^{77}Se nuclear magnetic resonance in di-tetramethyltetraselenafulvalene phosphorous hexafluoride [$(TMTSF)_2PF_6$] under pressure

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(Received 2 September 1982; revised manuscript received 15 February 1983)

We report measurements of the Knight shift, spin-lattice relaxation time, linewidth, and absolute susceptibility of ^{77}Se as functions of pressure, field, and temperature in the organic superconductor tetramethyltetraselenafulvalene phosphorous hexafluoride [$(TMTSF)_2PF_6$]. The results indicate that there is significant p-wave spin density at the Se sites and that the quenching of the spin-density wave (SDW) is a slow function of pressure. That is, there is a significant pressure regime where there is coexistence of a metallic and SDW state. The nature of this coexistence is discussed.

The organic superconductor tetramethyltetraselenafulvalene phosphorous hexafluoride [$(TMTSF)_2PF_6$] is a system with a rich variety of interesting properties including the onset of a spin-density-wave[1] (SDW) state at low temperature, the suppression of the SDW state to lower temperatures with application of pressure, and the occurrence of superconductivity[2] around 1 K and 7 kbar. Our motivation in this study was to employ a technique that would probe the detailed interplay between the metallic and SDW states. One question of particular importance is whether or not the metallic and SDW states coexist in the same regions of the crystal. Another possibility is that there is a mixed phase regime where different regions of the sample are in the metallic or SDW states. The nuclear magnetic resonance of the ^{77}Se is an ideal local probe to study these questions. We have organized the paper as follows. After discussing experimental details we present measurements of Knight shift, T_2 and T_1 in the high-pressure phase as functions of temperature and field. We then present results on the pressure dependence of ^{77}Se Knight shift, susceptibility, and T_1.

The preparation of the sample used in this study has been previously described.[3] The sample was a lightly pressed pellet of dimensions 0.15 cm diameter and 0.2 cm in length. Using He as the pressure medium[4] enabled us to vary the pressure from ambient up to 8.3 kbar under hydrostatic conditions. We observed no hysteresis or deterioration of the sample with pressure cycling. Superconductivity was observed at 6.9 kbar and 1.1 K at zero field via rf absorption measurements. The superconducting transition is very narrow, indicating that the bulk powder sample properties are unaffected by strains. Due to the very small size of our sample (limited by the pressure vessel) special techniques were needed to be used to improve the signal-to-noise ratio. Even with these techniques our lowest field was limited to 20 kOe. At this field the relaxation rate measurements took several days each. Temperature was measured by monitoring the vapor pressure of the helium bath surrounding the pressure vessel. Due to the small volume of sample used, a low-power transmitter[5] was sufficient for the experiments.

The Knight shift was measured by comparing the shift of the ^{77}Se nucleus to ^{63}Cu in the NMR coil. This was accomplished by using a frequency adding-subtracting scheme so that the spectrometer could be retuned to the ^{63}Cu signal in a short time. A Knight shift of 0.23% was assumed for the ^{63}Cu in the coil. Over the range of our experiments, namely, $20 \leq H \leq 105$ kOe, $1 < T < 4$ K, and $0 \leq P \leq 8.3$ kbar, we find the Knight shift in the metallic state to be $K = -0.09 \pm 0.01\%$; that is, K is independent of field, temperature, and pressure. The fact that K is negative (upfield) indicates that there is p-wave spin density at the Se site in $(TMTSF)_2PF_6$. This conclusion correlates very well with measured electron density profiles.[6]

Let us first consider the high-pressure metallic phase in the temperature range 1–4 K. We observe a Korringa relaxation rate (T_1T = constant) as shown in Fig. 1 characteristic of a metal. The pressure of 6.9 kbar is sufficiently high to be in the metallic phase as superconductivity is observed in zero field at 1.1 K. If the ^{77}Se nucleus were relaxed by s-state electrons, then the product K^2T_1T would be known[7]:

$$K^2T_1T = \frac{\hbar}{\pi k_B}\left(\frac{\mu_B}{g\mu_N}\right)^2 = 7.24\ \mu\text{s K} \ . \qquad (1)$$

