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NUCLEAR SPIN-LATTICE RELAXATION IN THE LINEAR CHAIN METAL, $NbSe_3$

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The nuclear spin-lattice relaxation time T_1 of ^{93}Nb in $NbSe_3$ has been observed as a function of frequency ν_N in the range 6-40 MHz at 4.2 K and of temperature T in the range 1.3-77 K at 10 MHz. $[T_1T]^{-1}$ is found to be proportional to $1/\sqrt{\nu}$ corresponding to characteristic divergence of spin correlation function in 1-D system. Below $\sim$10 MHz, a break down of the divergence is observed. The important features of the T dependence observed are a sharp minimum at $\sim$45 K and an asymptotical approach to the metallic relation, $T_1T = const.$ with decreasing T down to helium temperature. This $[T_1T]^{-1}$ minimum is explained by the destruction of the Fermi surface due to the CDW gap formation. The re-increase of $[T_1T]^{-1}$ below the CDW transition may suggest a partial recovery of the destructed Fermi surface.

INTRODUCTION

Niobium triselenide is a highly anisotropic metal which has been the subject of considerable attention. The crystal structure is made up of infinie chains of trigonal prisms extending parallel to the monoclinic crystal axis.[1] The electrical resistivity along the chains shows a metallic behavior from room temperature down to liquid helium range and has two anomalies at 145 and 59 K. These anomalies have been interpreted[2] in terms of two different charge density wave (CDW) formations.

Below these transitions, $NbSe_3$ shows the striking non-Ohmic behavior.[3] The measurements with a pressure of 7 kbar[4] have shown an increase in the superconducting transition temperature from $T_c \sim 0$ to $T_c \simeq 2.5$ K. The pressure also suppressed the CDW[5] and it has been suggested that the CDW formation and the superconductivity are antagonistic,[6] both competing for the electronic states near the Fermi surface (FS). These properties are also observed commonly on the most of low dimensional metals. Herein presented are experimental results on a nuclear magnetic resonance investigation to see what extent the electronic structure of $NbSe_3$ is one dimensional (1-D), and what happens on the electronic states near the FS at and below the CDW transition. The nuclear spin-lattice relaxation is related to the FS parameters and can yields information about the dynamic properties of the conduction electrons.

EXPERIMENTAL

Polycrystallines of $NbSe_3$ were obtained by the usual method[1] of heating stoichiometric amounts of niobium and selenium for several weeks in an evacuated quartz tube. A single crystal-like sample was prepared by arranging the fibrous crystals into a bundle with parallel b-axis.

The ^{93}Nb resonance spectrum measurements on the single crystal were made with b-axis parallel to the external magnetic field H_0 using a signal averager to obtain a sufficient S/N ratio. In this orientation (b-axis // H_0) and for the hexagonal symmetry, the spectrum of ^{93}Nb ($I = 9/2$) was composed of nine different lines whose frequencies are given by

$$\nu_{m \to m-1} = \nu_0(1 + K_{//}) - \nu_Q(m - 1/2) \qquad (1)$$

where $\nu_Q = 3e^2qQ/2I(2I-1)$, Q is the nuclear quadrupole moment, q the electric field gradient along the b-axis, and $K_{//}$ the parallel Knight shift. The observed first-order quadrupole spectrum yields an assignment of a quadrupole coupling constant $h^{-1}e^2qQ = 7.2 \pm 0.7$ MHz and $K_{//} = 0.10 \pm 0.05$ % at 1.3 - 4.2 K.

