# $^{13}C$ nuclear magnetic resonance in bis-tetramethyltetraselenafulvalenium hexafluorophosphide $[(TMTSF)_2PF_6]$ under pressure

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The nuclear spin-lattice relaxation rate, $T_1^{-1}$, of enriched $^{13}C$ nuclei in $(TMTSF)_2PF_6$ is measured in the high-pressure metallic phase at low temperature and high magnetic fields. $T_1^{-1}$ is found to depend logarithmically on applied field. These results are interpreted as nuclear relaxation to a charge carrier diffusing in two dimensions and are shown to be consistent with measurements on other nuclei in the material. By comparison with earlier measurements on $^{77}Se$ it is concluded that the spin-density-wave state interacts weakly with the carbon sites in the crystal.

The low-temperature properties of the organic superconductor bis-tetramethyltetraselenafulvalenium hexafluorophosphide $[(TMTSF)_2PF_6]$ have been under study recently due to claims of one-dimensional (1D) superconductivity,[1] the existence of a spin-density-wave (SDW) state[2] at low pressures, and the possible coexistence of metallic and SDW states. Our motivation in studying $(TMTSF)_2PF_6$ was to use an experimental technique that could probe directly the question of dimensionality of charge carrier motion. Nuclear magnetic resonance is an ideal probe because of its local nature. Also, the TMTSF molecule has three observable nuclei: $^1H$, $^{13}C$, and $^{77}Se$. In earlier publications[3,4] we presented results on the $^1H$ and $^{77}Se$ resonances. In the present paper we present NMR measurements on enriched $^{13}C$. Our results further support the viewpoint that $(TMTSF)_2PF_6$ in the high-pressure, low-temperature phase is a two- or three-dimensional metal.

The sample preparation details have been presented elsewhere.[5] The sample was a lightly pressed powder mounted inside a coil of dimensions 0.15 cm diameter and 0.2 cm long. The sample and coil were mounted inside the Be-Cu pressure vessel which was immersed in a liquid-helium bath whose temperature could be controlled. The solid helium pressure technique[6] resulted in no observed deterioration of the sample after repeated temperature and pressure cycles. Spin-lattice relaxation, Knight shift, spin-spin relaxation, and linewidth measurements were performed on the $^1H$ and $^{77}Se$ resonances and have been presented elsewhere.[3,4] The inner bridging carbons, denoted as C1 and C6 in Ref. 7, and shown in the figure were enriched approximately 70–80%. Therefore the measurements reported here give information on these carbon sites.

The detailed field (or frequency) dependence of the spin-lattice relaxation rate $T_1^{-1}$ of a nucleus that is hyperfine coupled to a charge carrier diffusing in $d$ dimensions has been shown in several cases[8] to reflect the effective dimensionality $d$ of the carrier. The reader is referred to several excellent references[8,9] that develop the theory. For our purposes, $T_1^{-1}$ varies as shown below:

$$\begin{aligned} &T_1^{-1} \propto H_0^{-1/2}, \quad d=1 \ ; \\ &T_1^{-1} \propto \ln H_0, \quad d=2 \ ; \\ &T_1^{-1} \text{ independent of field}, \quad d=3 \ . \end{aligned} \tag{1}$$

Here $H_0$ is the applied magnetic field.

A clear indication of one of the above behaviors establishes the dimensionality $d$ in a appropriate frequency regime. The two-dimensional result, i.e., $T_1^{-1} \propto \ln H_0$ has been observed[3] from 12 to 120 kOe by $^1H$ and $^{77}Se$ $T_1^{-1}$ measurements. A crossover to three-dimensional diffusion has been observed via proton $T_1^{-1}$ measurements on $(TMTSF)_2PF_6$. Physically, the crossover behavior is easy to understand. The magnetic field establishes a characteristic time scale, $\omega_e^{-1} = \hbar/g\mu_B H_0$. Suppose a system has two diffusion rates $D_2 > D_3$, which would be characteristic of a quasi 2D (two-dimensional) metal. $D_2$ represents an intraplane diffusion rate and $D_3$ an interplane diffusion rate. Then for $D_2 > \omega_e > D_3$ the carrier diffusion is effectively 2D and for $D_3 > \omega_e$ the system is effectively 3D. In other words, for long enough times the diffusion "looks" 3D.

