NMR relaxation rate in the superconducting state of the organic conductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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The ^{13}C nuclear spin-lattice relaxation rate, $^{13}T_1^{-1}$, has been measured in the superconducting state of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br in a field parallel to the conducting layers. The $^{13}T_1^{-1}$ exhibits an abrupt decrease just below the transition temperature without any indication of the Hebel-Slichter coherence peak. By separation of the vortex-dynamics contribution to $^{13}T_1^{-1}$ with the use of ^{1}H-NMR, the quasiparticle contribution to $^{13}T_1^{-1}$ is found to follow a T^3 law that is consistent with unconventional superconductivity with line nodes in gap parameter on the Fermi surface or highly anisotropic superconductivity. [S0163-1829(96)05621-4]

The mechanism of electron pairing in the organic superconductors is one of the fundamental but still open questions in condensed matter physics. In many cases, magnetic phases are known to abut on superconducting phases and the transition temperature, T_c, is highest near the boundary.[1,2] In quasi-one-dimensional tetramethyltetraselenafulvalene (TMTSF) systems, the magnetic phase is in a spin density wave (SDW) state, which is understood to result from nesting of a pair of open Fermi surfaces.[1] This ground state demonstrates that electron-electron interaction plays a non-negligible role as well as one dimensionality in the Fermi surface. In quasi-two-dimensional systems, κ-(BEDT-TTF)$_2X$, where BEDT-TTF stands for bis(ethylenedithio)tetrathiafulvalene, an antiferromagnetic phase (X=Cu[N(CN)$_2$]Cl) abutting on the well-known 10-K superconducting phase is found to have a different magnetic character from conventional SDW and suggested to be driven by strong electron correlation rather than the nesting of Fermi surfaces by ^{1}H-NMR study.[3] The ^{13}C-NMR also gives an indication of strong electron correlation still in the superconducting compounds [X=Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br].[4,5] The superconducting condensate in this situation intrigues interest in nature of the electron pairing.

Experimental research on symmetry of the pairing in κ-(BEDT-TTF)$_2X$ [X=Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br] has been done extensively through measurements of magnetic penetration depth with many kinds of experimental techniques; ac susceptibility[6] and microwave surface impedance[7,8] measurements below a lower critical field, H_{c1}, and μSR (Refs. 9 and 10) and magnetization measurements[11] far above H_{c1}. However, their results are quite controversial; some results suggest unconventional pairing[6,8,10] while others support conventional s-wave pairing.[7,9,11] Some delicate problems are involved in the measurements of penetration depth. The former two methods require severely high quality of the sample surface, although this method is ideal in a sense that the measurements are performed in the Meissner state, and for the latter two methods performed in the vortex state, the model of rigid Abrikosov lattice of vortices usually assumed in the analysis may be questionable because fluctuations of the order parameter in the vortex state is enhanced in quasi-two-dimensional systems as has been discussed in Cu oxides.

NMR is another probe characterizing the nature of the electron pairing. The NMR study has so far been conducted with ^{1}H probe in the donor molecule. The superconductivity in (TMTSF)$_2$ClO$_4$ was suggested to have line nodes in gap parameter on the Fermi surface by measurements of ^{1}H-NMR relaxation rate, $^1T_1^{-1}$.[12] For BEDT-TTF compounds, however, $^1T_1^{-1}$ showed below T_c an anomalously huge enhancement, which comes from field fluctuations due to vortex dynamics enhanced in quasi-two-dimensional superconductors.[13–15] This contribution to $^1T_1^{-1}$ overwhelms the quasi-particle contribution, of which the temperature dependence could not be extracted. This is because spin density of HOMO around ^{1}H sites is vanishingly small and consequently the hyperfine coupling of ^{1}H nucleus with quasiparticles is very small. This difficulty in ^{1}H-NMR may be overcome by ^{13}C-NMR at central carbon sites of BEDT-TTF, where spin density is much larger. Recent ^{13}C-NMR study of selectively isotope-labeled κ-(BEDT-TTF)$_2X$ [X=Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br] gave $(^{13}T_1T)^{-1}=0.1$ sec^{-1} K^{-1} at low-temperature limit in the normal state,[4] while $(^1T_1T)^{-1}$ is of the order of 0.001 sec^{-1} K^{-1}.[13–15] Namely, $^{13}T_1^{-1}$ is a hundred times more sensitive to quasiparticles than $^1T_1^{-1}$. On the other hand, $^{13}T_1^{-1}$ is 16 times more insensitive to field fluctuations than $^1T_1^{-1}$ because the relaxation rate is proportional to square of gyromagnetic ratio, γ_n, and $\gamma_{^1\mathrm{H}}/\gamma_{^{13}\mathrm{C}}$ is 4. Consequently, the relaxation contribution ratio of the quasiparticle to the vortex dynamics is expected to be more than thousand times larger in the ^{13}C-NMR than in ^{1}H-NMR.