In the measurement of the nuclear spin-lattice relaxation T_1, we must consider that we observe only the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ central transition. The relaxation behavior of the magnetization $M(t)$ for the transition is given by[7]

$$\frac{[M(\infty)-M(t)]}{M(\infty)} = a_1 e^{-2Wt} + a_2 e^{-12Wt} + a_3 e^{-30Wt} + a_4 e^{-56Wt} + a_5 e^{-90Wt}$$

where $2W = (T_1)^{-1}$ and a_i's are coefficients depending on the initial population of $2I+1$ levels. A theoretical calculation

for the initial conditions where (a) populations of $|m| > \frac{1}{2}$ levels are in thermal-equilibrium with the $|m| = \frac{1}{2}$ levels, and (b) $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition is saturated completely but the population of other spin levels are not effected, provides as

(a) a_1=0.152 a_2=0.140 a_3=0.153 a_4=0.192 a_5=0.363, and

(b) a_1=0.006 a_2=0.034 a_3=0.092 a_4=0.215 a_5=0.653,

respectively. Thus, in order to get the *2W* term, the fast relaxation terms should be suppressed by the initial condition imposed on the spin system. In the liquid helium temperature, we utilized a saturating comb composed of a few hundred *rf* pulses and obtained the *2W* component directly. Above 4.2 K, however, the comb method was not applicable since even a comb composed of a few *rf* pulses increased the sample temperature by Joule heating. Then we recorded full recovery behaviors $M(t)$ after single $\pi/2$ pulse and T_1 was assigned by getting the best fit of our data with the theoretical recovery curve for the initial condition (b). The agreement of T_1 values obtained at 4.2 K by this procedure with that by the comb method was good enough.

The T_1 of ^{93}Nb in the $NbSe_3$ polycrystalline was measured as a function of the nuclear resonance frequency ν_N from 6 to 38 MHz at 4.2 K. Data of $[T_1T]^{-1}$ vs. ν are shown in Fig. 1 in which the slope of a straight line is 1/2. We find here reasonable agreement of the data with this line. On the other hand, a level-off from the $1/\sqrt{\nu}$ line takes place below $\sim$10 MHz.

A few measurements of the T_1 on the single crystal were performed as a function of the angle θ between the b-axis and H_0. Results at 4.2 K are shown in Fig. 2 which represent a decrease by about 44 % in $[T_1T]^{-1}$ as the θ increases from 0 to $\pi/2$.

Fig. 3 shows the temperature dependence of $[T_1T]^{-1}$ and the resistive transition[3] in the insert. The principal feature is a sharp minimum at $\sim$ 45 K and a following asymptotical approach to a constant with decreasing T down to helium range.

DISCUSSION

Analysis of the Frequency Dependent Relaxation

The nuclear relaxation rate induced by the electron - nuclear interactions can be expressed as[8]

$$(T_1)^{-1} = \Omega_z G^z(\omega_N) + \Omega_+ G^+(\omega_e) \qquad (2)$$

where $\Omega_\alpha(\alpha = z,+)$ are the geometrical factors which depend on

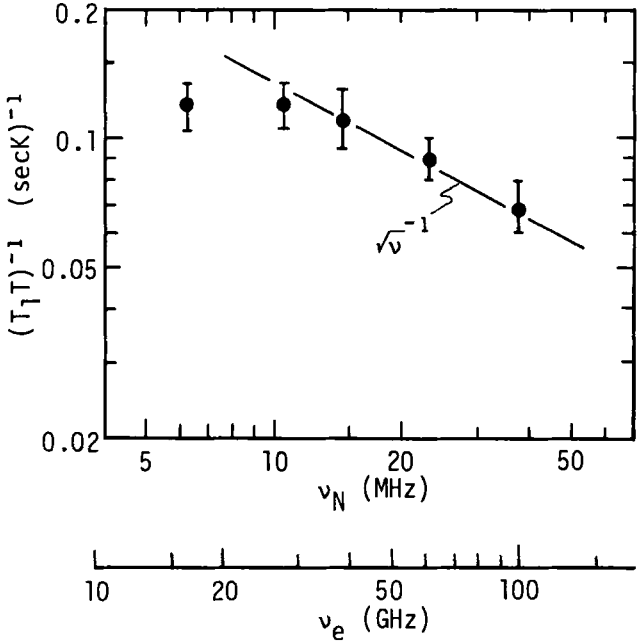

FIGURE 1 Variation of ^{93}Nb relaxation rate in $NbSe_3$ polycrystalline as a function of the nuclear (and electron) Zeeman frequencies at 4.2 K.

