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NMR in the 2D Organic Superconductors

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Abstract. — We review recent NMR studies of the layered organic superconductors of the
(BEDT)$_2$X family. First the normal state properties are discussed. The central issue is the
importance of the interplay between antiferromagnetism and superconductivity in these mate-
rials demonstrated by the observation of a pseudogap developing prior to the superconducting
transition. An extended analysis of the Knight shift and the nuclear relaxation rate gives an
evidence for strong antiferromagnetic fluctuations enhanced by Coulomb repulsion and the nesting
of the Fermi surface. The NMR data show some analogy with High $T_c$ superconductors however
the comparison is not straightforward as there is no clear evidence for spin-charge decoupling.
The use of high pressure to tune the amplitude of AF fluctuations enables us to draw a general
phase diagram of the family. In the second part the NMR experiments in the superconducting
state are presented. One of the fundamental questions addressed by these experiments is the
symmetry of the order parameter related to the pairing mechanism. The most spectacular NMR
measurements are those performed in the lock-in state, which give access to the density of super-
conducting excitations at low energy. These experiments suggest that the pairing state may
be unconventional featuring an anisotropic superconducting gap, possibly with nodes. Finally,
the NMR contribution to the understanding of the nature of the vortex state is discussed in the
context of recent results on $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br where the $^1$H relaxation was used as a probe
of the vortex density fluctuations.

1. Introduction

Quasi two-dimensional (Q2D) organic superconductors were issued as a result of a search for
new donor molecules replacing TMTSF in 1D organic salts in order to improve superconduct-
ing properties of these materials. This led to a new and completely different family of organic
conductors but paradoxically, the goal has been partially achieved since $T_c$ has been raised by
a factor of 10. Since then, the number of quasi two-dimensional organic superconductors has
grown very rapidly and actually the BEDT-based materials are the largest part among about
50 organic superconductors. These compounds, in spite of rather low critical temperatures

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(≈ 10 K) are very interesting as model materials for studying the mechanisms of superconductivity in the 2D superconductors.

Particular place in this family is occupied by the so called κ-phases which have been most extensively studied and appear to be representative for a quite large class of materials. Especially, they display a lot of properties similar to those observed in the high temperature superconductors (HTSC): high conductivity anisotropy or interplay between magnetism and superconductivity.

The general survey of the physical properties of 2D organic materials can be found in [1–4]. In this paper we concentrate rather on various aspects related to the application of the NMR and the electronic properties. The majority of results presented below are those obtained on κ-(ET)$_2$Cu[N(CN)$_2$]Br and which were published in [5–8]. This representative member of the κ-(ET)$_2$X family is one of the the best characterized up to date, it is also the 2D organic superconductor with the highest known $T_c$ (11.6 K) at ambient pressure [9].

The various topics covered in this paper are presented in three sections. The Section 2 is devoted to various applications of the NMR in the normal phase: spin density distribution, structural peculiarities and metallic properties. The emphasis is put on the apparent non-metallic behaviours revealed by this and other studies and which seem to be common to most κ-phase superconductors. For example, the resistivity often exhibits a maximum around 90 K and quite generally in the superconducting κ-phases a maximum of $dR/dT$ occurs near 50 K and tends to vanish under pressure [10–12]. Also the ESR spin susceptibility [13] shows a metallic behavior between 300 and 50 K but a dramatic drop below 50 K indicates an important suppression of the density of states at the Fermi level.

One of the advantages of the organic compounds is their high sensitivity to hydrostatic pressure. The application of pressure is a valuable tool since it increases the bandwidth and therefore it is in principle possible to directly measure how different physical quantities scale with the density of states at the Fermi level. This principle has been extensively employed in the context of (TMTSF)$_2$X and (TMTTF)$_2$X salts where the pressure scale was shown to be to some extent equivalent to the relative strength of electron-electron repulsion [14,15]. The situation is however more complex in 2D than in the 1D materials since also the geometry of the Fermi surface is subject to change under pressure. The feedback of this change on the density of states is not always easy to predict and this provides one of the questions we would like to answer with the use of NMR. Here we analyze the Knight shift ($K$) and spin-lattice relaxation time measurements carried out in a large interval of temperature and pressure. We interpret these results in terms of electronic correlations and spin density wave fluctuations above the superconducting transition.

The following sections deal with the NMR in the superconducting state.

In superconductors, the NMR relaxation can probe various types of fluctuations: superconducting excitations, normal carriers in the vortex cores, and motion of the vortex lines. An important achievement of the presented study is that all of these contributions could be properly separated. First, the exceptional advantage of κ-(ET)$_2$X superconductors consists in disposing two suitable NMR nuclei. On one hand, the spins of $^1$H nuclei located at the periphery of the large BEDT molecules, have a much weaker interaction with electronic spins than those of central carbons ($^{13}$C substituted) which contribute to build the conduction bands. On the other hand, the ratio of gyromagnetic ratios favours the relaxation of $^1$H by the fluctuating magnetic field of the vortex structure. Thus, we can well distinguish the contribution due to vortex motion from the others. Furthermore, the contributions due to normal electrons and superconducting excitations in the $^{13}$C relaxation could be separated in an elegant way, using the properties of the lock-in state. This enabled us to measure the Knight shift and the relaxation components due only to superconducting excitations, which is discussed in Section 3.
In the last section we present recent experimental and theoretical studies of vortex state by the \(^{1}H\) NMR relaxation for magnetic fields perpendicular to the conducting planes. New experimental results for the temperature and field dependencies of the NMR relaxation are confronted with existing models developed to understand the phase diagram of the mixed state of strongly anisotropic superconductors.

**Experimental Details.** — The measurements on \(\kappa-(ET)_{2}Cu[N(CN)_{2}]Br\) presented here were performed on a rhombic-shaped single crystals, approximately \(0.5 \times 1 \times 1\) mm\(^3\). The sample used for carbon NMR was 100\%\(^{13}\)C enriched on both central carbon atoms of the ET molecule. The quality of the sample has been tested by an inductive measurement of the superconducting transition. The critical temperature is \(11.6\) K with a transition width less than 1 K. Also, the NMR spectra analysis *versus* the orientation of the sample in the field shows that the sample was truly single crystal. Spin-lattice relaxation times have been measured applying a saturation comb and the signal intensity was measured using a spin echo for \(^{13}\)C and free induction decay for \(^{1}H\).

Measurements under pressure were performed in a small Cu-Be pressure cell. The pressure was applied using an isopentane medium through a capillary tubing. Doing so, we were able to adjust the pressure during cooling down to the isopentane solidification. At the solidification of the pressure medium, freezing and melting temperatures could be detected by watching the broadening of the isopentane NMR line.

### 2. Electronic Properties in Metallic Phase

2.1. NMR Shift Tensors. — \(\kappa-(ET)_{2}Cu[N(CN)_{2}]Br\) crystallizes in an orthorhombic structure with 8 ET molecules per unit cell (space symmetry Pnma) \[16\] therefore 8 central \(^{13}\)C pairs contribute to the spectrum. The spectrum of each carbon pair split by dipolar coupling is made up of 4 lines and thus we could expect in general to observe 32 lines in the spectrum. This number is however reduced by half due to the inversion symmetry of the structure which makes the two molecules of each dimer equivalent. Accordingly, we generally observe a spectrum with 16 lines in a general orientation.

Figure 1 shows the spectra obtained in three particular orientations of the crystal with respect to the field. When the field is parallel to the layer the reflection symmetry reduces the number of lines by half and when it is parallel to one of the axes a, b, c, all molecules become equivalent (the field is then invariant by all symmetry operations of Pnma) so that the spectrum reduces to 4 lines. There is one important practical implication of these observations: as we will see later the great anisotropy of the Knight shift tensor offers the possibility of an excellent alignment of the crystal in the field which will be of great help for measurements in the superconducting state.

In order to achieve an unambiguous line assignment two types of 2D-NMR \[17,18\] experiments were performed in several orientations: the dipolar couplings were measured taking J-resolved spectra and carbon pairs were identified using COSY experiments \[8\]. We have then determined the shift tensors of both carbon sites. For that we have assumed that the principal axes (\(X, Y, Z\)) are the symmetry axes of the ET molecule. \(X\) lies along the central C-C bond, \(Z\) is perpendicular to the molecular plane and \(Y\) completes the orthogonal frame. The origin of the shifts were based on the chemical shift in solid ET \[19\]. In principle it is not completely obvious that the chemical shift in the neutral ET is the same as in the metallic compound. There are however evidences that this choice for the origin of the Knight shift is correct within few ppm. First, as will be shown later, the line broadening observed below \(200\) K can provide an alternative determination of the origin of the Knight shift. Another independent method
was used by Hennig et al. [20] who performed the CP-MAS measurements on the \( \alpha-(ET)_2I_3 \) below the insulating transition and found that the observed shifts of the central carbons are close to that of pure BEDT. Furthermore, we will show that the pressure dependence of the Knight shift is consistent with this assumption.

