Evidence for the Role of Fluxoids in Enhancing NMR Spin-Lattice Relaxation and Implications for Intrinsic Pinning of the Flux Lattice in Organic Superconductors

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The authors report ^{1}H NMR spin-lattice relaxation rates, T_1^{-1}, in the quasi-2D organic superconductor κ-$(ET)_2Cu[N(CN)_2]Br$ ($T_c = 11.6$ K), for an aligned single crystal. The relaxation in the normal state obeys the Korringa law ($T_1 T$=const). In the superconducting state, for weak fields ($H_0 \approx 0.59$ T), T_1^{-1} is greatly enhanced and displays strong orientation dependence for field directions nearly parallel to the superconducting layers. This behavior indicates that motion of the fluxoid system is the cause of the extra relaxation, and is evidence for a "lock-in" transition of the flux lattice.

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The study of organic charge-transfer salts has attracted renewed interest with the discovery of several quasi-2D superconductors based on the organic donor molecule BEDT-TTF [bis(ethylenedithio)-tetrathiafulvalene, hereafter abbreviated as ET]. Although pressure is needed to suppress an insulating ground state for the ET-based compound possessing the highest transition temperature, κ-$(ET)_2Cu[N(CN)_2]Cl$ ($T_c = 12.8$ K at 0.3 kbar) [1], there is an isostructural compound, κ-$(ET)_2Cu[N(CN)_2]Br$, which undergoes a superconducting transition at ambient pressure with $T_c = 11.6$ K [2]. We consider only this latter superconductor in this Letter.

Nuclear spin-lattice relaxation rate (T_1^{-1}) measurements have proven very useful in studies of both metallic and superconducting systems. They have been extensively and successfully used to study conventional [3,4], heavy fermion [5], and CuO_2-based [6] superconductors. In a simple metal, the conduction electrons provide the dominant relaxation mechanism, and the well known Korringa law ($T_1^{-1} \propto T$) is obeyed. In the superconducting state, however, a gap opens up in the density of states at the Fermi level, which produces dramatic changes in $T_1^{-1}(T)$. Specifically, for traditional, orbital s-wave superconductors, there is an increase in the relaxation rate just below T_c. This effect, known as a coherence peak, was important in establishing the BCS theory [3]. At low temperatures ($T \ll T_c$), for an isotropic superconducting gap, the relaxation rate is expected to fall off exponentially.

In organic superconductors such as κ-$(ET)_2Cu(NCS)_2$ and β-$(ET)_2I_3$, it has been shown that there is an enormous enhancement of the relaxation rate in the superconducting state relative to the normal state Korringa value [7-9]. The physical cause of this peak has been the subject of considerable controversy. It is believed that the phenomenon observed is not the expected coherence peak, both because the magnitude of the enhancement is so large (a factor of ~ 10, as opposed to the expected value of ~ 2), and also because the maximum in T_1^{-1} occurs at the wrong temperature ($\sim 0.5 T_c$, as opposed to the expected $\sim 0.85 T_c$). Some of the theories offered to explain the anomalous relaxation include critical fluctuation effects in a second-order phase transition [7], a superconducting glass state in a granular system [9], a spin density wave (SDW) transition [8], a structural transition [10], and a flux line lattice melting transition [8].

Here, we report ^{1}H NMR spin-lattice relaxation rate (T_1^{-1}) studies in an aligned single crystal of κ-$(ET)_2Cu[N(CN)_2]Br$ for temperatures $4 \le T \le 340$ K and static magnetic fields $0.52 \le H_0 \le 8.1$ T. We have observed a relaxation peak in the superconducting state of the present system similar to that found in previous studies of other organic superconductors [7-9]. In addition, we have further elucidated the nature of the peak by performing our NMR experiments on a single crystal, rather than with unaligned polycrystalline samples. We find that the anomalously rapid relaxation can be suppressed in high fields and for certain precise orientations of the single crystal. We interpret these findings as evidence that the origin of this relaxation is motion of the fluxoid system.

Our measurements were performed on a single crystal with dimensions $1.6 \times 1.3 \times 0.6$ mm (mass=2.2 mg). The synthesis process has been described elsewhere [2]. The high and intermediate field measurements ($H_0 = 8.1$, 4.1 T) were performed in a 348 MHz Oxford superconducting solenoid and the low field measurements ($H_0 < 1$ T) were performed in a Varian electromagnet with a rotatable base. The nuclear magnetization was measured at a variable time (t_{wait}) after saturation (or inversion) of the resonance line. In all cases the recovery was single exponential above $T = 50$ K. In this case, we could unambiguously define T_1. For $T < 50$ K the crystal displays a strong metallic character, and the recovery has been fitted to a sum of two exponentials. The short time constant, T_{1s}, is taken as a spin diffusion time due to the rf skin effect [11] and the long time constant, T_{1L}, is taken as the intrinsic T_1, as it maps smoothly onto the data above $T = 50$ K.

