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PROTON SPIN-LATTICE RELAXATION TIME IN THE SUPERCONDUCTING INTERCALATION COMPLEX $\text{TaS}_2(\text{PYRIDINE})_{1/2}$

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Résumé. — La RMN des protons dans $\text{TaS}_2(\text{pyridine})_{1/2}$ montre que les molécules de pyridine constituent un réseau rigide avec de faibles mouvements moléculaires au-dessous de 300 K. Le T_1 des protons est associé aux interactions entre les phases métalliques et les phases de pyridine au-dessus de 80 K, au moins. Un plateau anormal de T_1 au-dessous de 80 K peut être éventuellement attribué à une apparition d'ondes de densité de charge. Au-dessus de T_C une augmentation importante de T_1^{-1} a été observée dans un échantillon monocristallin.

Abstract. — Proton NMR in $\text{TaS}_2(\text{pyridine})_{1/2}$ shows that pyridine molecules form a rigid lattice with slow molecular motions up to 300 K. The protons' T_1 is associated with interactions between the metallic layers and the molecular layers at least above 80 K. An anomalous T_1 plateau below 80 K might tentatively be attributed to the occurrence of charge density waves. Below T_C a large increase of T_1^{-1} has been observed in a single crystal sample.

Layered transition-metal dichalcogenides with organic molecules intercalated have been of considerable interest because of the extremely anisotropic properties of the conduction electrons in the metallic layers. The intercalation modifies the properties of the conduction bands and superconductivity, and greatly increases the already pronounced anisotropy of the host material. In 2 H-polytype TaS_2 ($T_C \simeq 0.8$ K), the separation δ between the metallic TaS_2 layers (~ 6 Å thick) can vary from 9 to 57 Å depending on the intercalated organic molecules [1-3]. A significant feature of superconductivity in these complexes is that T_C is strongly affected by the intercalation, whereas it is relatively insensitive to the magnitude of the separation δ up to 57 Å [2]. This suggests that the superconductivity is mainly a two-dimensional phenomenon. Fundamental theorems [4, 5] demonstrate that no phase transition occurs in two dimensions, but for many experiments on these complexes, phase transitions have been detected, as in three

dimensions. Therefore it is important to detect and understand the origin of any electronic coupling between the metallic layers and molecular layers. In this letter, we report ^1H NMR data in

which provides a microscopic probe for the present purpose. In this complex ($T_C = 3.5$ K) TaS_2 layers are separated by layers of pyridine molecules ($\delta \simeq 12$ Å) [1]. Another aim of the present study concerns the possibility of detecting the effects of superconducting fluctuations near T_C , which are expected to be enhanced in two dimensional systems. In a favorable case they may yield the dominant relaxation mechanism at low temperatures [6].

We prepared two powdered polycrystalline samples and one single crystal (labeled as p.c.I, p.c.II and s.c.I, respectively), all from different batches. Intercalation of pyridine was achieved by heating TaS_2 crystals and pure liquid pyridine in a sealed tube at 140 °C for two days. The intercalation complexes were sealed in the quartz tube under helium gas atmosphere and kept at liquid nitrogen temperature

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except for the experimental runs. The samples were controlled by measuring T_C utilizing the frequency changes of a marginal oscillator caused by the superconducting transition. Onset temperatures of the superconducting transition T_C were enhanced from 0.8 K for unintercalated TaS₂ to $\simeq 3.8$, $\simeq 4.5$ and $\simeq 4.2$ K for p.c.I, p.c.II and s.c.I, respectively. The transition widths for 90 % transition in the earth's field were 1.2, 1.3 and 0.7 K, respectively. These T_C values are somewhat higher than 3.5 K which has been reported for single phase crystals ($\delta = 11.85$ Å). The higher T_C indicates that the present samples are in the mixed phase (mixture of phases with layer separation $\delta = 12.01$ and 11.85 Å) [7, 8] which has higher T_C . (Incomplete pyridine intercalation gives a lower T_C than full intercalation.)

Proton spin-spin and spin-lattice relaxation times were measured from room temperature to liquid helium temperatures using transient NMR spectrometers. The decay curves of ¹H free induction after a 90° rf pulse follow the relation

$$M(\tau) = M_0 \exp[-(\tau/T_2^*)^2],$$

which corresponds to a Gaussian line shape. The observed value of T_2^* is 20 ± 2 (μs) and independent of the temperature in the normal state. In the powdered samples, T_2^* decreases by about 20 % in the superconducting mixed state (at 1.4 K) (for both $H_0 = 2.3$ and 4.7 kOe). In the single crystal sample, $T_{2\parallel c}^*$ decreases by about 25 % at 1.4 K, where the $T_{2\parallel c}^*$ were measured with the external field parallel to c -axis (normal to layer) of the crystal. This decrease

of T_2^* in the superconducting mixed state is associated with the periodic lattice of vortices. With the magnetic field perpendicular to the c axis a poor signal to noise ratio was obtained, due to the eddy current loss of the rf field (normal to the layer) and, therefore an accurate value of $T_{2\perp c}^*$ could not be obtained.