Using the isotropic chemical shift (\( \approx 111 \text{ ppm from TMS} \)) [19] the eigenvalues of the shift tensor for \( \kappa-(ET)_2Cu[N(CN)_2]Br \) are obtained by fitting the single crystal rotation patterns as shown in Figure 2. The fit gives \( \bar{K}^1 \equiv (K_{XX}, K_{YY}, K_{ZZ}) = (-20, 20, 550) \) and \( \bar{K}^2 = (-180, -110, 320) \) for the two sites C\(_1\) and C\(_2\). It is important to note that the fit is excellent for the site 1 in contrast with that of site 2. This could be due to the assumption made on the
principal axes, since in \( \kappa-(\text{ET})_2\text{Cu[N(CN)]_2}\text{Br} \) the symmetry of the ET molecule is broken by the dimerization so that the two tensors are likely to have slightly different principal axes as was also revealed by other studies [21].

Separating the isotropic and anisotropic parts of the shift tensor: \( \mathbf{K} = K_{iso} + K_{aniso} \) we obtain for the two sites: \( K_{iso}^{1} = 190, K_{iso}^{2} = 10, K_{aniso}^{1} = (-203, -163, 366) \) and \( K_{aniso}^{2} = (-190, -120, 310) \). At present the origin of such strong difference in the isotropic shifts of the two sites cannot be explained. In general we expect a slight difference in the spin density due to the relative shift of the two molecules of the dimer as shown in Figure 3. As was suggested by Kawamoto et al. [22] the large difference could be related to a slight mixing of 2s orbital to HOMO caused by the breakdown of the planar atomic coordination around \( C_1 \) atom, although this hypothesis was not confirmed by X-rays. On the other hand, it is also likely that the asymmetry was overestimated by neglecting the anisotropy of the chemical shift [23]. The labelling of the sites in Figure 3 was chosen according to the principle that the spin density should be higher for the sites which are close one to another and have stronger overlap of the atomic orbitals. Although the lack of spin density calculations for the present compound makes impossible to confirm this assumption, such rule was demonstrated for the TMTSF stacks in the \((\text{TMTSF})_2\text{X}\) family [14, 24].

DeSoto et al. [21] made similar studies but they have taken into account the anisotropy of the ET chemical shift to extract the Knight shift tensor. Also, they attribute the higher \( K_{ZZ} \) rather to the outer carbon sites \((C_2)\). based on the angular study of the hne positions and the linewidth. Their site assignment relies on the fact that the experimentally determined principal axes of the Knight shift tensor do not coincide exactly with those of the ET molecule. The misalignment is attributed to the proximity of the carbon atoms of the other molecule of the dimer and therefore is expected to be stronger for the site \( C_1 \) (see Fig. 3) However, as the effect is rather small (\(~6\ deg\)) it is not clear if the assignment obtained in this way is more reliable (the experimentally determined axes of the tensor are usually subject to an experimental error of the same order of magnitude).

The strongly anisotropic Knight shift on \( C_1 \) and \( C_2 \) sites comes from the \( 2p_z \) orbitals of the carbon and \( 3p_z \) of the sulfur atoms. The strong and positive \( K_{ZZ} \) as well as weaker and negative in-plane components of \( \mathbf{K} \) can be readily attributed to dipole field of the \( 2p_z \) conduction electrons. The interaction with electronic density of the neighbouring sulfur and carbon atoms accounts for the deviation from the pure dipolar shift due to \( 2p_z \) and proportional to \((-1,-1,2)\). The latter can be written as:

\[
1K_{2p_z}^{dp} = f_{C_1} \chi_p A_{2p_z}^{dp} \quad \text{with} \quad A_{2p_z}^{dp} = \frac{2}{5} \hbar \gamma_e \left\langle \frac{1}{r^3} \right\rangle_{2p_z}
\]

where \( f_{C_1} \) is the spin density on the \( 2p_z \) orbital of \( C_1 \), \( \chi_p \) is the electronic susceptibility per spin and \( \left\langle \right\rangle_{2p_z} \) means the space average weighted with the \( 2p_z \) electron density [25]. For an
isolated carbon atom we have [25]:

\[
\langle \frac{1}{r^3} \rangle_{2p_z} = 2 \text{ u.a.} = 1.35 \times 10^{25} \text{ cm}^{-3} \quad \text{and} \quad A^{\text{dip}}_{2p_z} = 100 \text{ kG/\(\mu_B\)} \quad (2)
\]

In the same way it is possible to estimate the dipolar field generated by the spins on the neighboring sulfur and carbon atoms:

\[
1K^{\text{dip}}_{C_1-C_2} = f_{C_1} \chi_p A^{\text{dip}}_{C_1-C_2} \quad \text{with} \quad A^{\text{dip}}_{C_1-C_2} = \hbar \gamma_e \left\langle \frac{1}{r^3} \right\rangle_{2p_z(C_2)} \simeq \hbar \gamma_e \frac{1}{r_{C_1-C_2}^3} \quad (3)
\]

\[
1K^{\text{dip}}_{C_1-S} = f_{S} \chi_p A^{\text{dip}}_{C_1-S} \quad \text{with} \quad A^{\text{dip}}_{C_1-S} = \hbar \gamma_e \left\langle \frac{1}{r^3} \right\rangle_{3p_S} \simeq \hbar \gamma_e \frac{1}{r_{C_1-S}^3} \quad (4)
\]

After having inserted the interatomic distances \(r_{C_1-C_2}\) and \(r_{C_1-S}\) [16] we obtain:

\[
A^{\text{dip}}_{C_1-C_2} = 7.5 \text{ kG/\(\mu_B\)} \quad \text{and} \quad A^{\text{dip}}_{C_1-S} = 3.75 \text{ kG/\(\mu_B\)} \quad (5)
\]

Summing up all contributions the anisotropic part of the shift tensor of the site \(C_1\) can then be written as:

\[
\bar{K}_{\text{aniso}} = K^{\text{dip}}_{2p_z} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & +2 \end{bmatrix} + K^{\text{dip}}_{C_1-C_2} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} + 2K^{\text{dip}}_{C_1-S} \begin{bmatrix} 1+3\cos \varphi & 0 & 0 \\ 0 & 1-3\cos \varphi & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad (6)
\]

\(\varphi\) is the angle (\(S_1C_1S_2\)). We have supposed that the two sulfur atoms have the same spin density (otherwise the tensor is not diagonal within the chosen frame).

The numerical estimations requires the knowledge of \(\chi_p\), \(f_{C_1}\), \(f_{C_2}\), \(f_{S_1} = f_{S_2}\) et \(f_{S_3} = f_{S_4}\). We take \(\chi_p = 5 \times 10^{-4} \text{ emu/mole.dimere} \chi_p = 8.3 \times 10^{-28} \text{ emu/spin from [26]}.\) Using the relaxation rate study presented in the next section we can assume that \(f_{C_1} \simeq 1.5f_{C_2}\). The spin density on the sulfur atoms is not known but it is reasonable to set [27] \(f_{S_1} = f_{S_2} = 3f_{C_1}\) and \(f_{S_3} = f_{S_4} = 3f_{C_2}\). The factor of 3 is somewhat bigger than the one resulting from band structure calculation, but the effect of Coulomb repulsion is to reinforce the spin density on the sulphur atoms whose \(3p\) orbitals are more delocalized that the \(2p\) orbitals of the carbons. The \(f_{C_1}\) is then obtained by fitting the theoretical expression of \(\bar{K}_{\text{aniso}}\) to the experimental results. With \(f_{C_1} = 0.023\) we obtain

\[
\bar{K}_{\text{aniso}}(C_1) = (-193, -165, 360) \quad \text{and} \quad \bar{K}_{\text{aniso}}(C_2) = (-112, -118, 231)
\]

The result for \(C_1\) fits well with the experimental values, on the other hand the discrepancy observed for \(C_2\) probably mean that in our determination of the experimental shift tensor we have overestimated the anisotropic part of this site.

The isotropic part of the Knight shift can be due either to the effect of the contact interaction with the electrons of \(1s\) and \(2s\) orbitals of the atom if these are mixed to the conduction band, or to the core polarization of the same orbitals by the conduction electrons. From the Hückel calculations [27], the mixing of the \(2s\) states to the HOMO band is below 1% but the hyperfine coupling constant is strong enough to provide a non negligible effect: \(A_{2s} = 3500 \text{ kG/\(\mu_B\)} [25]\) giving \(1K^{\text{contact}}_{2s} = f_{2s}\chi_p A_{2s} = 76 \text{ ppm}\). As for the core polarization, it is to note that it would give a contribution of the same order of magnitude. It is in general quite hard to calculate, but to have a rough estimate we can consider the effect of the exchange interaction between the \(s\) orbitals and \(2p_z\) for which the effective hyperfine field was estimated to [28] \(A^{\text{eff}}_{2p_z} \simeq +30 \text{ kG/\(\mu_B\)}\).
The resulting isotropic contribution would then be $1K_{2p_s}^{p,c} = fC_1xPA_{2p_s}^{p,c} = 60$ ppm. These estimations are rather crude but they confirm the existence of an isotropic shift of the order of hundred ppm.

Another $^{13}$C study was reported by Kawamoto et al. [22,26] who worked on a powder sample of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br. They adjusted the powder linewidth taking $fC_1 = fC_2 = 0.03$. Also, a similar estimation was obtained for $\beta$-(ET)$_2$I$_3$ from the analysis of $^{13}$C MAS spectra [23].

A complementary information on the spin density distribution can be obtained studying the anisotropy of the nuclear relaxation rate $1/T_1$ [8].

