PHYSICAL REVIEW B
CONDENSED MATTER

THIRD SERIES, VOLUME 26, NUMBER 9 1 NOVEMBER 1982

Nuclear resonance and relaxation in ditetramethyltetraselenafulvalenium salts

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(Received 22 February 1982; revised manuscript received 14 May 1982)

NMR (60-MHz) T_1 and T_2 data for tetramethyltetraselenafulvalenium salts, $(TMTSF)_2ClO_4$ and $(TMTSF)_2FSO_3$, over the temperature range 75 – 300 K, are presented and discussed along with existing data for the isostructural hexafluorophosphate salt. Molecular-motional assignments in $(TMTSF)_2PF_6$ are revised in the light of the new data on the ClO_4^- and FSO_3^- salts. T_1 minima in the $(TMTSF)_2PF_6$ salt within the temperature ranges 55 – 80 and 18 – 24 K are considered to manifest behavior of two species of methyl group, each with a characteristic barrier height to the onset of molecular motion. The sensitivity of proton linewidth to sample orientation is demonstrated for the $(TMTSF)_2X$ family of salts.

INTRODUCTION

An increasing amount of experimental evidence attests to the remarkable properties of the ditetramethyltetraselenafulvalenium (TMTSF) salts first synthesized by Bechgaard and others.[1–12] Magnetic resonance techniques have been informative.[2,6,7,9–11] For example, NMR measurements[6] on the hexafluorophosphate salt $(TMTSF)_2PF_6$ are believed to corroborate the presence of an antiferromagnetic order below the metal-insulator transition temperature $T_{MI} = 12.5$ K.[2,7,8] This temperature delineates markedly different NMR behavior above and below the transition. The linewidth is inhomogeneously broadened below T_{MI},[10] the ^{77}Se resonance "vanishes,"[6] and abrupt changes in T_1 occur.[6,9,10] Phenomena in the vicinity of T_{MI} have been interpreted in terms of the presence of a spin-density wave in the salt.[2] The Korringa-type behavior, where $T_1 \propto T^{-1}$ between 15 and 25 K, observed by Andrieux *et al.*,[6] does not figure in the subsequent data of Scott *et al.*[10]

Nevald and co-workers[13] observed a change in the ^{19}F linewidth of $(TMTSF)_2PF_6$ at 70 K which has been attributed to the onset of PF_6 rotation.[9] Andrieux *et al.*,[6] on the other hand, interpreted these ^{19}F data in terms of a disordering of PF_6^- ions at temperatures above 70 K. Some ordering is believed to set in below this temperature while still retaining free rotation. Structural measurements by Bechgaard *et al.*[1] have been interpreted in terms of ordered PF_6^- ions at room temperature and they alternatively suggest that the change in linewidth at 70 K may be due to a change in electronic states. There is evidence that PF_6^- is disordered at room temperature in our samples. This aspect of our work will be reported in a planned future publication.

As well as the change in T_1 near 12.5 K, attributed to fluctuations in the spin density, there are two additional minima in T_1 versus temperature in the PF_6^- salt. Typically, at 10.5 MHz, T_1 minima are observed at ~20 K and ~58 K, respectively.[9,10] The former is frequency dependent and is assigned to methyl group motion; the latter is reported to be frequency independent (within the range 10.5 – 20.2 MHz) and is assigned to ^{1}H-^{19}F interactions with the further suggestion of a structural phase transition involving rearrangement of CH_3 and PF_6^- groups.[9,10]

In this paper we report NMR T_1 and T_2 data for two isostructural members of the $(TMTSF)_2X$ family of salts, namely, $X = FSO_3^-$ and ClO_4^-. The aim of this work is twofold: First, to seek further information on the transition at 86 – 89 K observed in conductivity, magnetic susceptibility, and thermopower measurements on $(TMTSF)_2FSO_3$ (Ref. 12), and second, to examine the molecular motional assignments of Scott *et al.*[9,10] in $(TMTSF)_2PF_6$ in the light of our data and the well-studied characteristic behavior of methyl groups at low temperatures.[14–26]

EXPERIMENTAL

The crystals were grown by electrocrystallization[1] in trichloroethane. The electrolyte was the tetrabutylammonium salt of FSO_3^- or ClO_4^-. The latter was grown from chlorobenzene as solvent. Crystal growth was allowed to proceed over a period of weeks at 9 °C and 30–50 μA current using dry cells as power sources. Harvesting of crystals was done without special precautions other than the use of purified methylene chloride to wash off the excess electrolyte. The crystals were introduced into sample tubes suitable for NMR study, evacuated, and sealed.