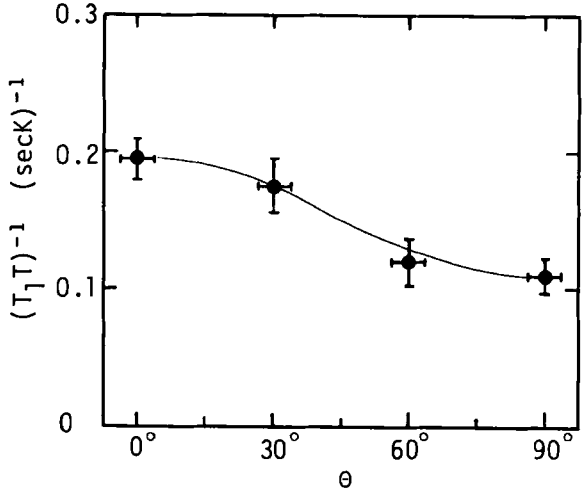

FIGURE 2 Dependence of ^{93}Nb relaxation rate in $NbSe_3$ single crystal on the angle θ between b-axis and H_0 at 10.5 MHz and 4.2 K.

the hyperfine interactions, $G^{\alpha}(\omega)$ is the Fourier transform of the spin correlation function, $\Gamma^{\alpha}(t)=<s^{\alpha}(t)s^{\alpha*}(0)>$, and for an isotropic Hamiltonian one has $2G^{z}(\omega) = G^{+}(\omega) = G(\omega)$.

Recent theoretical calculation[9] indicates the divergence of the correlation function, $G(\omega) \propto 1/\sqrt{\omega}$ as $\omega \to 0$, providing 1-D tight-binding Hamiltonian taking into account the electron-electron and electron-phonon interactions. This divergence comes from the very slow decay of $\Gamma(t) \propto 1/\sqrt{t}$ as $t \to \infty$ in 1-D,[10] and it corresponds to an important contribution, in another word , from the long wave length part of the momentum transfer ($q_{\perp} \simeq 0$) connecting two points on the FS in 1-D system.[11] This is in contrast with 3-D metals where the $q_{\perp} \simeq 0$ contribution is much smaller because of low density of states near $q_{\perp} \simeq 0$.

Consequently, the $(T_1)^{-1}$ value depends on the exchange spectrum at both frequencies ω_N and ω_e and has $1/\sqrt{\omega}$ divergence.

For the ^{93}Nb relaxation in $NbSe_3$, the d core-polarization and orbital interactions are dominant contributions over the s contact interaction since the Nb s-band lies even higher in energy above the Fermi energy E_F due to strong hybridization with the Se orbitals.[12] As the energy transfer by the core-polarization brings with simultaneous electron - nuclear spin flip-flop, the $(T_1)^{-1}$ depends on the exchange spectrum as, $G(\omega_e \pm \omega_N) \simeq G(\omega_e)$. On the other hand, $(T_1)^{-1}$ depends on $G(\omega_N)$ for the orbital interaction. Thus, the $1/\sqrt{\omega}$ dependence of $G(\omega)$ and the fact that the geometrical factor Ω is the same order in magnitude for the d core-polarization and orbital interactions, suggest strongly the dominant orbital contribution to $(T_1)^{-1}$, as $\omega_N \ll \omega_e$.