2.2. Proton NMR and Structural Transitions. — The conformational ordering has a strong impact on the metallic and superconducting properties of $\kappa$-(ET)$_2$X salts. It is well known that in those (TMTSF)$_2$X compounds where the anion does not share the inversion symmetry of the TMTSF crystal structure, the anion ordering plays an essential role in the stabilizing of different ground states [29]. In $\kappa$-(ET)$_2$X the analog role of the agent of interaction between metallic and insulating layers is played by ethylene groups at the end of the donor molecules. Due to the sp$^3$ hybridization of the carbon atoms of the (CH$_2$)$_2$ groups, these have two stable configurations called eclipsed or staggered, depending on relative orientation of the outer C-C bonds [30]. At high temperature the system is disordered by a thermally activated fast motion and at low temperature one of these configuration is adopted depending on the anion and compound structure [16,30]: staggered for $\kappa$-(ET)$_2$Cu(NCS)$_2$ and eclipsed for $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br and $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl.

The characteristic energy of the conformational motion can be monitored by $^1$H NMR. The relaxation time of the protons of the (CH$_2$)$_2$ groups induced by the strong dipolar field is dominant when the Larmor frequency is comparable with the frequency of the fluctuating dipolar field. According to the standard BPP theory (Bloembergen-Purcell-Pound [31]) the resulting relaxation rate is:

$$\frac{1}{T_1} \propto \left[ \frac{\tau_c}{1 + \omega_N^2 \tau_c^2} \right]$$

where $\tau_c$ is the characteristic frequency. For a thermally activated process we have:

$$\tau_c = \tau_0 \exp \left( \frac{E_a}{kT} \right)$$

where is $E_a$ the activation energy.

In Figure 4 we have plotted $1/T_1$ vs. $T$ at different fields. The data are very well fitted with the theoretical expression giving $C = 9.5 \times 10^8$ s$^{-2}$, $\tau_0 = 7 \times 10^{-13}$ s and $E_a = 2650$ K.

From the field dependence of the peak it is clear that the motion starts to freeze around 200 K. Such structural transition is indeed observed by X-rays [16,32]. However, while according to the X-rays the modulation induced by the ethylene groups is commensurable with the lattice, the NMR seems to indicate that a kind of disorder is present in the system at low temperatures. In fact, as was already reported in different experiments [5,21], the $^{13}$C NMR linewidth starts to broaden below 150-180 K. On the other hand this broadening is rather insensitive to pressure up to 4 kbar though the compressibility of the $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br is high enough to expect a shift of the transition to higher temperature. This phenomenon is therefore not well understood and requires further studies. A similar effect was observed in $\beta$-(ET)$_2$I$_3$ at 200 K [19] in which a phase transition occurs with an incommensurate modulated structure. The authors attribute the line broadening to an Anderson localization modifying locally the electronic density and driven by the modulation of the electrostatic potential induced by different configurations of ethylene groups.
Fig. 4. — $^1$H relaxation rate in $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br due to ethylene group motion at 1 T, 3 T and 9 T. The electronic contribution to the relaxation obtained from the rescaled relaxation of $^{13}$C has been subtracted. The solid curves are fitted with the theoretical expression as explained in the text.

Fig. 5. — $^{13}$C spectra of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br for the magnetic field parallel to the planes at different temperatures.
Although, as we see from the results discussed above, the underlying physics of the phenomenon is not yet quite clear, the NMR experiments show undoubtedly that the line broadening is simply caused by a distribution of hyperfine shifts in the sample. This is well shown in Figure 5. The width vary strongly among different lines and it is found that the width of each line is proportional to its Knight shift (for example the line c in Fig. 5 has zero Knight shift for the given field direction and thus remains narrow down to low temperatures).

This is analyzed more quantitatively in Figure 6 where the ratio linewidth/Knight shift is plotted in function of temperature. Challenging different reports by X-spectroscopists about the wave vector of the lattice modulation, the only interpretation of Figure 6 we can give is that there is an incommensurable modulation of the electronic density. The investigation of the anisotropy of $T_1$ in the spectrum [21] led to similar conclusions. It will be therefore interesting in the future to look for such a broadening in other compounds and especially in $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl and $\kappa$-(ET)$_2$Cu(CN)[N(CN)$_2$] where the structural transition is absent.

2.3. Antiferromagnetic Fluctuations Seen by $^{13}$C NMR. — The NMR investigation of the electronic properties in metallic state of the ET compounds involves mainly the $^{13}$C Knight shift and relaxation measurements in function of temperature and pressure. As was shown in previous section, NMR properties of this nucleus are only determined by hyperfine interaction with conducting electrons therefore its Knight shift and relaxation reflects the evolution of the local static or dynamic susceptibility. These studies address some key questions in the field of 2D electronic structures such as the competition between magnetism and superconductivity or the role of Coulomb repulsion.

In Figure 7 the shifts of 6 lines (labelled a, b, c, d, e and f as in Fig. 1 of Ref. [5]) of $^{13}$C in $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br have been plotted versus pressure. The shifts exhibit linear decrease with pressure up to 5 kbar, all lines in the spectrum having the same relative slope $d\ln(K)/dP$. This confirms that the evolution of the Knight shift under pressure follows the variation of the density of states at the Fermi level $n(E_F)$ (or the transfer integrals) since the chemical shift is pressure independent.

The variation of the Knight shift is evaluated to be about -6 %/kbar in the pressure interval studied. It is noteworthy to compare this value with the analogous pressure coefficients in other
organic conductors having similar compressibility, e.g. in the Q1D conductor \((\text{TMTSF})_2\text{PF}_6\),
the variation of \(n(E_F)\) was estimated to about 2%/kbar [14]. Also, the structural study of \(\kappa\)-(ET)\(_2\)Cu(NCS)\(_2\) under pressure led to evaluate the variation to the bandwidth to 150 K/kbar or again \(\approx 2%/\text{kbar}\) [33].

This estimation suggests first that simple free electron susceptibility cannot account for such a variation of the Knight shift. Following the ideas developed for 1D metals we are tempted to think that the enhancement is the effect of electronic correlations. In a most naive picture one can estimate the expected enhancement of \(K(p)\) through the RPA approximation, introducing the on-site repulsion parameter \(U\). This will renormalize the spin susceptibility \(\chi\) by a Stoner factor:

\[
\chi = \frac{\chi_0}{1 - U n(E_F)} \propto \frac{n(E_F)}{1 - U n(E_F)}
\]

where \(\chi_0\) is the bare susceptibility. It follows that :

\[
\frac{d(ln \chi)}{dP} = (\frac{1}{1 - U n(E_F)}) \frac{d(ln n(E_F))}{dP}
\]

Taking a Stoner factor of 3 to explain the result and \(n(E_F) = 0.9 \text{ e}^-/\text{eV}/\text{ET molecule}\) [27] we obtain \(U \approx 0.7 \text{ eV}\) which is comparable to the bandwidth \(W \approx 0.6 \text{ eV}\). Without omitting the rather crude character of this calculation, we remind that a more elaborate analysis of NMR relaxation data in TMTSF and TMTTF salts has yielded \(U\) values close to 1 eV [14]. A comparison is meaningful here as the Coulomb repulsion strength is a molecular property and in both cases conduction bands are build on the same sulfur orbitals.

The situation seems however more confused if we go further into details of numerical estimations of the relaxation rate. In the NMR of correlated metals it is well known that one expects deviations from the Korringa relation due to collective effects and the problem was extensively studied in the context of 1D organics [14,15]. Here we were encouraged to make this kind of speculations by the observed linear dependence of \(1/T_1\) vs \(K^2\), see Figure 8. The quantitative measure can be given by the so-called Korringa ratio:

\[
\kappa = T_1 T K^2 (\frac{\gamma N}{\gamma_e})^2 \frac{4\pi k_B}{\hbar}
\]

Fig. 7. — Pressure dependence of the \(^{13}\text{C}\) lines shift at room temperature.
which is strictly equal to unity in the free electron model and more generally is defined for the component of the relaxation rate due to uniform \((q = 0)\) fluctuations of the hyperfine field [15].

For the current data of \(\kappa-(ET)_2\text{Cu[N(CN)]}_2\text{Br}\) we have

\[
T_1TK_1^2 \approx 1.2 \times 10^{-6} \text{ s K}
\]

at room temperature, where we have used \(K_1^2 = K_{zx}^2 + K_{zy}^2 + K_{xz}^2 + K_{yz}^2 + K_{yz}^2 + K_{yz}^2\) for the \(T_1\) measured \(H_0\) along the \(z\) axis [17, 18]. This gives \(K \approx 0.29\) in good accordance with the result of [21]. On the other hand, the usually expected effect of electron-electron correlations is to increase the experimental value of \(K\) [15, 17] and such enhancement was indeed reported for many 1D metals [14]. But, as in general only the zero wave vector component of \(1/T_1\) enters to the Korringa relation, this probably means that, unlike for 1D systems, the uniform part of the relaxation is not dominant even at high temperature. From the shape of the Fermi surface [27] we can indeed predict the existence of strong fluctuations at non-zero wave vector responsible for the reduction of the uniform susceptibility. We should point out here that the data in Figure 8 is very remarkable, it shows namely that the Korringa ratio does not vary with pressure. If the antiferromagnetic fluctuations dominate the relaxation, this would mean that their amplitude scales as the bandwidth, and that the geometry of the Fermi surface (especially the nesting quality) is not affected by pressure up to \(~5\) kbar.