In the normal state, the observed recovery of the magnetization after saturation was found to be non exponential and independent of the initial condition of saturation as shown in figure 1, where

$$[M(\infty) - M(t)]/M(\infty)$$

are plotted as a function of $t/T_1^{(e)}$ for the three samples. Here $T_1^{(e)}$ is the time at which $M(t) - M(\infty)$ has reached $1/e$ of its initial value. Within experimental accuracy, the recovery behaviour is independent of temperature, magnetic field and samples. This non exponential recovery of the magnetization might be linked with the mixture of phases in the samples as will be discussed later on. On the other hand, the recovery curves approach a single exponential as the complexes go into the superconducting mixed state.

Figure 2 shows the temperature and magnetic field dependence of $T_1^{(e)}$ of ¹H in the normal state. The same temperature dependences were obtained, of course, for $T_1^{\text{initial slope}}$ and $T_1^{\text{final slope}}$. A comparison of $[T_1^{\text{initial slope}}]^{-1}$ and $[T_1^{(e)}]^{-1}$ can be seen for example in figure 3. Characteristic results on $T_1^{(e)}$ are summarized as follows.

- $T_1^{(e)}$ and, therefore, T_1 is much larger than T_2 .
- From ~ 80 K to 300 K, $T_1^{(e)}$ increases mono-

FIG. 1. — Longitudinal magnetization recovery $[M(\infty) - M(t)]/M(\infty)$ versus $t/T_1^{(e)}$ at 4.2, 77, 300 K with different magnetic fields and samples, where $T_1^{(e)}$ is the time of the $1/e$ point of the magnetization recovery.

FIG. 2. — Temperature and magnetic field dependence of $T_1^{(e)}$ above 4.2 K for the three samples. $T_1^{(e)}$ is the time of the $1/e$ point of the magnetization recovery.

FIG. 3. — Temperature dependence of $(T_1^{(e)})^{-1}$ and $(T_1^{(\text{initial slope})})^{-1}$ in the normal state for sample p.c.I. A Korringa like relaxation dominates above 80 K.

tonically and is roughly proportional to T (see also fig. 3). One can estimate $T_1^{(e)}$ tentatively as 2.5×10^2 and 6.0×10^2 (s.K) for p.c.I and p.c.II respectively.

c) At 77 K and 300 K, $T_1^{(e)}$ is almost independent of the magnetic field H within the observed range.

d) Below ~ 80 K down to ~ 10 K, $T_1^{(e)}$ is quite insensitive to the temperature for all the samples.

e) At 4.2 K, $T_1^{(e)}$ depends on the magnetic field and increases with increasing H .

Figure 4a shows the temperature and field dependence of $T_1^{(e)}$ at low temperatures for p.c.I and p.c.II, where curves separate roughly the superconducting

FIG. 4a. — Temperature and magnetic field dependence of $T_1^{(e)}$ below 10 K for the two powdered samples. The drawn curves roughly separate the superconducting and normal states as estimated from $T_c(H)$ measurements.

and normal state, estimated from $T_c(H)$ measurements.

f) At low temperatures and at high magnetic fields (normal state), $T_1^{(e)}$ begins to increase again with decreasing temperature.

g) As the complexes go into the superconducting mixed state, $T_1^{(e)}$ decreases or remains nearly constant.

Figure 4b shows T_1 of the slow recovery part and the rapid recovery part of the recovery curves in s.c.I, where the T_1 were observed with the external magnetic field parallel and perpendicular to c -axis of the crystal at 2.3 and 4.7 kOe. Rapid drops of T_1 below the transition temperature $T_c(H)$ were observed clearly as can be seen in the figure. At 1.4 K, T_1 of the slow and rapid recovery part take the same value (single exponential recovery).

FIG. 4b. — Temperature and magnetic field dependence of T_1 obtained from the slow and rapid recovery components of the magnetization for the single crystal sample below 4.2 K. T_1 was measured with magnetic field orientations both parallel and perpendicular to the crystal c -axis.