Here $\hbar$ is Planck's constant divided by 2π; k_B, Boltzmann's constant; μ_B, the Bohr magneton; and $g\mu_N$,

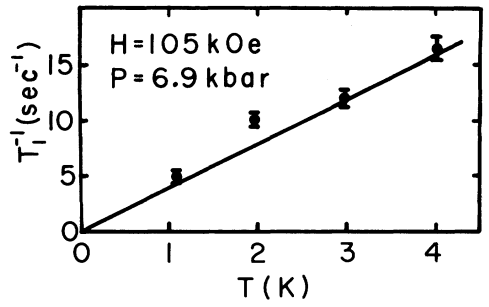

FIG. 1. Spin-lattice relaxation rate of ^{77}Se vs temperature at 6.9 kbar and 105 kOe. The departure from Korringa relaxation around 2 K is due to the enhancement of T_1^{-1} through the high-field phase transition (see Ref. 14).

the nuclear moment. Our experimental value of 0.24 μs K indicates that the relaxation is *not* due to the contact hyperfine interaction. We cannot, unfortunately, estimate the relaxation due to p-wave electrons since we do not know the hyperfine field and density of states. We can conclude, however, that the relaxation and Knight shift are dominated by p-wave electrons at high pressure.

We have plotted T_1^{-1} vs H in Fig. 2 for ^{77}Se at high pressure and $T = 1.08$ K. These results are entirely consistent with earlier results[8] on the field dependence of ^{1}H relaxation rates where a logarithmic high-field behavior is observed indicative of relaxation to a spin diffusing in two dimensions. Unfortunately, the error bars are too large to definitely establish the logarithmic field dependence that is observed in the proton relaxation rates in the same pressure and temperature ranges. We could not extend T_1^{-1} measurements to sufficiently low fields to observe the three-dimensional (3D) cutoff due to signal-to-noise limitations.

The magnitude and field dependence of the linewidth shown in Fig. 3 at 4.02 K are quite unusual.

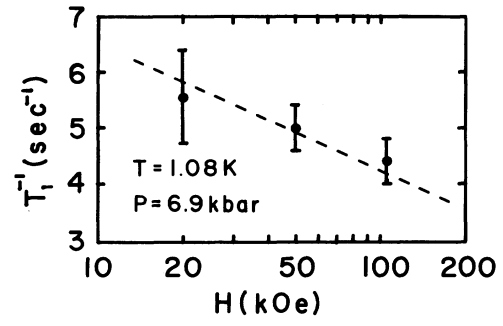

FIG. 2. Spin-lattice relaxation rate of ^{77}Se vs applied field at 1.08 K and 6.9 kbar. The dotted line is the theoretical logarithmic field dependence from the proton relaxation rate with only the hyperfine interaction adjusted.

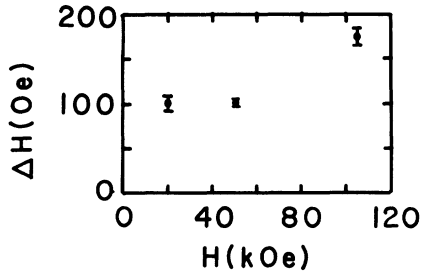

FIG. 3. Linewidth of ^{77}Se and 4.02 K and 6.9 kbar vs applied field.

The linewidth is nearly independent of temperature over our temperature range of 1–4 K. In the high-field regime the linewidth increases with applied field, and at low fields the linewidth approaches a constant indicating that there is some strong inhomogeneous broadening. The low-field linewidth of 100 Oe is much larger than the expected dipolar linewidth ($\mu/r^3 \sim 0.1$ Oe). Throughout the temperature and field range, T_2 is constant and has the value 440 μs. The most likely mechanism responsible for the linewidth is an indirect interaction with the SDW. If some of the Se sites in the unit cell are not involved with the formation of the SDW state their proximity to the sites with appreciable spin density can lead to a broad linewidth. As we show below, the SDW state coexists with the metallic state even at higher pressures.