The evolution of these properties in temperature was the next goal in our investigation of \(\kappa-(ET)_2\text{Cu[N(CN)]}_2\text{Br}\). Figure 9 shows the temperature dependence of the Knight shift between 10 and 300 K at 1 bar and 4 kbar. The error bars increase at low temperature because of the line broadening discussed before and also the overlapping of the lines. The ambient pressure data concides with that from ESR spin-susceptibility measurements [13]. Between 300 and 50 K, the Knight shift decreases slowly (\(\approx 8\% /100\) K). If we compare in \(\kappa-(ET)_2\text{Cu[NCS)]}_2\) the isotherm [33] and the isobar [34] expansion coefficients we can conclude that 100 K corresponds to 1.7 kbar. Hence, the variation of the spin susceptibility in high temperature region can be attributed to the lattice contraction.

Below 50 K we observe a sharp drop in the spin susceptibility which has been interpreted in terms of a pseudo-gap in the density of states [13]. At 4 kbar this pseudo-gap disappears and the compound exhibits a more common metallic behavior in agreement with the observations made on the resistivity under pressure [10].

Spin-lattice relaxation time measurements versus pressure and temperature are presented in Figure 10. At 1 bar, \(1/T_1T\) exhibits near 50 K an important enhancement, which can also

Fig. 8. — Relaxation rate vs. \(K^2\) (at room temperature, with pressure as the implicit parameter)
be observed on protons [35,36]. Clearly, this large peak in $1/T_1T$ is in some way related to the decrease of the susceptibility: it occurs near 50 K and is progressively spread out under pressure. At higher temperatures the susceptibility (corrected for the thermal expansion) becomes constant and at the same time a Korringa-like behaviour is restored for $1/T_1T$. 

Fig. 9. — Temperature dependence of the Knight shift (normalized by its room temperature value) at 1 bar (●) and 4 kbar (○).

Fig. 10. — $1/T_1T$ vs. temperature at different pressures: 1 bar (●), 1.5 kbar (△), 3 kbar (○) and 4 kbar (○).
The temperature profiles of $1/T_1 T$ and Knight shift show a rather striking similarity with those reported in $\text{YBa}_2\text{Cu}_3\text{O}_{6.63}$ for the $^{63}\text{Cu}$ [37] as well as some other HTSC materials [38]. This relaxation behaviour in HTSC has been often explained by the appearance of short range antiferromagnetic correlations in the CuO$_2$ planes leading to a pseudo-gap or a decrease in the density of states. Although a comparison with HTSC may be instructive here we must be careful and remember that some concepts and scenarios invoked to understand the electronic properties of copper oxide superconductors, do not apply in their organic analogs. First, the models based on the Fermi Liquid (FL) approach emphasize the role of the peculiar properties of the Fermi surface of cuprates. Accordingly, the van Hove singularity at the Fermi level, coupled with the AF nesting, produces the characteristic “double” divergences in response functions. Several authors make use of this mechanism to explain the linear temperature dependence of the resistivity and the high $T_c$'s. On the contrary, in ET-based superconductors neither does $n(E_F)$ diverge nor is $\rho(T)$ linear. Furthermore, in the HTSC there are arguments for the strong coupling regime and the model based on the “Luttinger liquid” theory. This approach postulates the possibility of spin-charge decoupling in 2D electron system. Accordingly, the peak of $1/T_1 T$ $\text{YBa}_2\text{Cu}_3\text{O}_{6.63}$ was interpreted as the appearance of a spin gap [38] since it is not followed by the resistivity. As far as the results presented here are concerned, it would be more difficult to accept the required postulate because there is a strong correlation between the relaxation rate and the resistivity which has a peak near 90K and one can distinguish different regimes in the $\rho(T)$ curves below and above 50K. Moreover this simultaneous peak of resistivity and $T_1$ seems to be one of immanent features of the BEDT salts since it has been observed in another compound of the family [26]. Therefore the possibility of the spin-gap scenario in the $\kappa$-(ET)$_2$X is not established.

On the other hand there is a common point with cuprates worth to exploit here, which is the influence of the shape of the Fermi surface on the magnetic properties. It is well known that the 1D AF nesting of the Fermi surface in (TMTSF)$_2$X compounds not only gives a huge contribution to the relaxation time but can affect the conductivity and make the system go into an insulating state [29,39]. In $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br the calculated Fermi surface [27] shows the existence of nested parts with two possible incommensurate wave vectors (Fig. 11).
Both nuclear relaxation and electron scattering are sensitive to the imaginary part of the local susceptibility $\chi''$. For the relaxation rate we have:

$$\frac{1}{T_1 T} \propto \sum_{\mathbf{q}} \frac{\chi''(\mathbf{q}, \omega_N)}{\omega_N}$$

(8)

where $\omega_N$ is the Larmor frequency. The introduction of correlations within the RPA approximation leads to modify the bare susceptibility as follows [15]:

$$\frac{\chi''(\mathbf{q}, \omega_N)}{\omega_N} \approx \frac{1}{(1 - U\chi_0(\mathbf{q}, \omega_N))^2} \frac{\chi''(\mathbf{q}, \omega_N)}{\omega_N}$$

(9)

Nesting of the Fermi surface occurring at a vector $\mathbf{Q}$ will thus enhance $\chi''(\mathbf{Q}, \omega_N)$ as well as $1/T_1$ because of the maximum of $\chi''(\mathbf{Q}, \omega_N)$ at $\mathbf{Q}$ [40].

The RPA description is no longer valid in presence of a strong divergence. The FL theories based on the nesting properties provide in general a better approach through the quasi-particle picture, introducing the notion of pseudo-gap as a decrease of the effective density of states at Fermi level [41,42]. Such pseudo-gap developing at low temperatures would affect the static and dynamic susceptibility explaining thus both the drop of $K$ and peak in $1/T_1 T$. Charfi-Kaddour et al. [42,43] have calculated the contribution to the relaxation rate at the nesting vector in a 2D interacting electron gas model. They show the existence of a maximum of relaxation as a function of temperature which depends on the nesting and on the strength of the correlations.

Also Kampf et al. [41] have shown that spin fluctuations in a two-dimensional metal with a nested Fermi surface lead to a pseudo gap in the electronic spectrum. Although these studies were made in the context of copper oxide superconductors, the main ingredients used in the calculation i.e. imperfect nesting and Coulomb repulsion, do exist as well in the organic systems we study here. Charfi-Kaddour et al. [42,43] in their model have defined the conditions for this pseudo gap to develop: good nesting, strong correlations and low temperature. The same authors have then calculated the electron scattering contribution due to the AF fluctuations. They show the existence of a crossover temperature for the resistivity strongly correlated to the maximum of $1/T_1 T$, in qualitative agreement with the experiments (Fig. 10, [10]). The measurements on $\kappa$-(ET)$_2$X meet the expectations of this theoretical model: the disappearance of the spin fluctuations under pressure is observed in the spin-lattice relaxation rate measurements parallel to the reduction of the pseudo-gap which manifests in the decrease of the Knight shift (Fig. 7).

Above 4 kbar all the properties become more usual for a metal. The nesting enhanced AF fluctuations are certainly more dependent on pressure than the effects coming only from the pressure dependence of the bandwidth, so that one would have to include the true Fermi surface shape of ET salts in order to get a quantitative account of the observed effects. Indeed, whereas in the previous analysis of the pressure dependence of the Knight shift we found that it varies by 6%/kbar, the relaxation is much more sensitive on pressure in the interval of temperature where the AF fluctuations are dominant. The effect of pressure would then be to reduce the quality of the nesting. This reminds the situation in 1D systems like (TMTSF)$_2$PF$_6$ where the application of pressure results in reduction of the SDW transition temperature. Such effect was attributed to the increased overlap of $\pi$ orbitals in the transverse direction which destroys the perfect 1D-nesting and inhibits the growth of $2k_F$ spin fluctuations at low temperature [29,39,44]. In our case the reduction of the nested parts can explain the reduction of spin fluctuations and the disappearance of the pseudo-gap. Furthermore, it is interesting to note that, similar to what is observed in the 1D systems, this evolution under pressure is accompanied by the
disappearance of the superconductivity. This observation emphasizes once again the relation between spin fluctuations and superconductivity.

Following the example of a unified phase diagram for 1D conductors [44], Mayaffre [8] proposed an implementation of such general $p-T$ phase diagram for the $\kappa$ phases. This is shown in Figure 12. The important feature of this phase diagram is the proximity of antiferromagnetism and superconductivity as already suggested by the observation of the relaxation peak but finally confirmed by the discovery of the antiferromagnetic ground state in $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl [22,45,46]. The fact that when applying pressure this compound becomes superconducting reminds the properties of the phase diagram of for the (TMTSF)$_2$X-(TMTTF)$_2$X family which shows in fact some similarities with the one of Figure 12. However, in 1D compounds, the mechanisms governing the low temperature behaviour are certainly different, since the 1D chain structure and the dimensionality crossover play a fundamental role. It was shown indeed that in 1D systems the 2D or 3D nesting leads to two different mechanisms relying on the interchain tunneling and competing for the stabilization of the ground state [39,44]. In the present case, although the nesting has a 1D character, the electron gas remain essentially two-dimensional for all temperatures. On the other hand, the above phase diagram is also similar to that of the underdoped YBa$_2$Cu$_3$O$_{x}$ (although the comparison is not straightforward since in our phase diagram the pressure affects only the bandwidth but not the band filling, whereas in the HTSC the role of “coupling parameter” is played by the doping which governs the carrier concentration). This comparison raises once again the question about the nature of the antiferromagnetism in the 2D organics: it shows at the same time some similarities with the localized antiferromagnetism of HTSC and with the itinerant, nesting-driven magnetism of low-dimensional systems. Probably, an extensive study of the antiferromagnetic state in $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl (which is commensurate despite of the incommensurate nesting vector) would be of great interest.