T_1 and T_2 proton resonances were recorded on a modified Bruker spectrometer operating at 60 MHz with a recovery time of ~5 μs. A Commodore PET® computer was used to signal average the weak resonances from the small quantities (50 mg) of material available. The 90°-τ-90° solid echo sequence,[27] with $\tau = 9$ μs, generated an approximation to the complete free-induction decay (FID) from which T_2 was chosen as the time at which the signal decayed to $1/e$ of the initial observed intensity. The 180°-τ-90° sequence provided T_1.[28] Temperature stability was ±1 K over the temperature range 73–300 K of our measurements.

RESULTS AND DISCUSSION

Proton T_1 and T_2 data for the ClO_4^- and FSO_3^- salts are presented as a function of temperature in Fig. 1. It is first noted that our T_2's are appreciably longer than the linewidth data of Andrieux *et al.*[6] and Scott *et al.*[5,9,10] for the PF_6^- salt. Typically, Scott *et al.* report a linewidth of 6 G and $T_2^* = 11$ μs between ~12 K and room temperature, while Andrieux *et al.* report a somewhat greater linewidth. Preliminary measurements on the PF_6^- in our laboratory indicate proton T_2's of ~18 μs at comparable temperatures. The discrepancy between the two earlier sets of data has been attributed to the different resonant frequencies of the two experiments. There may be alternative explanations. In the past[29] similar discrepancies have been associated with the recovery time of the spectrometer: The magnitude of short T_2's is sensitive when the latter is determined from the FID following a single 90° pulse rather than the solid echo sequence.[27] It may be noted too that the motion of the methyl groups in the $(TMTSF)_2X$ crystals is spatially highly anisotropic. Different linewidths will usually result from samples of different morphology. Earlier measurements were performed on polycrystalline powder samples (denoted case *A*) while measurements reported herein relate to needlelike crystals stacked almost vertically in the NMR sample tube (case *B*). On the reasonable assumption that *intra*contributions dominate methyl-group relaxation, classical rotation (or an equivalent tunneling mechanism) will lead to a reduction in the rigid lattice second moment for a powder, $M_2(A)$, by a factor of 4. For an array of crystals arranged vertically in the magnetic field H_0 the symmetry axes of the (rotating) methyl groups in the TMTSF salts are randomly disposed about the vertical axis which is perpendicular to H_0. Under these circumstances the second moment $M_2(B)$ is reduced by a factor of $\frac{5}{64}$ rather than $\frac{1}{4}$, and therefore

$$\left[\frac{M_2(A)}{M_2(B)}\right]^{1/2} = \frac{T_2(B)}{T_2(A)} = 1.78 \; .$$

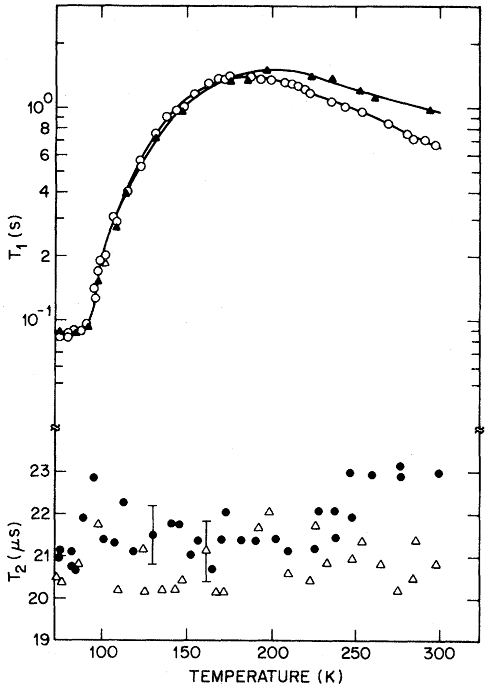

FIG. 1. T_1 and T_2 data at 60 MHz for the two $(TMTSF)_2X$ salts: For $X = ClO_4$, T_2 (△) and T_1 (▲); for $X = FSO_3^-$, T_2 (●) and T_1 (○).