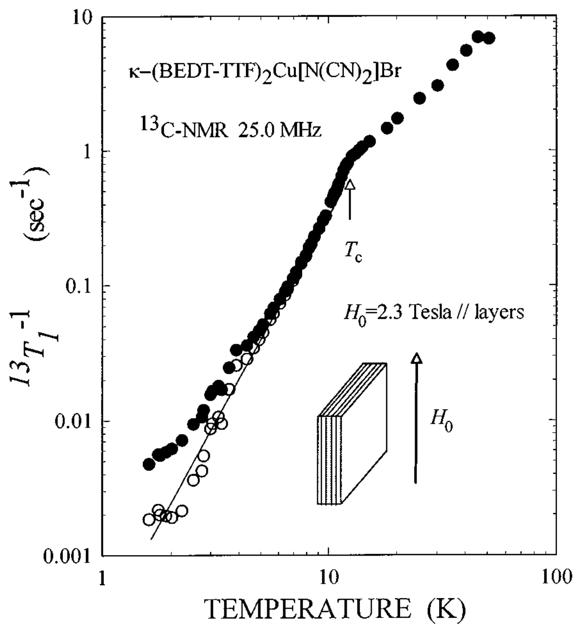

FIG. 1. ^{13}C nuclear spin-lattice relaxation rate. Closed circles; observed data of the relaxation rate. Open circles; quasiparticle contribution obtained by analysis with the use of the ^{1}H-NMR results (see text). The solid line represents a T^3 dependence.

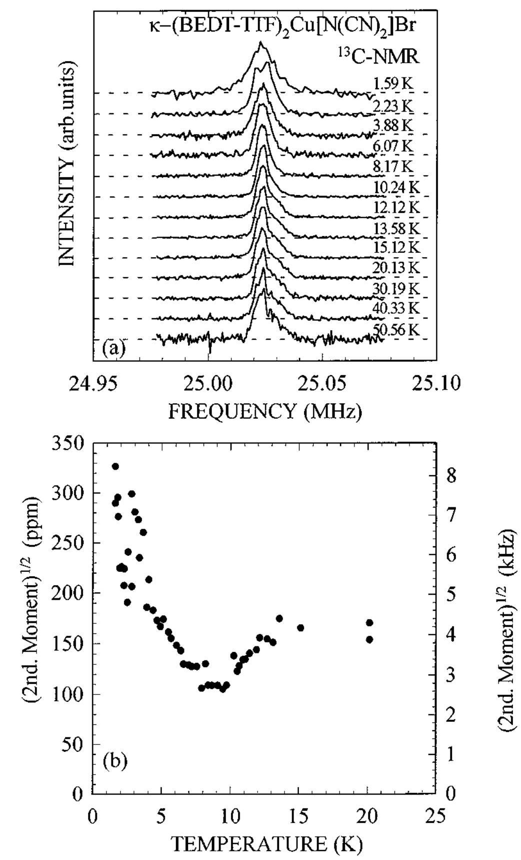

FIG. 2. (a) ^{13}C-NMR spectra and (b) square root of second moment of the spectra.