3. $^{13}$C NMR in the Superconducting State

There is still no general consensus on the mechanisms of superconductivity in quasi-two-dimensional organic superconductors. 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 [47, 48] and a more unconventional pairing [49–52] have been proposed. The latter was motivated by the fact that pronounced electron correlations appear to be a common property for cuprate high-$T_c$ or heavy fermion superconductors. On one hand the available studies of the temperature dependence of the superconducting gap and of the electromagnetic properties seem to exclude non conventional schemes such as local-pairing model. on the other hand there is no decisive arguments for neither BCS-type pairing nor for the pairing mechanism [53]. Crucial experiments and methods do not give convergent results, another example here is some number of isotope effect reports which so far did not converge into a consistent picture.

In the history of classical superconductors NMR supplied one of decisive experiments to establish the relevance of the BCS model. Certainly the best known NMR hallmark of a BCS superconductor is the observation of the Hebel-Slichter peak in the relaxation rate just below the transition and an activated behaviour of $1/T_1$ at low temperatures. This is not the case for materials studied here and different pictures are found to be consistent with the NMR data. However, we will see that NMR can provide a very "pure" probe of the electronic properties such as density of states in the superconducting state and from this point of view it is one of the most precious experimental tools.

$^{13}$C NMR is particularly adapted to probe the electronic properties, since the carbon atoms lie in the core of the conducting layers. In particular, it is important that it is not very sensitive to the relaxation due to flux line motions, responsible for the well known peak in $^1$H relaxation which will be discussed in the next section.

Below we discuss recent Knight shift and relaxation measurements made on $κ$-(ET)$_2$Cu[N\(\text{CN})_2]Br for two orientates of the crystal: field perpendicular (\(H_0 || b\)) and parallel (\(H_0\)) in the \((a-c)\) plane) to the conducting layers. The corresponding $^{13}$C spectra are those shown in Figure 1a and b (Sect. 2.1). The Knight shift has been measured as the frequency interval between two lines of the spectrum belonging to neighbouring carbon sites [6]. This method relies on the fact that both sites have nearly the same chemical shift and further has the advantage of avoiding a possible demagnetizing effect. The experimental error at low temperature is due to an inhomogeneous line broadening below 190 K proportional to the Knight shift (Sect. 2.2) and to the dipolar coupling [6]. The latter limitation becomes important at low field, consequently the Knight shift data has been available only for high field (7.8 T). Also, the extraction of a reliable set of $T_1$'s for the field and temperature dependence is not straightforward because of the dipolar coupling. As we already pointed out [6], only the average relaxation rate of two neighbouring carbon sites is free of parasitic temperature dependence resulting from dipolar coupling.

Let us consider first the results obtained in a field perpendicular to the conducting layers. These are presented in Figure 13 (Knight shift) and Figure 14 ($T_1$).

Anticipating the interpretation given further we expect the following scenario: in the mixed state there are two kinds of electronic spins interacting with $^{13}$C nuclei, those of normal electrons in the vortex cores and those of thermally broken superconducting pairs. As we will see later, in high field (7.8 T), the majority of $^{13}$C nuclear spins (80%) are inside vortex cores. In this case the measured Knight shift is due almost only to electrons in the metallic state. Indeed, the data in Figure 13 (black circles) show that there is no change at the superconducting transition and that the Knight shift decreases steadily from temperatures above $T_c$ (in fact, the slope remains almost constant below 50 K as we have seen the previous section). Using these data we can plot the term $AK(T^2$) (solid line in Fig. 14) where $A = 0.19 K^{-1}s^{-1}$ and $K$ is normalized to unity at 300 K. From the observation that the Korringa relation $(T_1T)^{-1} = AK^2$ is obeyed above $T_c$ (8 K at 7.8 T) we can assume that such relation gives a good description
Fig. 13. — Normalized Knight shift at 7.8 T in perpendicular field (black circles) and parallel field (open circles).

Fig. 14. — $(T_1T)^{-1}$ in perpendicular field. 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.

of the electronic behavior in the vortex cores. Nevertheless this is only a phenomenological approach and one must not forget that this linear behavior is not necessarily a true Korringa law, since as we have seen in the previous section $(T_1T)^{-1}$ is already enhanced above 20 K due to spin fluctuations with a non-zero wave vector. Notice here that 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 even at such low temperature.

As for $(T_1T)^{-1}$, presents a strong field dependence below $T_c$ and tends to saturate at low temperatures (Fig. 14). The field dependence is a signature of a relaxation due to normal electrons in the vortex cores: it merely reflects the variation of the vortex density with the field. This type of relaxation has been also observed by Silbernagel et al. [54] in a conventional type-II superconductor, $V_3$Si, and similar field dependence have been studied recently in HTSC
Fig. 15. — $(T_1 T)^{-1}$ at 4.2 K versus magnetic field. The dotted line corresponds to the 12 K value.

[55, 56]. In $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br the field dependence is particularly important because we are relatively close to $H_{c2}$.

To interpret the curves of Figure 14 we have considered a simple model, with two different sources of relaxation [6]. The first $(n T_1)$ comes from normal electrons in the vortex cores and the second $(s T_1)$ 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:

$$\frac{1}{T_1} = \frac{H_0}{H_{c2}} \frac{1}{n T_1} + (1 - \frac{H_0}{H_{c2}}) \frac{1}{s T_1}$$

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 contribution $n T_1$ can be estimated from the data at $T \ll T_c$ since then the relaxation from normal electrons is dominant. Therefore, assuming that the latter follows a Korringa law, we should observe :

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

The field dependence is analyzed in Figure 15, where $(T_1 T)^{-1}$ at 4.2 K is plotted versus the field. Taking for $(n T_1 T)^{-1}$ the value at 12 K (dotted line) we derive an estimate of $H_{c2}$. This estimate can be refined extrapolating the $T_1$ data to zero temperature [6] and yields $H_{c2} = 10$ T and $\xi_{ac} = 60$ Å. The obtained value of $\xi_{ac}$ is larger compared to those already published [57-59].

Other determinations of $H_{c2}$ were derived from the zero temperature extrapolation of $dH_{c2}/dT$ near $T_c$ which yield always $H_{c2} > 20$ T (except the measurements of Vulcanescu et al. [60] performed at low temperature and giving $H_{c2} \approx 18$ T). The present method of determination should in principle be more reliable because it directly involves the low temperature and high field measurements.

The used model works under the assumption that all nuclei are equally coupled to both sources of relaxation. Such hypothesis is first of all supported by the observation of single exponential decays [6, 8]. This is usually attributed to a rapid spin diffusion, however, the characteristic spin diffusion time on the vortex lattice lengthscale is too long to justify a relaxation averaging [6]. A mechanism which is found to be justified here is due to a rapid diffusion of vortex cores themselves, also invoked by Martindale et al. [56]. We will see in Section 4 that the measurements presented in Figures 13 and 14 were performed above the irreversibility line and therefore in the vortex-liquid state where a rapid diffusion of vortex cores ensures a good contact between a given nucleus and all relaxation sources.
The existence of a linear relation between the magnetic field and the “normal” component of the relaxation means that the number of normal electrons is proportional to the number of vortices. Let us mention here that it is not obvious in general to suppose that the contributions of different vortices are independent and additive. Volovik [61] has shown that for an anisotropic superconducting gap with zeros at the Fermi level a big part of the electronic density comes from the delocalized states outside the vortex cores. This lead to an average density of states varying as $\sqrt{H}$. The calculation of the relaxation rate is not given in [61] but one can expect it to be slower than linear in such case.

We now turn to the measurements performed in parallel field and presented in Figures 13 and 17 (Knight shift) and Figure 16 ($T_1$). The extremely weak angular width of the lock-in state was confirmed in the angle-resolved NMR study by De Soto et al. [36]. It was therefore a technical challenge in these measurements to get the perfect sample orientation and achieve a true lock-in state. The detailed study of the NMR spectrum revealed the large anisotropy of the shift tensors (Sect. 2.1) it was thus possible to use this property to align the crystal in the field to within $\pm 0.25^\circ$ [6,8].

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 configuration, as expected for a true lock-in state. The mentioned above “angular sharpness” of this state (see Sect. 4) is well demonstrated in Figure 16 where we have also plotted the results obtained with a misalignment of about two degrees (black squares). Such misalignment is enough to cause creation of pancakes vortices which highly enhance the relaxation at low temperature.

The possibility of performing NMR measurements in the lock-in state is highly attractive since it gives the possibility to perform unique studies on the 2D superconductor: the Knight shift gives the spin susceptibility in the superconducting state and the relaxation rate probes the density of superconducting pair excitations. This is because in parallel configuration the field penetrates completely into the insulating layers and is screened by Josephson currents without need for creating pancake vortices. It was shown that the presence of such “Josephson vortex” centered on the insulating layer do not change the amplitude of the order parameter in the conducting planes [62]. Apart from presenting the difficulty of aligning the sample, this
method of eliminating the problems of the mixed state is technically much easier than the classical approach based on NMR measurements with field cycling or NQR at zero field.