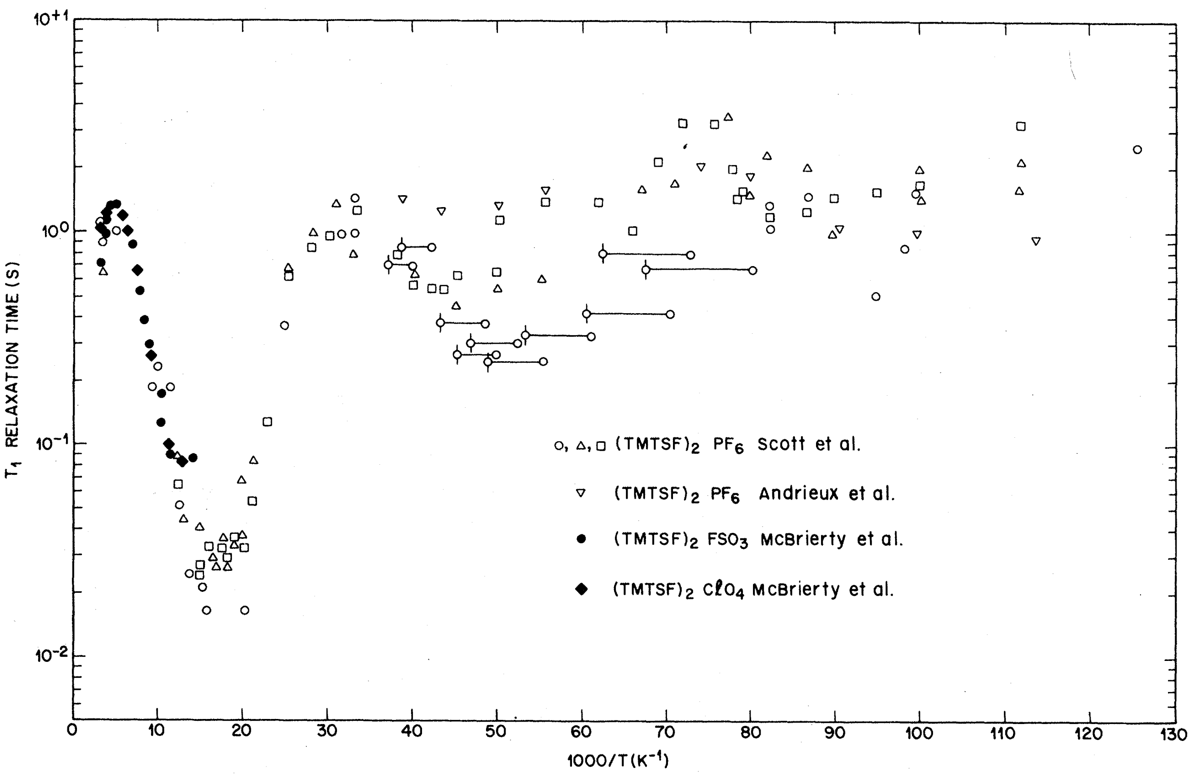

FIG. 2. Collated T_1 data for the $(TMTSF)_2X$ salts. Scott *et al.* (Ref. 10) suggest that their low-temperature data at 10.5 MHz may require a temperature correction of the order indicated. $\nu_0 = 10.5$ MHz (○); 14.9 MHz (△); 20.2 MHz (□); 45.0 MHz (▽); 60.0 MHz (●,◆).

Thus while other possible explanations may be invoked, differences in linewidth data can be rationalized in terms of orientational differences in the samples studied. Note that spin diffusion is responsible for the observation of comparable T_2's.[30]

Below ~200 K, the FSO_3^- and ClO_4^- salts exhibit identical T_1 versus temperature behavior indicating that methyl-group motion dominates relaxation, and that the formation of the T_1 minimum at ~80 K is therefore insensitive to the ^{19}F nucleus in the FSO_3^- salt. This statement will be generalized later to include the PF_6^- salt in this temperature region.