In the present work, the superconductivity in κ-(BEDT-TTF)$_2$Cu[N(Cn)$_2$]Br has been investigated by ^{13}C-NMR. Although ^{13}C-NMR has an advantage described above, the contribution of vortex dynamics to $^{13}T_1^{-1}$ becomes appreciable particularly at lower temperatures where the quasiparticle contribution diminishes rapidly. In this work, separation of the two contributions to $^{13}T_1^{-1}$ is attained by analysis of ^{1}H-NMR relaxation rate, $^1T_1^{-1}$, measured for the identical sample at the same field as in the ^{13}C-NMR. The temperature dependence of the quasiparticle contribution to $^{13}T_1^{-1}$ thus obtained is presented.

The BEDT-TTF molecules with selective substitution of ^{13}C isotope have been synthesized from $^{13}CS_2$ according to the method by Larsen and Lenoir[16] with slight modification. The salt of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br was prepared by conventional electrochemical oxidation. The relaxation rate and spectra were measured for a sample of five crystals, which were aligned with the conducting layers parallel to a magnetic field of 2.3 Tesla. This value of field corresponds to NMR frequencies of 25.0 MHz for ^{13}C-NMR and 99.5 MHz for ^{1}H-NMR. In this geometry and magnitude of field, T_c keeps nearly unchanged.[17] As for the effect of vortex cores, ac susceptibility study showed that vortices in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ are of the Josephson type.[18] This means that the normal-core contribution to T_1^{-1}, which is often not negligible in usual type-II superconductors, is minimized in the present compound. A small amount of normal cores may come from vortex discs due to misalignment between the field direction and layers and from possible excitation of vortex and antivortex discs due to two dimensionality enhanced by deterioration of out-of-plane coherence in a parallel field.

The data of $^{13}T_1^{-1}$ are plotted by closed circles in Fig. 1. In the normal state above T_c of 12 K, it shows a more rapid increase than a linear dependence with increasing temperatures up to 50 K, that reproduces the previous results.[4,5] A temperature range to which we pay a particular attention in this paper is below T_c. One of the remarkable features is the absence of the so-called Hebel-Slichter coherence peak below T_c; the $^{13}T_1^{-1}$ shows a sudden decrease just below T_c. At lower temperatures, the decrease is more moderate than an exponential function of temperature; it seems to follow a T^3 law down to ~5 K, below which it gradually deviates upward.

As was mentioned above, the measured $^{13}T_1^{-1}$ includes two kinds of contributions. Prior to the separation of them, we see the effect of vortex motions on NMR spectra. Figure 2(a) shows ^{13}C-NMR spectra. In the normal state above T_c, one can see asymmetrical line shapes, similar to the previous spectra for powders.[4] This asymmetry comes not from anisotropy of spin susceptibility, but from nearly uniaxial symmetry of hyperfine coupling tensor, which was discussed quantitatively in the previous papers.[4,5] In the present configuration of the field and crystals, the direction of the $2p_z$ orbital, from which the dipole field is a main term of the tensor, against the field direction is different for each crystal. This is the reason why the present spectra are similar to that of the powder pattern. The width of the spectra, which measures spin susceptibility, decreases below 12 K but increases at lower temperatures with symmetrical line shape. To characterize this feature quantitatively, square root of the second moment was plotted in Fig. 2(b). The decrease just below T_c is an evidence of singlet spin pairing in the superconducting condense. The increase of the width below 7 K is reasonably

