Dynamic properties of commensurate and incommensurate spin density waves as probed by 13C NMR

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DYNAMIC PROPERTIES OF COMMENSURATE AND INCOMMENSURATE SPIN DENSITY WAVES AS PROBED BY ^{13}C NMR

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ABSTRACT

We have measured ^{13}C NMR lineshape and nuclear spin lattice relaxation in the spin-density-wave (SDW) state of $(TMTTF)_2Br$ and $(TMTSF)_2PF_6$. The incommensurability of the SDW in $(TMTSF)_2PF_6$ is confirmed, and we show that the phason mode is dominant in the relaxation. However, we found that $(TMTTF)_2Br$ is commensurate and estimated that the SDW amplitude is small. No phason contribution to the relaxation is observed in this compound. We discuss some implications for theory.

INTRODUCTION

The isostructural families $(TMTTF)_2X$ and $(TMTSF)_2X$, with X = PF_6, SbF_6, Br, etc ... exhibit a wide variety of ground states, summarized in a generalised temperature-pressure phase diagram [1]. Among them, the compounds with a spin-density-wave (SDW) ground state are divided into two classes by their normal state properties. Some, like $(TMTSF)_2PF_6$, are conductors down to the SDW transition, while others, like $(TMTTF)_2Br$, exhibit charge localization around 100 to 200 K, and are very good insulators at the SDW transition temperature.

The dynamics of the $(TMTSF)_2PF_6$ like systems in the SDW state has aroused much interest lately and proves to be very similar to charge-density-wave dynamics. For instance, it exhibits non linear dc conductivity with a marked threshold field, low frequency pinned mode in ac conductivity and noise generation in the non linear regime [2]. This coherent set of transport properties is explained by the picture of an incommensurate SDW, *i.e.* no multiple of the wave vector of the electronic modulation is a vector of the reciprocal lattice. In this case, the collective translation mode (phason mode) is expected to have a small gap, due only to impurity pinning, and therefore dominates the dynamics of these systems.

The SDW dynamics has not been measured in the $(TMTTF)_2Br$ like systems, because of their prohibitively high resistivity at low temperature, due to the charge localization. NMR, on the other hand,

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is unaffected by this charge localization, because of the one-dimensional spin-charge decoupling [3]. Moreover, it has already proved useful in the study of incommensurate systems like distorsive crystals [4], CDW [5], and SDW [6–8], providing data on the incommensurability through lineshape analysis and on the dynamics through nuclear spin lattice relaxation (NSLR) measurements. It is therefore suitable for comparing the two classes of SDW systems.

We have measured the NMR spectrum and NSLR of both $(TMTTF)_2Br$ and $(TMTSF)_2PF_6$. We confirm that the $(TMTSF)_2PF_6$ SDW is incommensurate. We show that the characteristic parameters (amplitude and wave vector) of the SDW are probably quite similar in both compounds but $(TMTTF)_2Br$ turns out to be commensurate. As a result,the dynamics of these two compounds are very different. The significance of these results for the theoretical understanding of the SDW state is discussed.

EXPERIMENTAL

Our samples are selectively ^{13}C enriched on the central carbon sites usually labelled C(3) and C(13) [9] at 100 % for $(TMTTF)_2Br$ and at 10 % per molecule for $(TMTSF)_2PF_6$. The synthesis of the enriched compounds will be published shortly [10].

The $(TMTSF)_2PF_6$ samples have been checked by transport measurements. The SDW transition occurs at 12.5 K. The $(TMTTF)_2Br$ samples are notoriously more difficult to grow. We could not achieve good contacts for resistivity measurements, because of the poor surface quality, but the samples have been characterized by EPR. The transition occurs around 15 K.

The NMR measurements have been performed on single crystals in a 9.3 T field, which brings the ^{13}C resonance frequency to 99.63 MHz. All the data in the SDW state were obtained by an echo with phase cycling procedure. NSLR was measured by saturation recovery.

