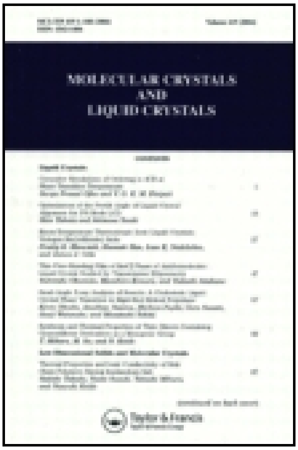

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COOPERATIVE PHENOMENA IN $(TMTSF)_2ClO_4$ NMR RELAXATION

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Abstract - ^1H and ^{77}Se NMR relaxation data on relaxed $(TMTSF)_2ClO_4$ are presented and an interpretation is proposed for the non-Korringa behaviour which is based on the existence of one-dimensional $2k_F$ spin correlations.

INTRODUCTION

The organic conductor tetramethyltetraselenafulvalenium-perchlorate $(TMTSF)_2ClO_4$ is well known for its conducting properties at ambient pressure for all temperatures and in a wide range of magnetic fields, provided great care is taken to cool the sample slowly (10 K/hour for the so-called R-state) [1]. We have performed NMR relaxation rate measurements on both ^1H and ^{77}Se (I = 1/2) nuclei in this metallic domain, in order to investigate the low-temperature response of the electron gas. As it was suggested in a previous work [2] we have found that the usual Korringa law is not verified in this system. In the present work, the T_1^{-1} behaviour at low temperature will be correlated with the predictions of standard quasi-1D models. The large T_1 anomaly between 1.2 and 40 K in fields extending from 1 kOe up to 64 kOe is interpreted as the existence of well developed one dimensional spin-density wave (SDW) cooperative phenomena, emphasizing that the temperature dependence of $1/T_1$ is not compatible with a single-particle description of the conduction state.

EXPERIMENTAL RESULTS

Details concerning the preparation and the structure of the $(TMTSF)_2X$ compounds can be found elsewhere [3]. For both ^1H and ^{77}Se nuclei, T_1 was determined recording the free induction signal after a π-$\pi/2$ sequence, changing the delay between the two pulses. An exponential decay was observed over more than one decade.

Data of ^{77}Se relaxation rates at various fields in relaxed $(TMTSF)_2ClO_4$ are collected in Fig. 1. the Korringa law is fairly well obeyed, without field dependence in the higher temperature regime 25-40 K. At lower temperature, the spin-lattice relaxation rate is strongly enhanced, compared to the expected Korringa behaviour, and a field dependence can be clearly detected (between 6 and 20 K). Below 6 K or so, another Korringa regime seems to be approached. The linewidth was found rather large compared to $1/\gamma T_2$ (22 G at 30 kG, 44 G at 64 kG) but almost linear in field and may be attributed to a distribution of Knight-shifts corresponding to different ^{77}Se sites.

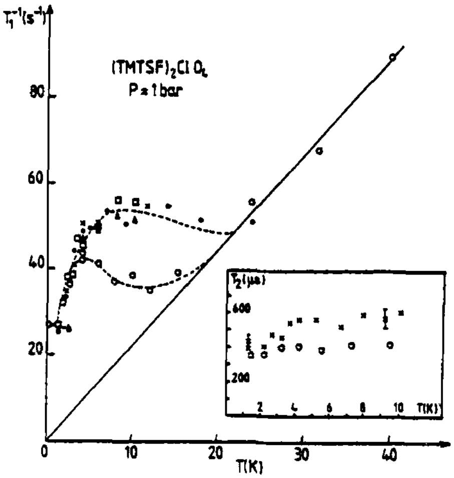

FIGURE 1

^{77}Se lattice relaxation rate in relaxed $(TMTSF)_2ClO_4$.

o $H_o = 64.2$ kG // b'

● $H_o = 31.9$ kG // b'

× $H_o = 21.0$ kG // b'