We see in Figure 13 (open circles) that the Knight shift decreases more quickly below $T_c$ and tends towards zero at low temperature. This gives an evidence that the spin paring 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 [63]. On the contrary, in a singlet state, the Knight shift should follow the Yosida function [64] which tends to zero at low temperatures. In principle also the symmetry of the gap function can be determined from the temperature dependence of the Knight shift. In Figure 17 we have plotted $K_s/K_n$ together with theoretical curves for an isotropic s gap [64] and a d-wave gap [65]. Unfortunately this result cannot be considered as decisive because of the experimental error.

The relaxation studies give more interesting information. Note first that the relaxation rate is not enhanced just below $T_c$, i.e. there is no Hebel-Slichter peak. The absence of coherence peak can be explained as the influence of AF correlations in the case of an anisotropic gap [65,66]. On the other hand, we observe that the variation of the relaxation rate $s$ faster just below $T_c$. This effect also observed in HTSC may be interpreted as the disappearance of the contribution of spin fluctuations at the superconducting transition.

But, probably the most valuable result of these studies was the discovery that $(T_1)^{-1}$ follows a $T^3$ law below $T_c$. The data of Figure 16 show undoubtedly that such law is valid over a very wide range of temperature. Such behaviour was first observed by Takigawa et al. [67], in a quasi-one-dimensional organic superconductor, (TMTSF)$_2$ClO$_4$. Hasegawa et al. [68] have proposed a theoretical model based on an anisotropic gap with lines of zeros at the Fermi surface. They found that the Hebel-Slichter peak is greatly reduced and that the relaxation rate follows a $T^3$ law at low temperature because of the linear density of states at low energy. This model was important because it gave a motivation for searching new types of pairing. Also
in HTSC, the $T^3$ law has been observed several times [56, 69] and has been often interpreted as a signature of d-wave pairing. Indeed, theoretical calculations involving a d-wave pairing are in general in good agreement with the experimental results [65, 66, 70]. Nevertheless, as Martindale et al. [56] 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 $\exp(-\Delta/k_BT)$ behavior with varying $\Delta$'s, for an anisotropic nodeless gap. In the present case we would have: $\Delta/k_BT_c = 0.3$ at the lowest temperatures and $\Delta/k_BT_c = 3.2$ near 10 K. These estimates would mean that if the gap is nodeless its anisotropy must be greater than 10.

In summary, these results provide a solid experimental evidence for a very anisotropic (possibly with nodes in the gap) spin-singlet pairing in this class of 2-D superconductors. The possibility for non-conventional pairing in 2-D organic superconductors has been pointed out by Bulaevskii [3]. This pairing could bear some resemblance with the spin fluctuation mediated interchain interaction proposed by Bourbonnais and Caron [39, 71] in the context of 1-D superconductors.

4. Vortex Dynamics by $^1$H NMR

NMR studies of the mixed state of layered superconductors are motivated by the sensitivity of this technique to the magnetic field created by vortices. It would be impossible here to present a general survey of the physics of the mixed state and the reader can refer to dedicated reviews like [72, 73] to access the vast bibliography.

A common property of layered superconductors is the existence in their phase diagram of the so-called irreversibility line defined by the characteristic field $H_{irr}(T)$. In cuprate superconductors there are some evidences that this line defines a phase boundary in the mixed state which separates a vortex-liquid and a vortex-solid states. This interpretation is consistent with a general observation that the onset of non-zero resistivity corresponds to the irreversibility line. The simplest picture corresponds to that of melting of a vortex lattice above some critical temperature which makes the collective pinning mechanism ineffective and lets vortices move and dissipate energy. Such effects have originally been attributed to High-$T_c$ superconductors due to their high transition temperature $T_c$ and a short in-plane correlation length $\xi$, making the superconductor less sensitive to pinning by localized defects. The observation of the same phenomena in organic superconductors shows that they may be more generally related to quasi-2D structures with weak inter-layer coupling.

Various explanations of the irreversibility line were proposed. Among the models involved one can distinguish those supposing a thermodynamic transition either to a vortex lattice or to a vortex glass state below $T_{irr}$ and those invoking a thermally assisted depinning of vortices [72]. So far there is no direct experimental evidence favouring any of them in organic superconductors.

A remarkable property of the NMR relaxation in the system of vortices is that although being local i.e. integrated over wave numbers, nevertheless it gives access to low lying long wave excitations of the vortex system, namely to sounds of the lattice and to the plastic hydrodynamics of intrinsic defects. Before discussing how NMR may well contribute to elucidate the fundamental questions it is important to understand the main differences between the usual transport and magnetization techniques sensitive to bulk properties and the local probe such as the NMR. The essential difference is due to different characteristic timescales of these experiments. The DC transport and magnetization experiments are performed at low frequencies and thus are sensitive to the pinning of the vortex system as a whole, whereas the NMR probes the fluctuations of vortices typically at frequencies of the order of $10^7 - 10^8$ Hz. In the relatively pure materials like $\kappa$-(ET)$_2$X the characteristic timescale corresponding to such high frequencies is usually smaller than the mean distance between pinning centers and thus
we can say that in some sense NMR is insensitive to phenomena related with pinning. This makes the use of NMR very attractive as a probe of vortex kinetics on a microscopic scale.

A spectacular effect is the observation [7,36,50,74] of the peak in dependence of $^1$H relaxation rate on temperature $T$ at given magnetic field $B$. It is now practically admitted that this peak is due to the magnetic fluctuations induced by motions of the flux lines, as was first suggested by Takahashi et al. [50] who studied the relaxation of $^1$H and $^{13}$C and concluded that such effect cannot be interpreted as a usual coherence peak. It is important to emphasize once again on a very weak interaction of $^1$H nuclei spins located at the end of the BEDT molecules with electronic spins. On the contrary, in High-$T_c$ materials the Korringa tail of the relaxation dominates over the orbital effects [75–77].

The direct evidence that proton relaxation is governed by the flux line motion was given by the experiment of De Soto et al. who performed an angular study on a single crystal of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br. The orientation dependence of $1/T_1$ (Fig. 18) reveals a sharp depression in a very small range around the position where the field is parallel to the layers. This is explained by the occurrence in this angle range of the “lock-in” state, in which the flux lines are pinned entirely between the conducting planes and their movement is drastically reduced. The existence of the lock-in state was predicted as a consequence of a discrete nature of 2D layered structure [72,78] and has been confirmed in $\kappa$-(ET)$_2$X materials by ac-susceptibility measurements [79].

The next important observation is that the peak position $T_m(B)$ follows the irreversibility line [7,50]. One is lead to think that it is related to critical effects at the transition between a solid and a liquid states of the vortex system. Nevertheless this question is not settled yet. The difficulty in the interpretation of the NMR is that it can hardly distinguish between the dependencies on the magnetic field and on frequency. For example, in the conventional interpretation of the irreversibility line in terms of thermally assisted depinning, the timescale of the experiment has an effect on the observed transition temperature: in this interpretation the relaxation peak is a frequency effect i.e. it is a simple relaxation enhancement when the characteristic time of the vortex motion matches the Larmor frequency [50]. This hypothesis leads to a BPP-like model, the use of such approach may indeed be encouraged by the simple field dependence ($B^{-1}$) of the amplitude of the relaxation peak. This kind of approach was recently used by Suh et al. [76] to analyze the relaxation peak observed in a High-$T_c$ material. However, as we stressed above, testing theoretical models would require a sufficient data set in order to decouple field and frequency effects.
Fig. 19. — \(^1\)H NMR relaxation rate for fields perpendicular to the conducting layers. The data at 0.59T are from De Soto et al. The continuous line is the exponential fit of the low temperature part of the curve, as discussed in the text.

In this respect, recent results on \(\kappa-(ET)_2\text{Cu}[\text{N(CN)}_2]\text{Br}\) [7] should bring a significant progress. These are shown in Figure 19 which presents the variation of the relaxation rate versus temperature at several fields ranging from 0.45 T to 9.3 T (the data at 0.59 T are from [36] and are in excellent agreement with our data for other fields). It was the first time that the relaxation peak could be followed on such a large range of fields. Moreover, the effect is amplified by the absence of any background relaxation, in contrast to results reported in High-\(T_c\)'s [76,77] where hyperfine relaxation is always dominant. Hence, the quality of the data allows to discover new remarkable features in the \((T, B)\) dependence which has not been seen before. The most striking observation is that the field dependence of \(T_1^{-1}\) disappears progressively below the transition line, leading to a single "master curve" \(W(T)\) at low temperature.

The remarkable feature of these results is the correlation between the relaxation peak and the VL melting. Plotting the position of the \(T_1\) peak in the \((B, T)\) plane we obtain a smooth line shown in Figure 20. This line goes very close to the magnetization irreversibility line [48] and to the transition line obtained from ac-susceptibility measurements [80], except for high fields where the NMR peak shifts to higher temperatures.