RESULTS

Since the four central carbon sites in the unit cell are related by inversion [9], there are only two unequivalent sites as far as NMR is concerned. We have determined the Knight shift tensor for both sites, using the strong temperature dependence of the spin susceptibility χ [11] and the standard method of rotating the crystal with different initial positions [12]. With this procedure, we find the principle axes close to $\bar{a}$ and to the molecular symetry axes with respective eigenvalues at room temperature given in table I.

	K_1	K_2	K_3
site 1	515	-225	-290
site 2	385	-170	-215

Table I : Knight shift anisotropy values in ppm at room temperature in $(TMTTF)_2Br$. The principal axes 1, 2, 3 are close respectively to $\bar{a}$, to the long molecular axis C(13)-C(3), and to the short molecular axis.

Because of the low enrichment of our $(TMTSF)_2PF_6$ samples, we were able to perform only an approximate determination of the Knight shift tensor assuming the axes are the same as in $(TMTTF)_2Br$ and using an assembly of several single crystals aligned along $\bar{a}$. The values we obtained are given in table II.

	K_a	$K_\perp$	$\Delta K_\perp$
site 1	260	-130	30
site 2	140	-70	15

Table II : approximate Knight shift anisotropy values in $(TMTSF)_2PF_6$ (in ppm, at room temperature). We assumed the axes are about the same as in $(TMTTF)_2Br$. $K_\perp$ is the mean value in the plane normal to $\bar{a}$, and $\Delta K_\perp$ is the anisotropy in this plane

The total width of the lineshape of $(TMTTF)_2Br$ at 4.2 K, in the SDW state (Fig. 1 a), is about five times larger than in the normal state. The contribution of the two sites is split up into four very different resonances, symmetrically shifted with respect to the common chemical shift value. This splitting is obviously due to the presence of the staggered magnetization $\bar{M}_j$ (The subscript j denotes that $\bar{M}$ is not uniform), and from the absence of continuous distribution, we conclude that the SDW is commensurate.

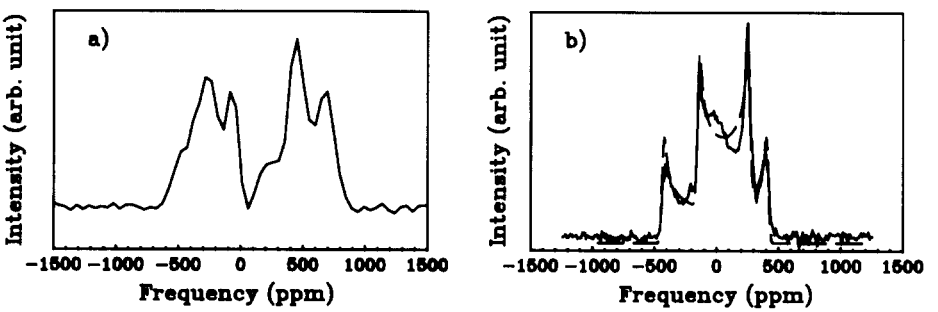

Fig. 1 : single crystal lineshapes in the SDW state at 4.2 K. (The reference is TMS)

a) of $(TMTTF)_2Br$.

b) of $(TMTSF)_2PF_6$. The dotted line is a fit using a sum of two functions f (defined in the text) with different parameters ω_0. It gives equal intensity to each site.

However, the ratio of the relative peak positions is different from the Knight shift ratio we measured by a factor of 30 %. Thus, we suppose that a slight molecular spin density redistribution occurs in the SDW state. As a result, the exact peak assignment is doubtful. Depending on the details of the redistribution, the wave vectors $(1/2, 1/2, 0)$, $(1/2, 0, 0)$ or$(1/2, 1/4, 0)$ in the $(\bar{a}^\star, \bar{b}^\star, \bar{c}^\star)$ basis are equally compatible with our data. For more about the peak assignment, see [13].