We will now briefly summarize our data taken in the normal state, i.e., for $T > T_c$. The crystal structure of κ-$(ET)_2Cu[N(CN)_2]Br$ is orthorhombic, with the conducting organic layers (composed of ET molecules) and the inorganic anion layers (composed of zigzag polymeric chains of $\{Cu[N(CN)_2]Br\}_\infty$) both lying in the a-c plane, but staggered along the b axis at intervals $s = 15$ Å [12]. The results of strong field (8.1 T) and intermediate field (4.1 T) measurements with $\mathbf{H}_0 \| \mathbf{b}$ are shown in Fig. 1. As in other ET-based organic superconductors, the increase of T_1^{-1} above $T = 160$ K is thought to be due to a thermally activated motion of the terminal ethylene groups of the ET molecule [9]. Using the Bloembergen-Purcell-Pound (BPP) model [13] we calculate the activation energy to be $T_0 = 1400$ K with a correlation time $t_c = 8 \times 10^{-12}$ s. The peak in the relaxation rate is depressed and shifts to a higher temperature as the external field is increased from $H_0 = 4.1$ T to $H_0 = 8.1$ T, as predicted within the BPP theory. This interaction obscures the nuclear relaxation due to the conduction electrons above $T = 160$ K.

Referring to Fig. 1, there is a crossover range ($50 < T < 160$ K), below which the relaxation rate follows the Korringa relation (T_1T = const), indicating relaxation by conduction electrons. There is a small enhancement of the relaxation rate in weak field (0.59 T). This type of magnetic field dependence has been observed in quasi-1D organic conductors and was attributed to spin diffusion in low dimensional systems [14]. This is a small effect for the present study and we only mention it. From a least-squares fit we obtain $T_1T = 900 \pm 50$ K s for the Korringa constant, which is comparable to that of other ET-based superconductors [8]. This relatively large value indicates rather weak coupling of the ^1H nuclei with the π conduction electrons. This is in agreement with both scanning tunneling microscopy (STM) [15] and NMR Knight shift [16] studies which find that the conduction electron density is concentrated near the central part of the ET molecule. The ^1H nuclei under observation form part of a terminal ethylene group and thus interact weakly with the electrons.

We now turn to our results for the superconducting state. Figure 2 shows the relaxation data for two values of the magnetic field for a single crystal with the static magnetic field $\mathbf{H}_0 \| \mathbf{b}$ (i.e., perpendicular to the conducting planes). Below T_c there is a dramatic peak in the relaxation rate measured in a weak field, with an increase of a factor of 10 in T_1^{-1} near the lowest temperatures measured. The peak is broad: It begins just below T_c and rises rapidly with a maximum occurring at $T/T_c \approx 0.5$. However, the peak is suppressed in an intermediate field. As stated previously, the peak seen in low field is not the usual coherence peak.

Instead, we postulate an explanation based on motion of the fluxoid system to account for this relaxation process. To test for such a mechanism, we investigated the orientation dependence of the relaxation rate. We expect that a fluxoid relaxation process should be highly anisotropic in a layered superconductor. Flux-lattice dynamics should be qualitatively different for magnetic fields parallel and perpendicular to the set of superconducting planes. For example, in another layered superconductor, $YBa_2Cu_3O_{7-x}$, measurements which are influenced by fluxoid dynamics such as resistivity [17], torque [18], and critical current [19] all show strong angular dependence below T_c.

To test our hypothesis of fluxoid relaxation, we measured the orientation dependent $T_1^{-1}(\theta)$ [where θ is defined as the angle between the static magnetic field $\mathbf{H}_0$ and the normal to the layers (b axis)] for an aligned single crystal in the superconducting state at a temperature nearly corresponding to the peak in T_1^{-1} seen in Fig. 2 (i.e., $T = 6$ K). If the relaxation mechanism in question were due to some type of coupling of the hydrogen nuclei to the conduction electrons, we would expect a smooth

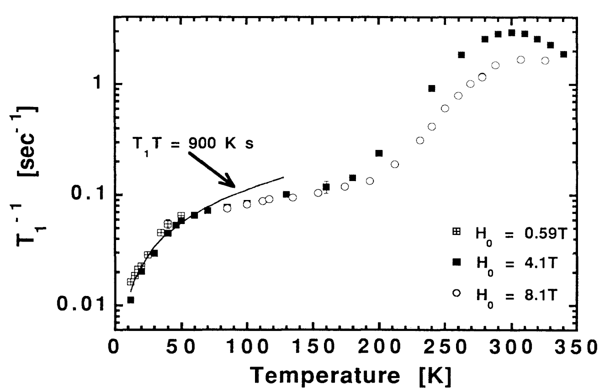

FIG. 1. Temperature dependence of T_1^{-1} in the normal state for three values of the external field. The BPP mechanism is dominant above $T = 160$ K, and the Korringa relation is followed below $T = 50$ K.