The transition observed at 86–89 K in the FSO_3^- salt does not show up in any clear way in the NMR data. This temperature region unfortunately coincides with the rapid rise in T_1 on the high-temperature side of the minimum (~80 K). The T_2 data suggest the presence of a small increase, of the order of 0.5 μs, in the 86–89 K temperature region, but this observation is speculative at best in view of the scatter in the T_2 result. Note, however, that $(TMTSF)_2FSO_3$ exhibits a weak T_2 transition at ~250 K which does not show up in the data for $(TMTSF)_2ClO_4$. There is a concomitant decrease in T_1 versus temperature at a rate which is more rapid than that observed in the ClO_4 salt, again indicating enhanced relaxation in the FSO_3^- salt. It is interesting to note the upturn in T_2^* versus temperature in this temperature region in the measurements of Scott *et al.*[10] on the PF_6^- salt. Motion of the ^{19}F nucleus or a change in the electronic states are likely causes. Berthier *et al.*[31] have showed that the electronic contribution to T_1 in the related material (tetramethyltetrathiafulvalene tetracyanoquinodimethanide) TMTTF-TCNQ(D_4) increases with temperature and attains a rate of 5 s^{-1} at 300 K. A similar mechanism may well operate in the $(TMTSF)_2X$ salts. Alternatively, or concurrently, the ^{19}F nuclei may be contributing to T_1 relaxation.

Let us now turn to a consideration of the proton T_1 behavior in $(TMTSF)_2X$ salts for which the available experimental data are depicted as a function of inverse temperature in Fig. 2. The appearance of two and, on occasion, three T_1 minima is not an uncommon manifestation of methyl-group behavior.[25,32] Tunneling theory predicts two minima, corresponding to *E*-*E* and *A*-*E* transitions, which are resolved at sufficiently high tunneling frequencies ($\gtrsim 0.5$ GHz).[26] Of course, multiple minima can also arise from the presence of different types of methyl groups with characteristic barrier heights to the onset of motion.[25] Indeed, 1,2,4-trimethylbenzene, which, in common with $(TMTSF)_2PF_6$ has two species of methyl group, exhibits a T_1 versus temperature response that is generally similar to that portrayed in Fig. 2.[32] (There may well be another minimum associated with methyl-group behavior at temperatures <18 K. However, no attempt will be made to interpret events in this temperature region in view of the additional complications arising from the metal-insulator transition.) Assignment of the observed minima to different types of methyl group in $(TMTSF)_2PF_6$ clearly provides the most straightforward interpretation of the T_1 response.

Recently Clough *et al.* have demonstrated that tunneling phenomena may be interpreted in terms of a "universal law" that takes no account of the phonon spectrum of the host lattice.[26] The law is based upon the strong correlation between the barrier height V (or tunneling frequency), the rate constant τ^{-1} for thermally activated methyl-group reorientation, and the absolute temperature Θ. In simple terms the tunneling frequency for different species of methyl group, reorienting independently, may be deduced from the temperature $\Theta_{\min}$, at which a T_1 minimum occurs. The validity of this approach has been tested satisfactorily for a sizable number of methyl-containing materials characterized by widely different phonon spectra.

For example, consider the 20.2-MHz data for $(TMTSF)_2PF_6$ for which $\Theta_{\min}$ is 23 ± 1 K and 56 ± 2 K, respectively. The corresponding tunneling frequencies are 1.5 ± 0.3 GHz and 82 ± 12 MHz. The fact that the ratio of the tunneling frequencies is comparable to the ratio of the magnitudes of the corresponding T_1 minima implies, albeit to a considerable approximation, that the two species of methyl groups are present in equal numbers.[15,17,24] In short, the shallow minima in the temperature range 18–24 K are a consequence of large tunneling frequencies, while the higher-temperature minima at 55–80 K more nearly conform to a Bloembergen-Purcell-Pound description.[33] The Lorentzian character in both temperature regimes is consistent with current theories of tunneling.

The spin-spin relaxation time manifests its usual behavior in that motions that are fast compared to the linewidth will produce narrowing. Thus when the tunneling rate also exceeds the linewidth (~ 100 KHz), narrowing will be observed, as is the case here.

In summary, the earlier interpretation of the T_1 minimum at 58 K in $(TMTSF)_2PF_6$ in terms of heteronuclear ^{1}H-^{19}F interactions is rejected and an alternative description in terms of methyl-group rotation is proposed. The transition observed at 86–89 K in $(TMTSF)_2FSO_3$ does not figure in any distinctive way in NMR T_1 or T_2 data. Variations in linewidth data from different laboratories for the PF_6^- salt can be reconciled on the basis of orientational differences in the samples studied.

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