In our set-up the $\bar{a}$ axis is kept perpendicular to the external field. Therefore, we assume the orientation of the electronic spin magnetization stays perpendicular both to the external magnetic field and the $\bar{a}$ axis, since the former is much larger than the spin flop field (0.5 T) and the latter is close to the hard magnetic axis. This is consistent the behaviour of the shift we observed when rotating the crystal around $\bar{a}$.

Using the assumption, our Knight shift and SDW shift data and the room temperature spin susceptibility $\chi = 5.3\ 10^{-4}$ emu/mole [14], we calculate that the magnetic moment is more than $7\ 10^{-2}\mu_b$ per electron and less than $1.7\ 10^{-1}\mu_b$ per electron, depending on the peak assignment. This is consistent with the $8\ 10^{-2}\mu_b$ per molecule (or $1.6\ 10^{-1}\mu_b$ per electron), calculated in Ref. [15].

The $(TMTSF)_2PF_6$ spectrum at 4.2 K (Fig. 1 b) is in sharp contrast to the previous one. It features two wide distributions of resonance frequencies, each associated with one unequivalent site. The lineshape reflects the spatial distribution of the local field at the nuclear sites. If we assume an incommensurate plane wave modulation, this distribution is

$$f(\omega) = \begin{cases} \frac{1}{\pi}\frac{1}{\sqrt{\omega_0{}^2-\omega^2}} & \text{if } |\omega| < \omega_0 \\ 0 & \text{otherwise,} \end{cases}$$

were ω_0 is the distribution width related to the magnetization amplitude. Thus, our spectrum confirms the incommensurate nature of the SDW in $(TMTSF)_2PF_6$. However, in our case, the lineshape is independent of the SDW wave vector. The analysis of the behaviour of the lineshape upon rotation is less straightforward in this case, because the anisotropy axes are different [15]. Relying on our approximate measurement of the shift tensor and the width of the spectrum when the easy axis $\bar{b}'$ is normal to $\vec{H}_0$, and using the room temperature susceptibility $\chi = 2.4\ 10^{-4}$ emu/mole [16], we tentatively estimate the magnetization amplitude to be about $6\ 10^{-2}\mu_b$ per electron. Other estimates give $8\ 10^{-2}\mu_b$ per molecule [6,7] and $16\ 10^{-2}\mu_b$ per molecule [15].

The temperature dependence of the NSLR of ^{13}C has also been measured in both samples. The NSLR of $(TMTSF)_2PF_6$ as a function of temperature (Fig. 2 b) exhibits two definite characteristics: 1) it diverges at the phase transition 2) it remains large and constant below the critical region. Similar results have already been obtained by proton NMR [8]. The plateau in our data, obtained by ^{13}C NMR, is much clearer than in ref.[8], however, probably because the ^1H NSLR includes a strongly temperature dependent methyl group rotation contribution. This behaviour contrasts markedly with the NSLR measured on $(TMTTF)_2Br$ (Fig. 2 a), which decreases by two orders of magnitude between the transition temperature and 4.2 K.

Great care was taken when processing the data to integrate a narrow frequency width. In the case of $(TMTSF)_2PF_6$, we selected regions in which only one site contributed to the spectrum. The resulting relaxation curves, however, were strongly non exponential in the SDW state, whereas no departure from exponentiality was observed in the normal state. Therefore, we used a stretched exponential function $M(t) = M_0(1-\exp[-(\frac{t}{T_1})^\beta])$ with an exponent $\beta = .65$ to fit the data in the SDW state, identical to the exponent observed in dielectric relaxation [17]. A stretched exponential is analysed in terms of some inhomogeneity inside the sample, which induces a spatial distribution in the relaxation mode density of states and therefore a continuous distribution of T1s. Strong pinning in the incommensurate SDW of $(TMTSF)_2PF_6$ is readily invoked to explain this inhomogeneity.