Δ $H_o = 6.0$ kG powder

□ $H_o = 31.9$ kG // c*

For ^{1}H, the results are quite similar though as already studied before [4-5-2], it is necessary to estimate the contribution to the relaxation rate due to the quantum tunnelling of methyl groups at low temperature. This contribution was extrapolated with the assumption of an activated behaviour [6]. Figure 2 displays the only points for which the relaxation is due to interaction with the

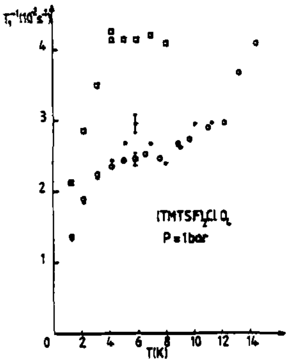

FIGURE 2

^1H spin lattice relaxation in relaxed $(TMTSF)_2ClO_4$.

□ H_0 = 1.1 kG powder
● H_0 = 4.0 kG // b'
o H_0 = 12.2 kG // b'

electron spins. At this stage, the ^{77}Se and ^1H results scale together with a ratio of hyperfine constants $[a(Se)/a(H)]^2 \sim 2.10^3$. Although the field dependence between 4 and 12kOe is reliable, the large enhancement of the relaxation rate at 1 kOe cannot be easily attributed to an intrinsic electronic effect, since parasitic relaxation due to magnetic impurities cannot be completely ruled out at low fields. However, no important effect of paramagnetic impurities has been reported so far via susceptibility measurements[7] in these materials prepared by electrochemical method, and this effect may be attributed to the proximity of the superconducting transition.

THEORY

Clearly, these data are not consistent with the single-particle description of the conducting state and here, we will try to correlate the results with the predictions of a low-dimensional theory. The general expression of T_1^{-1} is[8] :

$$T_1^{-1} = \gamma_N^2 \; |A|^2 \sum_{\vec{q}} \frac{\chi''_\perp(\vec{q},\omega_N)}{\tanh(\omega_N/2T)} \quad , \qquad (1)$$

where A is the contact hyperfine matrix element taken as q independent, γ_N gives the gyromagnetic ratio of the nucleus and $\chi''_\perp$ stands for the imaginary part of the retarded SDW correlation function. We have calculated, in the g-ology picture, the contribution of the $1D\text{-}2k_F$ component of $\chi''_\perp$ (the $q \sim 0$ component being negligible to the T_1^{-1} enhancement since the uniform magnetic susceptibility is constant below 50 K [7]). In order to predict SDW enhancement, we assume that the interactions can be described within the "g-ology" picture and we will focus our attention on the repulsive and gapless (g_1, g_2, g_3) domain where both SDW and triplet pairing can occur [9-10-11-12].

We keep in mind that the three-dimensional (3D) electronic motion will take place at low temperature, due to interchain single electron hopping. The cross-over temperature T_x was shown [13] to be reduced in comparison with the non-interacting electron gas value $T_x^\circ = t_\perp/\pi$ [14-15], because of strong intrachain correlations : $T_x = T_x^\circ\,(t_\perp/E_F)^{\alpha/1-\alpha}$ where $1>\alpha>0$ depends on the interactions [16].

In the 1D regime, the formula (1) can be modified, using the Kramers-Krönig relation :

$$\frac{\chi''_\perp\,(q+2k_F,\omega_N)}{\omega_N} \simeq \frac{2}{(\eta+1)}\,\bar{\chi}'_\perp(T) \qquad \text{for } \omega_N \ll T;\ |V_F q| < T \quad (2)$$

where $\bar{\chi}'(T) = \dfrac{\partial\chi'_\perp}{\partial\ell n(E_o/T)}$ and $\chi'_\perp$ is the real part of the total retarded susceptibility. The sum around 2 k_F ($|V_F q| < T$) leads to :

$$T_1^{-1} = \frac{4\gamma_N^2\ |A|^2}{\pi^2 V_F(\eta+1)}\ .\ T\ .\ \bar{\chi}'_\perp\ (T) \qquad (3)$$

This is obtained from the asymptotic properties of $\chi'_\perp(T,q,\omega) \sim (\mathrm{Max}(T,V_F q,\omega)/E_o)^{-\eta}$ [9-16]. E_o is a cut-off energy (temperature)for strong intrachain SDW enhancement characterized by a positive power law exponent η. Scaling arguments for $\bar{\chi}'_\perp$ with E_o tell us that $0<E_o<E_F$. E_o is very difficult to predict for organic compounds and it will be taken as an adjustable parameter of the problem. For $T_x<T<E_o$ the expression for T_1^{-1} becomes : $T_1^{-1} = CT(T/E_o)^{-\eta}$. Here C is a constant which gives the slope of T_1^{-1} vs T at T > E_o.