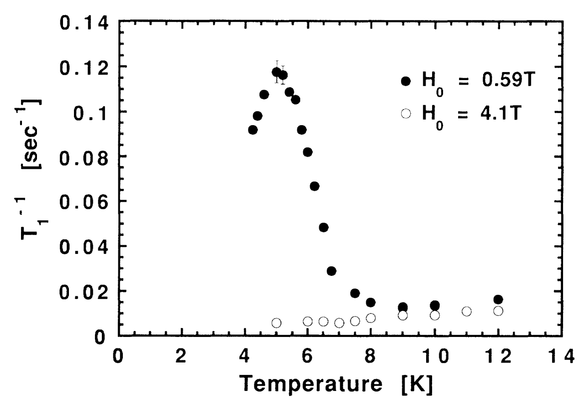

FIG. 2. Temperature dependence of T_1^{-1} in the superconducting state for two values of the external field, $H_0 = 0.59$ T (closed symbols) and $H_0 = 4.1$ T (open symbols). The transition temperatures are $T_c(H_0 = 0.59\ \mathrm{T}) = 10.4$ K and $T_c(H_0 = 4.1\ \mathrm{T}) = 8.8$ K [21].

orientation dependence [e.g., $T_1^{-1} \propto \cos^2(\theta)$], based on the principal axes of the electronic system. The results for data taken in a weak ($H_0=0.52$ T) field are shown in Fig. 3. We also plot data taken for the normal state ($T=14$ K) to obtain the orientation dependence when fluxoids are not present.

In the normal state, the relaxation is nearly isotropic, with only a slight variation of 20% in $T_1^{-1}(\theta)$. In the superconducting state, there is a gradual rise in $T_1^{-1}(\theta)$ with increasing angle until $\theta \simeq 40°$. Then there is a gradual decrease in $T_1^{-1}(\theta)$ until $\theta \approx 87°$, where there is a dramatic plunge in the relaxation rate, reaching a minimum at $\theta=90°$. The relaxation rate decreases by *an order of magnitude* in a window of only $\sim 3°$ from $\theta=90°$, the orientation corresponding to the field being parallel to the superconducting layers. In fact, for $\theta=90°$, the rate actually dips below the normal state value (which would be expected for $T \sim 0.5T_c$ if only an electronic mechanism were in effect). It appears that the relaxation mechanism in question is present for a broad range of orientations, but becomes very ineffective for a narrow interval near $\theta=90°$ (i.e., for parallel magnetic fields). As stated previously, no electronic relaxation mechanism could have such a steep angular dependence. Therefore, this result strongly indicates that fluxoid motion is the physical cause of the extra relaxation. Furthermore, it appears that there is a "lock-in" transition of the fluxoid system, with the fluxoids effectively locked in position when $\theta=90°$.

Such a lock-in transition was predicted by Tachiki and Takahashi [20] and later observed in resistivity measurements on $YBa_2Cu_3O_{7-x}$ by Kwok *et al.* [21]. In this theory [20], the superconducting order parameter varies periodically normal to the layers, with a minimum in the "normal" (or weakly superconducting) layers. The fluxoid cores minimize their free energy by lying in the normal, as opposed to the superconducting, layers of atoms. A necessary condition of the theory is that the perpendicular coherence length $\xi_\perp$ (which corresponds to the radius of the normal core of the fluxoid) is smaller than the interlayer periodic distance s. This condition is fulfilled in κ-$(ET)_2Cu[N(CN)_2]Br$, with $\xi_b(T=0) \approx 4$ Å [22] $\ll$ $s=15$ Å. We point out that in this model, the fluxoids are pinned by the crystal structure itself (i.e., *intrinsic pinning*), as opposed to the normal pinning mechanisms such as grain boundaries, defects, twinning planes, etc.

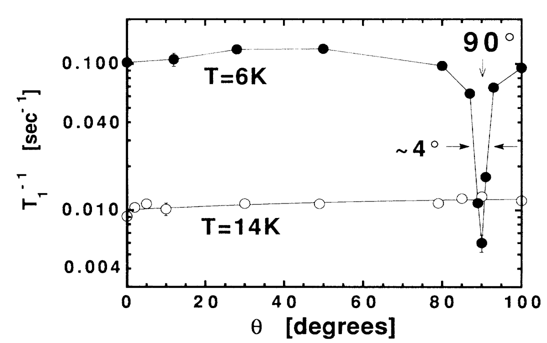

FIG. 3. Orientation dependence of T_1^{-1} in the superconducting state ($T=6$ K) and the normal state ($T=14$ K). Lines are to guide the eye.