The determination of the orientation of pyridine molecules in $\text{TaS}_2(\text{Py})_{1/2}$ is important in order to understand any electronic coupling between the metallic layers and pyridine molecules. In $\text{TaS}_2(\text{Py})_{1/2}$, both perpendicular and parallel orientation of the pyridine ring plane are consistent with the unit cell dimensions of the complexes [1], and the determination of the exact crystallographic structure has not yet been made. The measurement of the second moment of the proton NMR might be useful for this purpose. Experimental value of the second moment $\langle \Delta H^2 \rangle^{1/2}$ estimated from T_2^* of ^1H in the powdered samples is 2.64 ± 0.26 (Oe). The calculation of the powder average second moment for parallel orientation, perpendicular orientation with the lone pair orbital parallel to the layer plane, and perpendicular orientation with the lone pair orbital perpendicular to the plane are 2.42 ± 0.20 , 2.04 ± 0.15 and

$$2.52 \pm 0.3 \text{ (Oe)},$$

respectively. Thus this last structure is more or less in accord with the experimental result [9]. Unfortunately, no decisive evidence could be obtained from single crystal data as preliminary measurements of T_2^* at 4.2 K (normal state) for s.c.I show that the variation of T_2^* with the orientation of the c -axis with respect to H is comparable with the experimental error bar.

In the superconducting mixed state, the penetration of flux through the periodic lattice of vortices yields an inhomogeneous distribution of local magnetic fields in the sample. The second moment of this field distribution is approximately given by [10]

$$\langle \Delta H^2 \rangle^{1/2} = \frac{\varphi_0}{\lambda^2 \sqrt{16 \pi^3}}, \quad (1)$$

where λ is the penetration depth and φ_0 is the quantum of flux. This gives rise to a field independent decrease of T_2^* . Using equation (1), and estimated values $\lambda_{\perp c} \sim 3 \times 10^3 \text{ \AA}$ and $\lambda_{\parallel c} \sim 10^5 \text{ \AA}$ from reference [11] give $\langle \Delta H^2 \rangle_{\parallel c}^{1/2} \sim 10$ (Oe) and

$$\langle \Delta H^2 \rangle_{\perp c}^{1/2} \sim 10^{-3} \text{ (Oe)},$$

respectively. Therefore, in the superconducting mixed state $T_{2\perp c}^*$ should not change, while $T_{2\parallel c}^*$ should decrease to about 1/5 of its value in the normal state. This estimated decrease of $T_{2\parallel c}^*$ is much larger than the experimental result. Our data might rather indicate that $\lambda_{\perp c} \sim 10^4 \text{ \AA}$.

Among the many different possible contributions to the spin-lattice relaxation it is important first to consider any eventual relaxation due to paramagnetic impurities, as the magnetization recovery has been found non exponential, and T_1 is sample dependent. The induced relaxation time for a proton at distance r from a magnetic impurity is given by [12]

$$[T_1(r)]^{-1} = \frac{2}{5} \frac{\gamma_e^2 \gamma_n^2 \hbar^2}{r^6} S(S+1) \frac{\tau_c}{1 + \omega_n^2 \tau_c^2} = \frac{C}{r^6}, \quad (2)$$

where τ_c is the correlation time of the impurity spin S . The absence of a field dependence for T_1 above ~ 10 K indicates that impurities, if any, should be in the short correlation time limit $\omega_n \tau_c \ll 1$. Therefore T_1 should be an increasing function of T as τ^{-1} usually increases abruptly with T (at least as T^2 due to a Raman process). Therefore above 77 K the observed relaxation cannot be attributed to paramagnetic impurities. Below 77 K one could only interpret the results if spin lattice relaxation is limited by spin diffusion, in which case [12]

$$T_1^{-1} = \frac{8\pi}{3} N(C)^{1/4} (D)^{3/4}, \quad (3)$$

where D is the proton spin diffusion constant and N the number of paramagnetic centres per unit volume. In such a case the frequency dependence observed at 4.2 K could be associated with a transition from $\omega_n \tau_c \ll 1$ at 77 K to $\omega_n \tau_c > 1$ at 4.2 K, the temperature variation of T_1 being therefore quite small in this range because of the 1/4th power of equation (3). If values $S = 5/2$, and $D \sim 10^{-12} \text{ (cm}^2/\text{s)}$ are assumed, equation (3) yields $N \sim 3 \times 10^{16} \text{ (cm}^{-3}\text{)}$ which corresponds to a concentration of about 3 ppm of impurities per $\text{TaS}_2(\text{Py})_{1/2}$ unit. Although magnetization measurements have been performed by Geballe *et al.* [14] their experimental sensitivity was not high enough to allow such small amounts of impurities to be detected.

Finally the behaviour below $T_c(H)$, at least in the single crystal sample (s.c.I), cannot be attributed to paramagnetic impurities as T_1 strongly depends upon the orientation of the magnetic field with respect to the c -axis of the crystal. We shall therefore consider separately the three temperature regions.

