anisotropy must be greater than ten.

In summary, we have reported new details of the electronic properties in the superconducting state of κ -(ET) $_2$ Cu[N(CN) $_2$]Br. First, for perpendicular fields, the strong field dependent T_1^{-1} points out the predominance of normal state electronic excitations in the vortex cores and leads to a direct determination of the low temperature critical field [$H_{c2}(0) = 10$ T]. Furthermore, the relaxation can be described by a Korringa-like law with the evidence for a persistence of spin fluctuations at a finite wave vector. Secondly, the parallel field situation, which can be achieved with great accuracy thanks to the strongly angle-dependent ^{13}C -NMR spectrum at room temperature, has revealed a remarkable, very sharp lock-in of T_1^{-1} . In this case, the dominant source of relaxation is provided by quasiparticle excitations in the superconducting layers. The temperature dependence of T_1^{-1} ($\propto T^3$) and Knight shift down to $0.14T_c$ provides solid experimental evidence for a very anisotropic (possibly with nodes in the gap) spin-singlet pairing in this class of 2D superconductors. The possibility for nonconventional pairing in 2D organic superconductors has been pointed out by Bulaevskii [23]. This pairing could bear some resemblance with the spin fluctuation mediated interchain interaction proposed by Bourbonnais and Caron [24] in the context of 1D superconductors.

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- [1] A.M. Kini *et al.*, Inorg. Chem. **29**, 2555 (1990).
 - [2] D.R. Harshman *et al.*, Phys. Rev. Lett. **64**, 1293 (1990).
 - [3] M. Lang, N. Toyota, and T. Sasaki, Synth. Met. **55-57**, 2401 (1993).
 - [4] J.P. Le *et al.*, Phys. Rev. Lett. **68**, 1923 (1992).
 - [5] T. Takahashi, K. Kanoda, and G. Saito, Physica (Amsterdam) **185C-189C**, 366 (1991).
 - [6] S.M. De Soto, C.P. Slichter, H.H. Wang, U. Geiser, and J.M. Williams, Phys. Rev. Lett. **70**, 2956 (1993).
 - [7] H. Mayaffre, P. Wzietek, D. Jérôme, C. Lenoir, and P. Batail, Europhys. Lett. **28**, 205 (1994).
 - [8] T. Klutz, I. Hennig, U. Haeblerlen, and D. Schweitzer, Appl. Magn. Reson. **2**, 441 (1991).
 - [9] S. Schäublin, A. Höhener, and R.R. Ernst, J. Magn. Reson. **13**, 196 (1974).
 - [10] A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **74**, 3455 (1995).
 - [11] B.G. Silbernagel, M. Weger, and J.E. Wernick, Phys. Rev. Lett. **17**, 384 (1966).
 - [12] F. Borsa *et al.*, Phys. Rev. Lett. **68**, 698 (1992); K. Ishida, Y. Kitaoka, and K. Asayama, Solid State Commun. **90**, 563 (1994); G. Zheng, Y. Kitaoka, K. Asayama, and Y. Kodama, Physica (Amsterdam) **227C**, 169 (1994).
 - [13] J.A. Martindale *et al.*, Phys. Rev. B **50**, 13 645 (1994).
 - [14] W.K. Kwok *et al.*, Phys. Rev. B **42**, 8686 (1990); H. Ito *et al.*, J. Phys. Soc. Jpn. **60**, 3230 (1991); M. Lang, F. Steglich, N. Toyota, and T. Sasaki, Phys. Rev. B **49**, 15 227 (1994).
 - [15] J.R. Clem and M.W. Coffey, Phys. Rev. B **42**, 6209 (1990).
 - [16] P.A. Mansky, P.M. Chaikin, and R.C. Haddon, Phys. Rev. Lett. **70**, 1323 (1993).
 - [17] A.J. Leggett, Rev. Mod. Phys. **47**, 331 (1975).
 - [18] K. Yosida, Phys. Rev. **110**, 769 (1958).
 - [19] M. Takigawa, H. Yasuoka, and G. Saito, J. Phys. Soc. Jpn. **56**, 873 (1987).
 - [20] Y. Hasegawa and H. Fukuyama, J. Phys. Soc. Jpn. **56**, 877 (1987).
 - [21] T. Imai, T. Shimizu, H. Yasuoka, Y. Ueda, and K. Kosuge, J. Phys. Soc. Jpn. **57**, 2280 (1988); Y. Kitaoka *et al.*, Physica (Amsterdam) **153C-155C**, 83 (1988).
 - [22] D. Thelen, D. Pines, and J.P. Lu, Phys. Rev. B **47**, 9151 (1993); N. Bulut and D.J. Scalapino, Phys. Rev. Lett. **68**, 706 (1992); H. Monien and D. Pines, Phys. Rev. B **41**, 6297 (1990).
 - [23] L.N. Bulaevskii, Adv. Phys. **37**, 443 (1988).
 - [24] C. Bourbonnais and L.G. Caron, Europhys. Lett. **5**, 209 (1988).