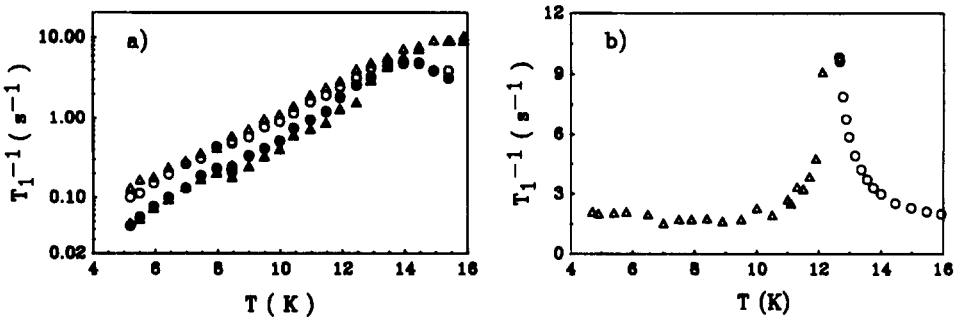

Fig. 2 : Nuclear spin lattice relaxation rate T_1^{-1}

a) of $(TMTTF)_2Br$ in the SDW state, for the four peaks

b) of $(TMTSF)_2PF_6$. ($\triangle$ for the SDW state, $\bigcirc$ for the faster peak in the normal state).

Unexpectedly, we have also found a pronounced non-exponentiality in the $(TMTTF)_2Br$ relaxation, which we tentatively ascribe to the peak inhomogeneity.

DISCUSSION

In the case of $(TMTSF)_2PF_6$, the concept of SDW is more readily understandable : the electron-electron repulsion leads to an electronic instability. The single electron interchain motion stabilises the ordering, which is forbidden for a strictly 1D system. Therefore, the details of the instability, like the wave vector of the modulation, are determined by the Fermi surface. Yet, for the $(TMTTF)_2Br$ class of compounds, which have a gap in the electronic charge degrees of freedom, another theory had to be developed to explain the SDW ground state. It is based on a coherent interchain tuneling of electron-hole pairs [18], and predicts that despite the different mechanisms, the macroscopic properties in the SDW are essentially the same in both classes of compounds : for instance, the expected SDW wave vector is also determined by the same best nesting condition of the fictitious Fermi surface [19]. In the case of $(TMTSF)_2PF_6$, the NMR measurements of the SDW wave vector [6,7] and the estimate calculated from the band structure [20] were in good agreement. In $(TMTTF)_2Br$, we found that the magnetization amplitude has the expected small magnitude. Moreover, the result of the wave vector calculations at room temperature (for which transfer integral estimates are available) gives 0.37 or 0.26 for the $\bar{b}^*$ component of the wave vector [20], which may be consistent with our observations.

As far as the NSLR is concerned, the divergence at the phase transition is known to signal the divergence of the relevant magnetic susceptibility [8]. We want to emphasize its temperature independence below the critical temperature region. Although magnetic impurities can yield a stretched exponential relaxation shape and a NSLR independent of temperature, we point out that the relaxation shape is very different above and below the SDW transition. Moreover, no magnetic impurity contribution to the EPR susceptibility has been detected in our usual $(TMTSF)_2PF_6$ samples. As a result, we rule out magnetic impurity relaxation, and believe the temperature independence of the NSLR reflects the predominance of the phason mode fluctuations in the NSLR. Such a behaviour

has already been observed in the incommensurate distorsive crystals [4]. Therefore, the absence of this mode in the commensurate $(TMTTF)_2Br$ is not surprising since commensurability is expected to introduce a significant gap, or to totally suppress the phason mode. Thus, in this latter compound, the relaxation is probably driven by magnons.

CONCLUSIONS

We have shown that in the incommensurate SDW system $(TMTSF)_2PF_6$, the phason mode dominates the NSLR. We observed that $(TMTTF)_2Br$ has about the same magnetization amplitude as other SDW compounds, yet exhibits a commensurate order. As a result, the phason mode is not significant for relaxation in this compound. The wave vector may also be consistent with the theory.

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