In the 3D-anisotropic model, the melting line derived from the Lindemann criterion is expected to follow a \(B_m \sim T_m^{-2}\) law whereas it is expected to be nearly vertical for the melting of a quasi-2D vortex lattice at a nearly constant temperature \(T \approx T_{2D}\). Here, the slope becomes very large above \(B \approx 2\) T: if we fit the whole curve with a power law we obtain instead \(B_m \propto T_m^{-4.5}\) (see solid line in Fig. 20). Therefore, it is likely that our phase diagram is compatible with an essentially quasi-2D picture: it is possible that at high fields the layer decoupling occurs at much lower temperatures, giving rise to a 2D melting transition which is almost field independent. Following this interpretation, the transition line should have two regimes: a vertical line at high fields and a 3D melting \(T^{-2}\) law at low fields.

Our findings correlate with recent studies of the phase diagram of the HTSC. The moderately anisotropic YBaCu compounds demonstrated the expected 1-st order phase transition between the crystal and the liquid of continuous vortex lines. Even then, the deviation from the vortex line melting picture have shown itself at high fields as disappearance of the 1-st order transition
line or its transformation to the II-nd order one. In BSCCO compounds the recent studies by traditional methods [81] and confirmed by original local measurements [82], reveal a completely different scenario. The difference seems to be due to interplane coupling strength.

Hence, the dimensionality of the system is the key question if we are to discuss different regimes of the vortex motion and their contribution to the relaxation. The situation is complicated by controversial data on the degree of anisotropy in organic superconductors in compare to referent HTSC. In recent two years the degree of anisotropy has been dramatically reconsidered both for organic superconductors and for the High-\(T_c\) BSCCO family. The ratio \(\Gamma = \lambda_c/\lambda_{ab}\), once thought to be \(\Gamma < 10\) for BEDT and \(\Gamma \sim 20 \div 50\) for BSCCO, may actually reach the values \(\Gamma \sim 150 \div 300\) according to recent measurements [83,84].

An essentially quasi 2D nature of the BSCCO compounds has been confirmed [81,82] by observations that with increasing \(B\) the melting line disappears at fields as low as 300 G which is of the order of \(H_d\) for that material. A natural candidate for such a low crossover field has been found [81] in the decoupling scenario [85,86]. According to this picture, even weak vortex fluctuations below the 2D melting are sufficient to destroy the inter-plane Josephson coupling at \(B > B_{cr} = C\Phi_0/\Lambda^2\), \(\Lambda = \Gamma d\). Here \(\Lambda\) is a so called Josephson coupling length and \(d\) is the inter-plane distance. With \(d = 15\) Å \(\Gamma > 100\) would ensure us that at our lowest fields \(\approx 1\) T we always sweep the 2D part of the phase diagram.

In 2D regime, a Berezinskii-Kosterlitz-Thouless (BKT) type of the melting phase transition occurs at \(T_{2D} \approx 0.05T_0\) where \(T_0 = (\Phi_0/4\pi\lambda)^2d/2\) is the energy scale for a Pancake Vortex (PCV) [72,87]. For BEDT with \(\lambda \approx 6000\) Å we find \(T_0 \approx 40\) K hence \(T_{2D} \approx 2\) K which is plausible to identify with the transition line observed at \(T = T_m(B) \approx 3 \div 6\) K. A sharp \(T\) dependence of the curve \(B = B_m(T)\), Figure 20, agrees with the expected weak field dependence of \(T_{2D}\). Computer simulations [88] also seem to confirm the decoupling regime: if rescaled from \(\lambda = 1500\) Å to \(\lambda = 6000\) Å, their results give \(T_{2D} \approx 3\) K and \(T_{dc} \approx 0.03\) K. The presented NMR experiments have been performed at fields \(B \geq 1\) T and at \(T > 1\) K, hence assuming the moderately high values of \(\Gamma\) we expect to test the 2D part of the phase diagram and to approach the 2D melting temperature which really seems to happen at \(T_m \approx 3 \div 6\) K.

The recent transport study in the vortex liquid state of \(\kappa-(ET)_2Cu(NCS)_2\) indicated the existence of 2D-3D crossover around \(B \approx 1\) T [89], which follows the above estimations.
However, similar experiments carried by the same authors on \( \kappa-(ET)_2\text{Cu[N(CN)]}_2\text{Br} \) [90] would rather indicate that the crossover is shifted to higher fields in this compound. Therefore, the question of dimensionality at low fields (1 T) is still opened. However, it seems that it is not necessary to be strictly in decoupled regime in order to be allowed to apply the 2D treatment. As was pointed out by the authors [7, 91], at finite temperature the vortex segments of adjacent layers are aligned only in average, allowing density fluctuations in each layer to be quasi independent (this state is named “flux density wave” in [91]).

It is widely believed that, according to [85, 86], even at \( B > B_{cr} \) a finite temperature \( T > T_{dc}(B) \) is required to decouple the planes. However, let us mention here that some arguments may be presented [91] that planes are decoupled at all finite \( T \) as long as \( B > B_{cr} \).

As for the theoretical studies, the work [75] was the first to address the NMR relaxation by the fluctuating motion of vortices, although in High-\( T_c \) materials the effect was rather structureless. Since then a number of different approaches have already been devoted to this question. The Langevin dynamics simulations [88] seem most promising in the fact that it can reproduce a softening in the dynamic structure factor of the lattice without any hypothesis a priori about the nature of the transition. However, in the published results the relaxation peak has a frequency dependence which is not confirmed experimentally, also the maximum of \( 1/T_1 \) is broad and has no clear relation to the melting line. Note that many other numerical simulations have been published, but unfortunately most of them give only access to the static structure factor of the system and cannot be used to study the NMR properties. Another way to produce a peak in \( 1/T_1 \) is to invoke the BPP relation for the correlation functions of the vortex density [76]: 

\[
1/T_1 \propto \tau/((\omega \tau)^2 + 1)
\]

implying that \( \tau \) is a monotonic function of \( T \) so that the maximum is attained at \( \tau \sim \omega^{-1} \). However this interpretation does not take into account the relation of the peak to the melting transition. Otherwise the harmonic approximation for the vortex motion in the solid phase have been exploited [75, 92, 93]. The emphasis was given to the averaged [75] and the local inhomogeneous [93] regimes of the relaxation by thermal fluctuations in the 2D vortex crystals bound by the magnetic coupling and to the quantum fluctuations of vortex lines in the isotropic system [92].

At first sight any consistent treatment using general laws of the vortex kinetics may provide a crude description of the effect. Indeed, a low temperature increase of \( T^{-1}_1 \) will always behave at least as \( T \) due to equipartition principle for fluctuations (as was observed and calculated for High-\( T_c \) materials [75]). At higher \( T \) the effect should disappear approaching \( T_c(B) \), altogether with the vortices, hence one always obtains a non monotonic \( T \)-dependence provided other sources of relaxation are negligible. Nevertheless this basic approach cannot give account, even empirically, for such an important feature as the peak sharpness and its positioning on the melting line.

Taking into account the presented results, selecting the appropriate regime of the vortex motion should now be guided by well distinguished features:

(i) a pronounced magnitude of the effect and the peak sharpness;

(ii) the peak location at the phase transition line with the absence of evidences for both the first order phase transition and phase separation;

(iii) a superlinear increase in a wide region of low temperatures and the “master curve” \( W(T) \) for the family of lines \( W(T, B) \).

In order to see how different ingredients of the vortex state contribute to the NMR relaxation let us first recall the basic formalism [75, 91]. The relaxation of a nuclei at the point \( \mathbf{R} = (r, z) \) is given by the mean square fluctuation of the in-plane magnetic field \( \delta \mathbf{B}^{xy}(\mathbf{R}, t) \) at the NMR frequency \( \omega \) for the applied field \( B \) in the \( z \) direction. In its turn \( \delta \mathbf{B}^{xy} \) is due to the density fluctuations \( \delta \rho(\mathbf{R}, t) \) of the vortices. In inhomogeneous system the relaxation rate depends on the position of the nuclei: \( W = W(\mathbf{R}) \). Suppose there is an intensive diffusion of nuclear
magnetization or of vortices so that the diffusion time over a distance \( \alpha \) is shorter than the resulting \( T_1 \). Then the relaxation rate \( W \) averaged over the volume \( V \) is observed as the inverse relaxation time \( T_1^{-1} \). This case is usually supposed in the literature, except for \[93\].

Following general principles \[17\] the NMR relaxation at the point \( \mathbf{R} \) is

\[
W(\mathbf{R}) = \gamma_N^2 \int \int dt \, d\mathbf{R}_1 \, d\mathbf{R}_2 \, \delta \mathbf{B}^{zy}(\mathbf{R} - \mathbf{R}_1) \delta \mathbf{B}^{zy}(\mathbf{R} - \mathbf{R}_2) \, D_\rho(\mathbf{R}_1, \mathbf{R}_2, t) \cos[\omega t]
\]

where \( \mathbf{R} = (r, z) \), \( D_\rho(\mathbf{R}_1, \mathbf{R}_2, t) = \langle \delta \rho(\mathbf{R}_1, 0) \delta \rho(\mathbf{R}_2, t) \rangle \) is the correlation function of the vortex density fluctuations \( \delta \rho \), \( \delta \mathbf{B}^{zy}(\mathbf{R}, t) \) is the in-plane magnetic field generated by a single pancake vortex \( \gamma_N \) is the gyromagnetic ratio of the nucleus.