In Fig. 1 we show $T_1^{-1}$ vs $H_0$ for $^{13}C$ at 6.9 kbar which complements our earlier results on $^1H$ and $^{77}Se$. The relaxation rate is observed to follow a logarithmic field dependence indicative of relaxation to a spin diffusing in two

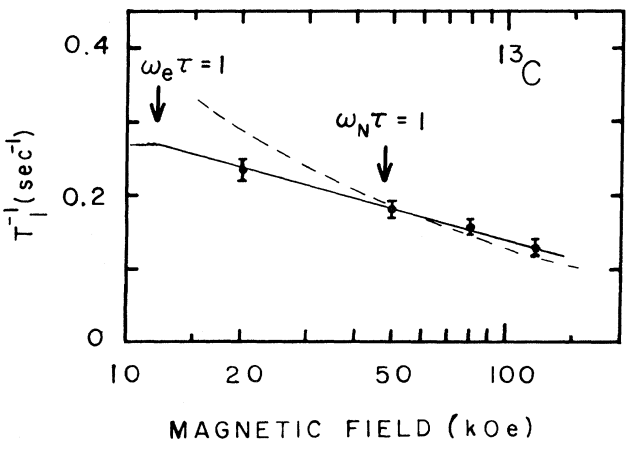


FIG. 1. Spin-lattice relaxation rate of inside bridging $^{13}C$ at 6.9 kbar, 4.02 K vs applied field. The appropriate electronic and nuclear cutoff frequencies are shown. The dashed line shows a fit of the data to one-dimensional diffusion.

 

dimensions. The cutoff to three dimensions may be governed by either $\omega_N = D_3$ or $\omega_e = D_3$ where $\omega_N$ and $\omega_e$ are the nuclear and electronic Larmor frequencies and $D_3$ the interplane diffusion rate. The details of the hyperfine coupling determines which cutoff is appropriate. In the case of $(TMTSF)_2PF_6$, $\omega_e = D_3$ is the appropriate cutoff for the following reason. The cutoff for the $^1H$ relaxation rate[3] is observed at 12 kOe. If $\omega_N = D_3$ determined the cutoff, then $H_0 = 48$ kOe would be the cutoff for $^{13}C$, as shown by the arrow in Fig. 1. This is observed to not be the case. Unfortunately, due to signal-to-noise limitations we could not extend measurements to low enough fields to observe the expected cutoff at 12 kOe.

These data are completely consistent with the $^1H$ and $^{77}Se$ results, which give the same logarithmic field dependence to $T_1^{-1}$. The only difference is the value given to the hyperfine coupling constant. Therefore we conclude that $(TMTSF)_2PF_6$ is at least a quasi 2D metal.

We now turn to a discussion of the SDW state. One important question is the determination of where the spins reside in the SDW state. It has been shown[4] that in the SDW state a large magnetic field ( $\gtrsim 5$ kOe) exists at the Se sites in the crystal causing a large drop in $^{77}Se$ amplitude from line broadening. No such effect is observed for the $^{13}C$ (C1 and C6) sites as there is no line broadening or change in nuclear magnetization as the sample passes into the SDW at low pressure. The Knight shift at the carbon site, $0.016 \pm 0.005\%$, is much smaller than that observed[4] for the $^{77}Se$. Furthermore, the linewidth is much smaller than that observed for $^{77}Se$ and is mainly limited by magnetic field inhomogeneities. Finally, the value of $T_2 = 560$ $\mu$s (80 kOe, 4.02 K) is that expected for the dipolar coupling between C1 and C6. Our conclusion, then, is that most of the SDW amplitude resides at the $^{77}Se$ sites in $(TMTSF)_2PF_6$.

In conclusion, we have shown from nuclear magnetic resonance experiments on $^{13}C$, $^1H$ (Ref. 3) and $^{77}Se$ (Ref. 4) that $(TMTSF)_2PF_6$ is a 2D metal in the high-field regime, a 3D metal in the low-field regime, and that the SDW state interacts most strongly with the Se sites in the crystal.

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