High temperature region ($\sim 80\text{--}300$ K). The absence of a frequency dependence for T_1 , and the fact that $(T_2)^{-1}/(T_1)^{-1} \gtrsim 10^5$ indicate that there is no significant contribution to the proton relaxation rate from rapid diffusion of molecular species. This result is in contrast with that in $\text{TaS}_2(\text{NH}_3)$ in which, at room temperature, significant contributions of the two dimensional diffusion of NH_3 molecules have been evidenced [13]. In this temperature range T_1^{-1} is dominated by some interaction between the metallic layer and the pyridine molecule. The absence of a field dependence and the Korringa like variation of T_1 indicate that such a coupling would allow energy transfers from the nuclear spin system to the conduction electrons. The dominant molecular-host interactions are therefore a direct dipole coupling between the conduction electrons and the proton nuclei and/or overlaps between the conduction band states and the molecular states through a significant admixture of sulphur character to the conduction Ta d-bands. In this temperature range, the non exponential recovery of the magnetization can only be attributed to the mixture of phases in the sample. Experimentally the observed magnetization recoveries in the normal

state (4.2-300 K) can be divided into two main components with roughly equal intensity, which is consistent with the fact that $\text{TaS}_2(\text{Py})_{1/2}$ intercalated with pure pyridine is usually composed of two phases (nearly 50-50 composition with $\delta \simeq 12.01 \text{ \AA}$ and $11.85 \text{ \AA}$). [7, 8]. Therefore the protons in the different phases might have different T_1 values, as the above mentioned interactions might be significantly affected by the arrangement of the pyridine molecules in $\text{TaS}_2(\text{Py})_{1/2}$.

Low temperature region in the normal state (below $\sim 80 \text{ K}$). As discussed above the plateau of T_1 below 80 K might be associated with magnetic impurities. However, a) the magnetization recovery shape has been found to be independent of T up to 300 K , b) The T dependence is the same for all samples. These two facts rather indicate that the relaxation proceeds through the same coupling from 300 K down to $\sim 10 \text{ K}$. Thus the experimental data implies that some intrinsic transition which affects T_1 would occur in the complex around 80 K . The only anomalous behaviour which might be related with the present result is the unusual peak observed by Geballe *et al.* for the susceptibility at $\sim 80 \text{ K}$ [7, 14]. This peak was however much weaker than that observed in pure TaS_2 at the onset of the charge density wave (CDW). According to Maki *et al.* [15], T_1^{-1} would be enhanced just below this onset temperature of CDW, and then increase monotonically (this effect would be similar in nature to that observed below T_C in superconductors, because the superlattice phases become stable by opening gaps at Brillouin zone boundaries near the Fermi surface). Though the occurrence of CDW in $\text{TaS}_2(\text{Py})_{1/2}$ has not been clearly evidenced up to date, this seems to us a plausible explanation for the anomalous T_1 behaviour below 80 K .

For T near or below the superconducting transition. Below $\sim 10 \text{ K}$ the measured relaxation rates become field dependent. In the single crystal a very large decrease of T_1 is observed below $T_C(H)$, for the two field orientations with respect to the c -axis. This increase of the relaxation rate is quite similar to that

observed in more classical three dimensional superconductors, but the magnitude of the dip (especially for the longer decay part) is much larger than for the usual case where it does not exceed a factor 2, decreases with increasing magnetic field, and is even reduced in most cases by a gap anisotropy. As the magnetization recovery curves have been found to approach an exponential with decreasing temperature, the relaxation below $T_C(H)$ might proceed through different coupling from that at high temperatures. The increase of T_1^{-1} in the powdered samples is not as clear as in the single crystal, which might be linked with the distribution of T_C in the powdered samples, associated with the random orientations of the crystals. Finally the variation of T_1 with field and temperature just above $T_C(H)$ might be linked with superconducting fluctuations although the possibility of a dominant contribution of paramagnetic impurities in this temperature range cannot be eliminated at present.

In conclusion, proton NMR in $\text{TaS}_2(\text{Py})_{1/2}$ provides some important informations concerning the electronic properties of the superconducting layered complex. Unlike in $\text{TaS}_2(\text{NH}_3)$ the relaxation is dominated by interactions between the host metallic layers and the pyridine molecules. A plateau of T_1 below $\sim 80 \text{ K}$ which might be associated with the occurrence of CDW, and a strong decrease of T_1 below $T_C(H)$ have been evidenced here. Although more experiments on well characterized samples are needed in order to understand the influence of the crystallographic phase on the hyperfine coupling and the eventual role of paramagnetic impurities, these preliminary experiments demonstrate that proton NMR is a good probe for the study of these materials. We also intend to investigate in more detail whether the field dependence of T_1 just above T_C is linked with superconducting fluctuations.

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