In addition, the theory predicts a critical angle α_c for magnetic fields almost parallel to the 2D planes, such that the flux lines will be intrinsically pinned for all orientations $90-\alpha_c < \theta < 90+\alpha_c$. Using the theory of Maslov [23] based on the Lawrence-Doniach (LD) model [24], we estimate that $\alpha_c \approx 0.04°$, where we have used $\lambda_{ac} = 7200$ Å [25], $\xi_b = 5$ Å [21], and $H_0=0.52$ T. In Fig. 3, the width of the notch in the relaxation rate is $\sim 2°$, which should be an upper limit for the actual critical angle α_c. In a real crystal, the observed critical angle ($\alpha_{c,\mathrm{obs}}$) will be broadened by, among other causes, the mosaic spread of the sample, typically a few tenths of a degree.

We now turn to the question of the likelihood of a fluxoid spin-lattice relaxation mechanism occurring in the present system. In principle there are two ways in which fluxoids in a type-II superconductor can influence spin-lattice relaxation. The first involves rapid spin-lattice relaxation at the normal metal rate in the fluxoid cores, followed by spin diffusion to more distant nuclei in the superconducting region via a cross relaxation process [26]. Such a mechanism cannot account for the present data because we measure relaxation rates that are actually much faster than the normal state value. The second mechanism is thermal motion of the fluxoids directly causing spin-lattice relaxation. This could conceivably be important for a nucleus with no other highly efficient relaxation route. This phenomenon was first reported in a ^{1}H NMR study of hydrated V-Ti alloy by Ehrenfreund, Goldberg, and Weger [27]. The authors reported a relaxation rate faster than that predicted by the BCS theory for $T \ll T_c$ and attributed the additional relaxation to a dynamic fluxoid process.

The spin-lattice relaxation process requires that there be a fluctuating magnetic field transverse to the direction of the static field, that is, perpendicular to the axis of quantization of the nuclear spins. In addition, there must be a component of the fluctuation at the nuclear Larmor frequency, $\omega_n \approx 10^8$ s^{-1}. Any theory based on the proposed fluxoid mechanism would have to consider the time dependence of the bending and twisting of the fluxoids as they move through the crystal, which will depend on the orientation of the external field with respect to the superconducting layers. It is not clear at present whether collective motion of the fluxoid lattice or independent fluctuations of each fluxoid should be considered, or whether the fluxoids themselves should be thought of as continuous lines as in the original Abrikosov lattice, or as 2D "pancake" vortices well confined to each superconducting layer.

In Fig. 3, it is interesting to note that the maximum relaxation rate does not occur at $\theta=0°$, as might be expected. Rather, there is a shallow minimum at this orientation, with the maximum rate occurring with the external field $\mathbf{H}_0$ inclined at $\approx 40°$ with respect to the b axis. A comparison with the crystal structure of κ-$(ET)_2Cu[N(CN)_2]Br$ shows that this field direction nearly corresponds with the inclination of the ET molecules within each layer (37° with respect to the b axis at $T=20$ K) [12]. Perhaps the fluxoid dynamics for this orientation are such that the relaxation is stronger than at normal orientation (T_1^{-1} is 40% faster).

It is worthwhile to compare our results with those of high-T_c superconductors such as $YBa_2Cu_3O_{7-x}$. Although an increase in the relaxation rate below T_c is not observed in these systems (in contrast to our results), nevertheless there is a strong magnetic field dependence of T_1^{-1}. Martindale *et al.* [28] have found that for $YBa_2Cu_3O_{7-\delta}$, $T_1^{-1}(\theta=0°)$ (or "$\frac{2}{3}W_{1c}$" in their notation) displays a strong field dependence at low temperatures (where fluxoid effects may become stronger than the electronic interactions) while $T_1^{-1}(\theta=90°)$ (or "$\frac{2}{3}W_{1a}$") has a weak field dependence. This is in accord with our finding that $T_1^{-1}(\theta=0°)$ is strongly influenced by fluxoid dynamics, while $T_1^{-1}(\theta=90°)$ is not. The absence of a fluxoid peak in T_1^{-1} below T_c in the CuO_2-based systems can be partly attributed to the masking behavior of the very high relaxation rate intrinsic to the electronic system. In contrast, for the ^1H nucleus in the present system, which is very weakly coupled to the conduction electrons, strong fluxoid effects are observed. Indeed, by exploiting the relatively weak contact between the conduction electrons and the ^1H nuclei, which allows the protons to be sensitive probes of other sources of fluctuating magnetic fields (such as fluxoids), NMR in organic superconductors can be a powerful technique of studying the bulk properties of fluxoid dynamics in layered, type-II superconductors.

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