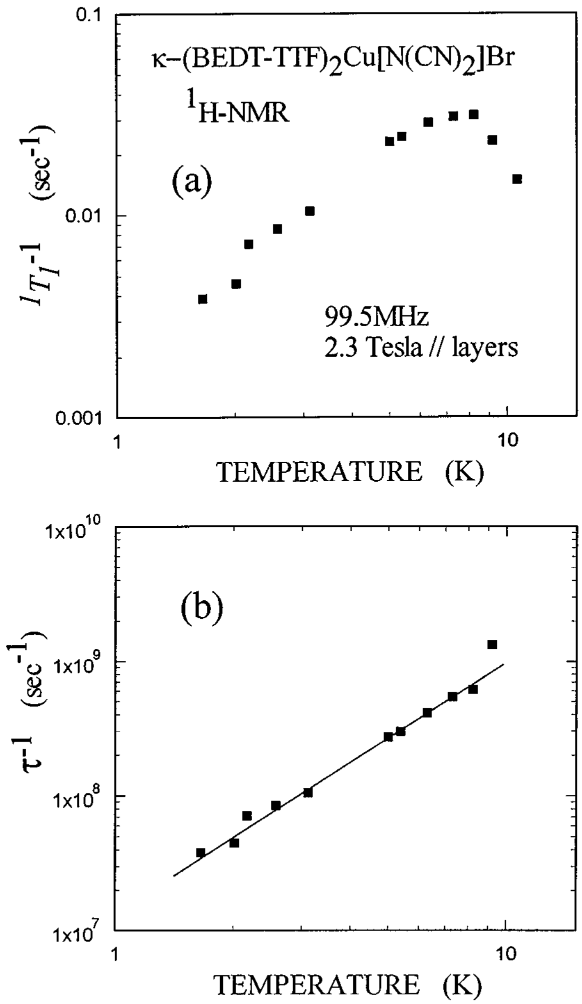

FIG. 3. (a) ^{1}H nuclear spin-lattice relaxation rate in the same field and geometry as in the ^{13}C-NMR measurements and (b) inverse of the correlation time of the field fluctuations (see text).

attributed to generation of local-field inhomogeneity due to gradual freezing of vortex motion. The value of 7 kHz at the lowest temperature corresponds to field inhomogeneity, ΔH_0, of about 7 G. It is noted that ΔH_0, although the data are scattered, does not tend to saturate even at low temperatures available, indicating progressive but still incomplete freezing of the motions. This implies that excitation of vortex motion is continuous or low lying in energy.

Figure 3(a) displays ^{1}H nuclear spin-lattice relaxation rate, ${}^1T_1^{-1}$, measured below T_c at the same geometry and magnitude of field as in the ^{13}C-NMR measurements. The ${}^1T_1^{-1}$ is determined by a single-exponential fitting of the recovery of nuclear magnetization below 50%, where it does not show an ideal exponential curve. With decreasing temperature, ${}^1T_1^{-1}$ increases and gives a broad peak around 7–8 K. Because the relaxation rate by quasiparticles should decrease rapidly below T_c, following the temperature dependence of ${}^{13}T_1^{-1}$, the relaxation rate we observed in ^{1}H-NMR is due to vortex dynamics. Our next step is to convert these values of ${}^1T_1^{-1}$ into corresponding values of ${}^{13}T_1^{-1}$. An important point to be considered here is that ${}^1T_1^{-1}$ probes the local field fluctuations at a frequency of 99.5 MHz while ${}^{13}T_1^{-1}$ does at 25.0 MHz. What we need is frequency dependence of the relaxation rate. Some theoretical works proposed spectral form of the fluctuations and the relaxation rate, where dynamics of the pancake vortices are assumed to cause the nuclear relaxation.[19,20] In the present geometry of the field, dynamics of Josephson vortices in the insulating layers as well as pancake vortices in the conducting layers due to the field misalignment contribute to the nuclear relaxation. Unfortunately, the role of the former is an open question at the present stage. As for the latter, a characteristic spectrum of the vibrational field fluctuations is calculated at least in the lattice state[21] and the temperature dependence of the relaxation rate is predicted to be linear. A peak formation of ${}^1T_1^{-1}$ around 7 K and a larger exponent ($\alpha \sim 1.5$) of ${}^1T_1^{-1} \propto T^{\alpha}$ at lower temperatures in Fig. 3(a) imply presence of diffusionlike dynamics in the present experiments. (The T-linear dependence with nature of vortex phonon, if any, may be visible at further lower temperatures.) In this paper, we assume a well-known formula which is relevant to the random field fluctuations,[22]

$$T_1^{-1} \cong \gamma_n^2 h^2 \frac{\tau(T)}{1+\omega^2 \tau(T)^2}, \tag{1}$$

where γ_n and ω are gyromagnetic ratio of the nuclei used and angular frequency tuned in the NMR measurement. The h and $\tau(T)$ are amplitude and temperature-dependent correlation time of the field fluctuations in the component perpendicular to the applied field. As is seen below, it is at low temperatures that the correction of the vortex contribution to ${}^{13}T_1^{-1}$ becomes effective. At low temperatures where $\omega\tau > 1$ holds, Eq. (1) reduces to a form of $T_1^{-1} \propto \gamma_n{}^2 \omega^{-2}$, namely, ${}^{13}T_1^{-1}/{}^1T_1^{-1} = (\gamma_{13_C}/\gamma_{1_H})^2(\omega_{13_C}/\omega_{1_H})^{-2} = 1$, where h and τ in Eq. (1) are only implicit parameters.