We now turn to a systematic study of the ^{77}Se NMR at lower pressure. In order to monitor the onset of the SDW as the pressure is lowered, we chose to carefully measure the absolute susceptibility of the ^{77}Se nucleus as a function of pressure. We used the Schumacher-Slichter method[9] with the calibration nucleus being the ^{13}C. This scheme is a variant of the usual Schumacher-Slichter experiment where the absolute electronic susceptibility is measured by comparison with a known NMR signal. The ^{13}C (1 at.% abundant) serves as a convenient calibration since its resonant field at constant frequency is only $\sim$30% less than that of ^{77}Se. It is important to use a calibrating nucleus whose resonance field is near ^{77}Se to minimize possible errors due to a field-dependent skin depth. All measurements described here were performed at 105 kOe and in the temperature range 1–4 K. There are ten carbon nuclei (three inequivalent sites) in the TMTSF molecule. There is the possibility that the bridging carbons are shifted or broadened strongly through interaction with the SDW. In order to check this we measured the ^{13}C NMR on a powder sample which had the bridging carbons enriched. The results indicate that the SDW interacts weakly with the bridging carbons so that we may assume that all the ^{13}C nuclei are observed at all pressures (note that exclusion of the bridging carbons

only leads to a 20% error). Further support of the interpretation that little or no SDW resides on the bridging carbons comes from the observation that T_1 is very slow (~ seconds). The ^{77}Se and ^{13}C resonances were measured by monitoring the echo amplitude. Care was taken to pulse so as to not saturate the resonances and adjustment of the pulse lengths appropriate for the nucleus under study were made. Corrections were also made for the different spin-spin relaxation times of the nuclei.

The susceptibility results are plotted in the lower part of Fig. 4 where the absolute susceptibility of the ^{77}Se is plotted versus pressure. $X = 1.0$ corresponds to observation of all the ^{77}Se nuclei, that is, four Se nuclei for every ten C nuclei with assumption of 7.5 at.% ^{77}Se abundance and 1.11 at.% abundance of ^{13}C. Several features are apparent. First, there is a broad pressure region (2–6 kbar) where the ^{77}Se susceptibility changes rather slowly. This is in contrast with the measured conductivity on typical single-crystal samples which rises sharply only at pressures around 7 kbar. Secondly, there is a small remaining susceptibility even at zero pressure. This is in contrast with earlier measurements[10] at ambient pressure as a function of temperature where it was implied that the ^{77}Se susceptibility drops to zero in the SDW state.

We do not observe any broadening of the linewidth of the observed ^{77}Se as the pressure is decreased. Evidently, whenever the SDW interacts with (or resides on) a Se site the effect is to completely wipe out the resonance. We have done a careful search for any shifted ^{77}Se resonance from zero field up to 120 kOe and do not observe any resonances. Our sensitivity was such that if a reasonable fraction (~ 50%) of the ^{77}Se had a linewidth less than about 500 Oe

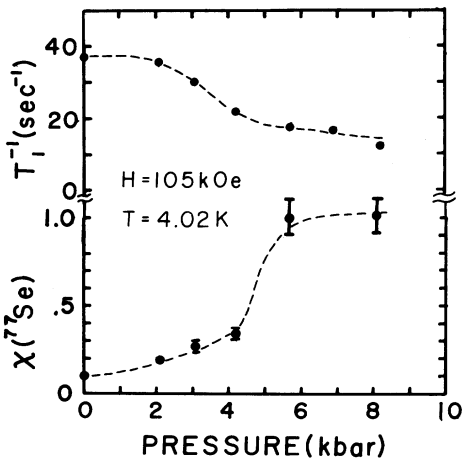

FIG. 4. Spin-lattice relaxation rate (top) and absolute susceptibility (bottom) of ^{77}Se vs pressure at 105 kOe and 4.02 K. The lines are guides for the eye. $X = 1.0$ corresponds to all the ^{77}Se in the sample.

they would have been observed. The interpretation, then, that the ^{77}Se is broadened beyond measurement range when it interacts with the SDW is probably correct.