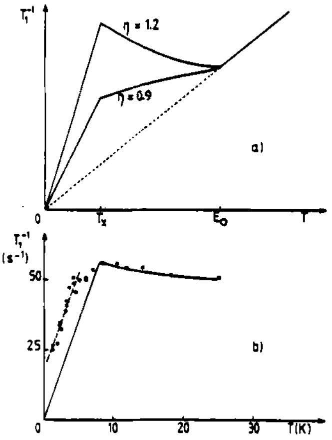

FIGURE 3

When $T \to T_x$, the enhancement saturates at $(T_x/E_o)^{-\eta}$ because of 3D couplings, and if we neglect the possibility of a true phase transition below T_x, the spin lattice relaxation rate approaches a 3D renormalized Korringa behaviour down to T = 0. This typical behaviour of T_1^{-1} is shown on Fig. 3a for the value of η ($\eta = 0.9$; $\eta = 1.2$).

DISCUSSION

From the low field experimental data (Fig. 3b), a departure from the Korringa behaviour is clearly seen at $E_o \approx 25$ K. Using the T_1^{-1} expression, the fit of the power law enhancement for $T < E_o$ gives $\eta \approx 1.1$, indicating the presence of strong SDW effects. The crossover temperature appears to be at $T_x \sim 8$ K. From the accepted values of T_x° found in the litterature [15] for $(TMTSF)_2ClO_4$ ($T_x^\circ = t_\perp/\pi \approx 30..80$ K), this means strong 1D collective effects. With the accepted range of anisotropy $t_\perp/E_F \sim 1/10..1/30$ [17-18] $T_x \simeq 8K$ implies $\alpha = 1/4...1/2$ which is compatible with η and quite reasonable for organic conductors. Furthermore, the enhancement factor $(T_x/E_o)^{-\eta} \sim 3.5$ agrees pretty well with the observed one which is equal to 3 or so. Beside the apparent residual component of T_1^{-1} as $T \to 0$, the relevant linear shape is essentially parallel to the one predicted.

The effect of large magnetic field (64 kOe) may be understood as orbital effects which reduce $t_\perp$ and consequently the crossover temperature. One must also note that the magnetic anisotropy of couplings is increased at low temperature and high field, and this can modify the SDW enhancement. The field dependence reported by Azevedo et al. on $(TMTSF)_2PF_6$ [19-20] has to be reinterpreted taking into account these new phenomena. Moreover, recent data at room temperature [21] rule out the possibility of spin diffusive processes for the T_1^{-1} field dependence at low temperature.

CONCLUSION

We have presented new NMR results which cannot be explained by usual single particle theory. However, the good agreement between experiment and a quasi-1D theoretical approach of T_1^{-1} strongly suggests that 1D cooperative phenomena are effective down to 8 K or so in $(TMTSF)_2ClO_4$. We want to emphasize that, from the 1D theoretical point of view, electron-hole SDW fluctuations can coexist with triplet pairing ones. Therefore, the strong T_1^{-1} enhancement for fields smaller than the superconducting critical field ($H_o \sim 1$ kOe) observed at low temperature may reflect some magnetic character for the precursor effects occuring in the vicinity of the superconducting instability which have been also revealed by other studies [23]. Furthermore, this work suggests that 1D physics should be taken into account down to low temperatures.

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$$T_1^{-1} = c\left[\frac{\tau_c}{1+\omega_o^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_o^2\tau_c^2}\right] \text{ with } \tau_c = \tau_o \exp\left(\frac{E_a}{kT}\right)$$

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