Since the magnetic penetration depth, which determines amplitude of field fluctuations in the vortex state, does not show significant temperature dependence except the vicinity of T_c, we assume h to be a constant. Applying a relation of $(T_1^{-1})_{max} = (\gamma_n{}^2 h^2)/2\omega$ to the ^{1}H-NMR case in Fig. 3(a), one obtains an amplitude of $h = 0.24$ G. This value is far smaller than the field inhomogeneity, $\Delta H_0 \sim 7$ G, estimated above. This is reasonable because the ΔH_0 probed by the NMR spectra corresponds to undulation of the field in the component parallel to the applied field while the h value deduced from the nuclear relaxation is the perpendicular component, which is a tilting component of the vortex fluctuations and therefore should be much smaller.

The inverse of τ obtained from Eq. (1) with the γ_{1_H} and ω_{1_H} values is shown in logarithmic scales in Fig. 3(b). The results are approximated by a power law of $\tau(T)^{-1} = 1.3 \times 10^7 \times T^{1.87}$ sec^{-1}, instead of activation type, as is guided by solid line in the figure, suggesting that the excitation in the vortex motion is low lying or gapless. This feature is consistent with the implications of the nonsaturating behavior in ΔH_0 described above. Now, we can calculate the ${}^{13}T_1^{-1}$ equivalence of ${}^1T_1^{-1}$ using Eq. (1) with the values of γ_{13_C}, ω_{13_C} and $\tau(T)$ obtained above. This is a contribution of the vortex dynamics to ${}^{13}T_1^{-1}$. Subtracting the values from the raw data of ${}^{13}T_1^{-1}$ (closed circles in Fig. 1), we finally obtain the quasiparticle contribution to ${}^{13}T_1^{-1}$, which is shown by open circles in Fig. 1. As seen in the figure, the vortex contribution, namely the difference between closed and open circles, becomes appreciable at lower temperatures. The resultant temperature dependence of the quasiparticle contribution follows a T^3 law, which supports existence of line nodes of gap parameter on the Fermi surface. The electron pairing in the compound in question is very likely of non-*s* wave in nature, although conventional pairing with extreme anisotropy cannot be ruled out. The overall results are in agreement with the recent works performed at a low-field of 0.6 T (Ref. 23) and high fields up to 7.8 T.[24]

In conclusion, we presented two distinctive aspects in ^{13}C nuclear spin-lattice relaxation rate, $^{13}T_1^{-1}$, in the superconducting state of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. One is the absence of the Hebel-Slichter coherence peak just below T_c. By the analysis of ^{1}H nuclear spin-lattice relaxation rate, the measured $^{13}T_1^{-1}$ was found to contain appreciable contribution of field fluctuations due to vortex dynamics at low temperatures. Subtraction of this contribution uncovered another fact that the quasiparticle contribution to $^{13}T_1^{-1}$ follows a T^3 temperature dependence. These two characteristics of NMR relaxation rate show that the superconductivity in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is an unconventional one with line nodes in gap parameter on the Fermi surface or highly anisotropic. Singlet pairing is also suggested by the ^{13}C-NMR spectra.

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[21] According to Ref. 19, spectrum density of the field fluctuations in the vortex lattice state has a $1/\omega^2$ dependence for $\omega > \omega_s$ and a weaker ω dependence for $\omega < \omega_s$, where ω_s is a characteristic frequency of the shear mode. Assuming, for example, that the field misalignment is 2° in the present experiment, ω_s is estimated at 1 GHz for our compound. On the other hand, a characteristic frequency of the tilting mode, ω_t, which is field independent, is estimated at 14 MHz. So, our experimental frequency is situated in between.
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