The broad region where the ^{77}Se susceptibility changes from ~10% to 100% indicates that the SDW is suppressed rather slowly as pressure is increased, more slowly than conductivity measurements suggest. This is perhaps not surprising as dc conductivity only tells one when the sample is metallic continuously over macroscopic distances. The picture emerges, then, of the coexistence of the SDW and metallic states over a large-pressure regime. The meaning of coexistence here is that some regions of the crystal are metallic and other regions are in the SDW state. Further support of this conclusion comes from the observation of several groups that ^{1}H spin-lattice relaxation rates become nonexponential[11] in the SDW state at low pressures. If the SDW and metallic state were really coexistent in identical regions of the samples, one would expect the stronger relaxation mechanism to be dominant with the result that only one exponential would be observed. The two exponentials observed indicate that different regions of the crystal have different states and that the protons monitor the two states with two relaxation rates. The ^{77}Se T_1, on the other hand, is always characterized by an exponential recovery and a Korringa rate at all measured temperatures, fields, and pressures.

The apparent inconsistency of the comparison between ^{1}H and ^{77}Se is easily explained. The protons are rather decoupled from interactions with either the conduction electrons characterizing the metallic state or with the SDW due to their positions in the crystal structure. As a result, only dipolar interactions are involved and the proton resonance can be observed and relaxed in vicinity of *either* the SDW or metallic state. In other words, its interaction with the SDW is not so strong as to strongly shift or broaden the resonance. The ^{77}Se, on the other hand, interacts with the SDW so strongly that the resonance is "wiped out" and only those ^{77}Se nuclei that interact with the metallic state or indirectly with the SDW state are observable. This interpretation is also borne out by the fact that the measured T_1^{-1} versus pressure of the ^{77}Se only increases slightly in the SDW state as shown in the upper part of Fig. 4, whereas the proton T_1 decreases by more than an order of magnitude over the same pressure range. This small pressure dependence is due to the fact that the ^{77}Se nuclei that are SDW broadened can still interact with the remaining metallic ^{77}Se through T_2 interactions, thus affecting T_1 slightly.

If we take the increase in the ^{77}Se T_1^{-1} at low pressure to be due to a T_2 mechanism we can estimate the fluctuating field at the ^{77}Se site. The spin-lattice relaxation rate for a nucleus experiencing a fluctuating field of magnitude h_0 with correlation time τ_0 is

given by[12]

$$T_1^{-1} = \frac{2\gamma_n^2 h_0^2}{3} \frac{\tau_0}{1+\omega_0^2\tau_0^2} \ , \tag{2}$$

where γ_n is the gyromagnetic ratio and ω_0 the resonance frequency. If we let the correlation time be given by $\tau_0 = h/J$ with $J/k_B \sim 200$ K as given by spin-wave experiments[13] then $\omega_0\tau_0 << 1$, and Eq. (2) reduces to

$$T_1^{-1} = \frac{2\gamma_n^2 h_0^2 \tau_0}{3} \ . \tag{3}$$

Substituting in the values yields $h_0 \sim 5$ kOe for the field at the ^{77}Se site in the SDW state, consistent with our experimental observations stated above that a large hyperfine field at the ^{77}Se site wipes out the resonance.

In conclusion, then, measurements of the Knight shift, T_1^{-1}, and susceptibility of ^{77}Se as functions of pressure, field, and temperature support the view that the SDW and metallic states coexist in different regions of the sample over a broad range of pressure. Also, there is significant p-wave spin density at the ^{77}Se site and the SDW interacts weakly with the carbon sites in the crystal. Finally, a hyperfine field of at least 5 kOe exists at the ^{77}Se site in the SDW state.

ACKNOWLEDGMENTS

We wish to thank D. L. Overmyer for his expert technical assistance. We also thank R. L. Greene, J. F. Kwak, W. G. Clark, and P. M. Richards for useful discussions. This work was performed at Sandia National Laboratories, and supported by the U.S. Department of Energy under Contract No. DE-AC04-76-DP000789.

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