Then the space-averaged relaxation rate \( \overline{W} \) can be expressed as

\[
\overline{W} = \omega^2 \int dt \, d\mathbf{R}_1 \, d\mathbf{R}_2 \cos\omega t \mathcal{K}(\mathbf{R}_1 - \mathbf{R}_2) \, D_j(\mathbf{R}_1, \mathbf{R}_2, t)
\]

\[
\mathcal{K}(\mathbf{R}) = \frac{a^2 \ddagger}{8 \pi \lambda^4} \left( \frac{r^2}{R^3} - \frac{z^2}{R^2 \lambda} \right) \exp\left[-\frac{R}{\lambda}\right]
\]

where we introduced the correlation function \( D_j = \langle j(\mathbf{R}_1, 0) j(\mathbf{R}_2, t) \rangle \) of the longitudinal flows of vortices \( j = \nu \mathbf{v} \) where \( \mathbf{v} \) is the local vortex velocity. The form-factor \( \mathcal{K}(\mathbf{R}_1 - \mathbf{R}_2) \) gives the overlap of the in-plane magnetic field generated by two vortices at points \( \mathbf{R}_1 \) and \( \mathbf{R}_2 \) \[72\] and \( \lambda \) stands here for the in-plane penetration depth. The dependence of \( W \) on vortex-vortex correlation functions and the overlap of magnetic fields comes from the non-local character of the vortex-nucleus interaction.

These expressions tell us first that the 3D correlations along the vortex line suppress the NMR relaxation because of vanishing weight \( \mathcal{K} \sim g_s^2 \) whereas for decoupled planes \( g_s \approx a^{-1} \) is large. Moreover, we see that in 2D the divergence of \( \int d^2r/r \) will make \( W \) very sensitive to the in-plane correlation radius of \( D_j \), we expect thus a divergent behavior of \( W \) near \( T_m \). In conclusion, we can expect the effect of the fluctuations on \( W \) to be in general much stronger in the 2D regime. This is easy to understand. The relaxation comes from fluctuating fields parallel to the planes. In 3D such field may only be created by bending of the vortex lines which is limited by the stiffness of the lattice. On the other hand, local density fluctuations in a 2D layer will create an important magnetic field penetrating a large number of other layers.

Let us now compare theory and experiment quoting results for different regimes of the vortex motion. The problem is in fact reduced to the calculation of the correlation function \( D_j \) for different models.

In harmonic regime we can apply the well known results for elastic response functions \[72, 75\]. We find for the 3D regime of correlated vortex lines (valid at \( \Gamma < 30 \) \[7, 91\]):

\[
W_{3D} \sim 10^{-2} \Gamma \frac{\omega^2 \ddagger}{\omega_1} \frac{d^3}{\xi T_0} \sim 10^{-4} \frac{\Gamma T[K]}{(B[T])^{1/2}}
\]

Here \( \omega_1 \) is the frequency of longitudinal relaxation related to the vortex line viscosity \( \eta \) as

\[
\omega_1 = \frac{8 \pi T_0}{\ddagger} \frac{\omega}{\omega_1} \sim 10^{-3}
\]

where the numerical estimation implies the Bardeen-Stephen result for \( \eta \) \[7, 91\].

In the 2D regime

\[
W_{2D} \sim \omega \left( \frac{a}{\lambda} \right)^4 \frac{d}{\xi T_0} \exp\left[-\frac{T}{T_2D}\right], \quad T_\omega \approx \frac{6T_{2D}}{\ln(16\pi \omega_1/\omega)} \approx \frac{T_{2D}}{2}
\]  

(10)
where \( \xi_1 \) is the effective PCV core size and the last factor comes from the scaling laws characteristic for the BKT state \([91]\).

We see first that both \( W_{d1}^{2D} \) and \( W_{d1}^{3D} \) show a strong field dependence \( \sim B^{-1/2} \), in disagreement with the experimental master curve (near \( T_{2D} \) we have \( \xi_1 \sim a \) but at low \( T \) when \( \xi_1 \approx \xi \) the dependence of \( B \) is even stronger \( W_{2D}. \) \( W_{3D} \sim B^{-1} \)). Moreover the numerical estimation shows a lack of 2 or 3 orders of magnitude in the amplitude of \( W_{d1}^{2D} \) at low \( T \). Contrary to \( W_{2D} \), the magnitude of \( W_{2D} \) is large but it increases sublinearly with \( T \) contrary to experiment.

All together these discrepancies motivated us to look for another mechanism related to the defects of the vortex structure \([7,91]\). In 2D, at \( T < T_m^{2D} \), we suggested that the fluctuations other than those due to elastic distortions can be originated by mobile plastic deformations: symmetric defects and bound pairs of dislocations or unbound dislocations. The dislocations at \( T \geq T_m^{2D} \) are expected to have the lowest activation energies (of the order of \( T_m^{2D} \)) since only share deformations are involved. But in view of low lattice compressibility they almost do not disturb the vortex density at distances larger than the mean VL spacing, hence the generated fluctuating magnetic fields are small. The point defects are expected to have larger activation energies \( (T_{2D} < E_d < T_0) \), nevertheless their motion generates the strongest fluctuations of the magnetic field, covering the volume \( \sim \lambda^3 \), in contrast to \( a^3 \) for other defects and penetrating over the largest number of planes \( \sim \lambda/a \). It makes their contribution dominating at intermediate temperature when the defect concentration is not negligible.

Considering defects as classical particles occupying preferential positions in the lattice we expect that the concentration of defects per one PCV is \( n_d \propto \exp(-E_d/T) \) where \( E = E(T) \) is the characteristic energy. We obtain thus an activated law for the relaxation:

\[
W_d \approx \frac{\omega d n_d}{\sqrt{\omega t_\lambda + 1}} \exp \left( -\frac{E_d}{T} \right) ; \quad t_\lambda = \frac{\lambda^2}{2D \omega \Delta T} \sim 10^{-7}s
\]

where \( D \) is the diffusion coefficient of defects. At small \( B \) or at large \( D \) we have \( \bar{W} \sim n_d \lambda^3 \) does not depend on anything but the concentration of defects and on \( \lambda \) at given \( T, B \), then we have a field independent “master curve” \( W(T) \sim n_d(T) \). Otherwise at large \( B \) or small \( D \) we have \( W_d \sim n_d \sqrt{D/\omega}/\lambda^4 \) which falls with increasing \( B \). The crossover between the two regimes happens when the diffusion length \( \sqrt{D/\omega} \) of the defect over the NMR period is about \( \lambda \), which requires \( D \sim 10^{-11}cm^2/s \). The contribution of defects has another useful feature important in connection with experimental observation at \( T < T_m \) since it does not contain ill-defined parameters like \( \Gamma \) and \( D \), hence we get a direct access to a concentration of point defects and the numerical estimation of \( W_d \) can be considered as rather reliable. We find \( W_d \sim 10 \exp(-E_d/T) \) in a reasonable quantitative agreement with experiment. Notice that the whole curve could not be fitted with a constant activation energy. Being fitted at low temperatures where data have high accuracy it shows a superexponential shape at higher \( T \). This feature may be due to a natural decrease of \( E = E_d(T) \) near melting point or due to unidentified critical effects in compressibility of the defect gas. The decrease of \( W \) at high \( T \) slope may be explained in various ways. The most integrated scenario comes from the observation that the point defects may be transformed to a bound pair of dislocations. Unbinding of dislocations at \( T_{2D} \) may reduce critically the lifetimes of point defects, in their turn dislocations do not participate as effectively to the NMR relaxation because they create nearly incompressible configurations with only local magnetic field. Another, complementary description involves pretransitional fluctuations in vortex liquid, which should exist if the transition is not of the pronounced first order. More details can be found in \([91]\).

In conclusion, the NMR relaxation by the thermal motion of vortices gives access to their correlations and especially to the plastic hydrodynamics of the intrinsic defects. The existence
of a close correlation between the relaxation peak and the melting transition shows undoubtedly that the sharp grow of $1/T_1$ near $T_m$ has a critical character. We can state in general that only 2D regime can provide the observed magnitude of the effect. In the high field domain $B > B_{cr}$ the inter-plane correlation is destroyed at least at $T > T_{dc}(B)$ and these conditions are met at least for the most of the presented experiments. In the BKT state of a decoupled plane below the melting temperature $T_{2D}$ the fluctuations are originated either by harmonic distortions of the local crystalline order or by the local thermally activated defects. We supposed that the low temperature development of the relaxation anomaly is due to a progressive softening of the vortex lattice in a broad temperature range below $T_m$ we then analyzed contributions from harmonic and plastic fluctuations of the lattice to the nuclear relaxation. The former shows a strong magnetic field dependence which is not observed in our experiments. The latter provides a more favorite picture in which the softening proceeds locally via excitation of symmetric defects. The persistence of the phenomenon at low temperatures would then give evidence of small activation energy and large mobility of defects, leading us to say that the vortex lattice is strongly delocalized already below the melting.

Concluding Remarks

Despite of the important experimental effort employed, many of the basic questions are still open. In the normal state, it is not always easy to distinguish the non-metallic behaviours which correlate with structural peculiarities and those which are inherent of the 2D electronic system. It seems that these questions will require a very systematic comparative study of different compounds of the family. For example, as we suggested in Section 2.3. a similar studies on $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl and $\kappa$-(ET)$_2$Cu(CN)[N(CN)$_2$] are required to establish the relevance of the “pressure scale” on the strength of AF fluctuations. The same systematic approach would be welcome in the superconducting state where the it should reveal how the anisotropy factor influences the phase diagram in the mixed state.

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