For the case of the orbital relaxation, following the calculation by Ehrenfreund *et al.*,[11] we obtained as

$$[T_1T]^{-1} = 2\pi\hbar k_B[\gamma_N N(E_F)H_{hf}(orb)]^2\{\S(q\simeq 0)+\S(q\simeq 2k_F)\}p \quad (3)$$

where $H_{hf}(orb)$ is the orbital hyperfine field and p is a reduction factor. $\S(q\simeq 2k_F) = 1$ for free electrons, and $\S(q\simeq 0) = (2\omega_N\tau)^{-1/2}$ for the possible case of finite mean free path.[11]

The experimental $\omega^{-1/2}$ dependence of $[T_1T]^{-1}$ indicates the important contribution of the $\S(q\simeq 0)$ term as discussed above and provides an evidence for the existence of 1-D flat Fermi surface even at the liquid helium temperature.

The reduction factor p can be calculated as a function of admixture parameters c_i of the d wave functions at E_F and found to be dependent of the angle θ between the b-axis and H_o as

$$p = p^{(1)} + p^{(2)} sin^2\theta \quad (4)$$

with

$$p^{(1)} = c_2(3c_1 + 2c_3) \quad \text{and} \quad p^{(2)} = c_2^2 - 3c_1c_2 + 4c_3^2 - 2c_2c_3,$$

where $c_1 \in d_{3z^2-r^2}$, $c_2 \in d_{xz,yz}$, $c_3 \in d_{xy,x^2-y^2}$, with a relation $c_1 + 2c_2 + 2c_3 = 1$. A solid curve in Fig.2 was drawn following eq,(4) with $(p^{(1)} + p^{(2)})/p^{(1)} \simeq 0.56$. The orientation dependence of $[T_1T]^{-1}$ also shows the dominant orbital interaction since the core-polarization relaxation should be independent of the angle θ. In order to obtain the ratio as $p^{(2)}/p^{(1)} \simeq -0.44$, one should put a limitation on the admixture parameters at E_F as follows;

$$c_1 \simeq 0.2 - 0.5, \quad c_2 \simeq 0.1 - 0.4 \quad \text{and} \quad c_3 < 0.15.$$

Experimentally the $[T_1T]^{-1}$ saturates below $\sim$ 10 MHz as shown in Fig. 1. This result indicates that in $NbSe_3$ the divergence of $G(\omega)$ breaks down and can be interpreted by introducing a cutoff process in the spin correlation.[9,10] The $G(\omega)$ could be calculated by taking Fourier transform of the self-correlation function which was constructed by[9,13]

$$\Gamma(t,\tau_c) = \Gamma(t)exp[-t/\tau_c] \tag{5}$$

where a function $\exp[-t/\tau_c]$ is introduced to get a fitting with the experimental $[T_1T]^{-1}$ plateau. From the eq.(5), $G(\omega)$ can be obtained as

$$G(\omega) \propto (\tau_c/2\omega)^{-1/2} \quad \text{for} \quad \omega\tau_c \gg 1, \quad \text{and}$$
$$G(\omega) \propto (\tau_c)^{-1/2} \quad \text{for} \quad \omega\tau_c \ll 1.$$

Thus, from the experimental $[T_1T]^{-1}$ behavior, we obtained a cutoff frequency as 2.3×10^7 Hz which gives a decay rate at which the spin correlation deviates from its 1-D behavior.

Nuclear Spin Relaxation and CDW Formation

The general characteristic of 1-D metals is in their instability towards the formation of the CDW which creates an energy gap at the E_F. This should result in a decrease of the density of states $N(E_F)$ and, therefore, a decrease of $[T_1T]^{-1}$ just below the CDW transition temperature T_c. For an ideal 1-D conductor, the CDW formation transforms the material into a semi-conductor because of the topology of FS. The metallic behavior of the $NbSe_3$ below T_c has been explained by the existence of plausible knots on the flat FS which does not satisfy the nesting criterion.[3]

As shown in Fig.3, the experimental value of $[T_1T]^{-1}$

provides a minimum at ~ 45 K indicating the reduction of $N(E_F)$ by about 60 % at least from the value at 77 K. This result gives an evidence for the destruction of portions of the FS due to the CDW formation as the second resistivity peak occurs also at 49 K.[3]

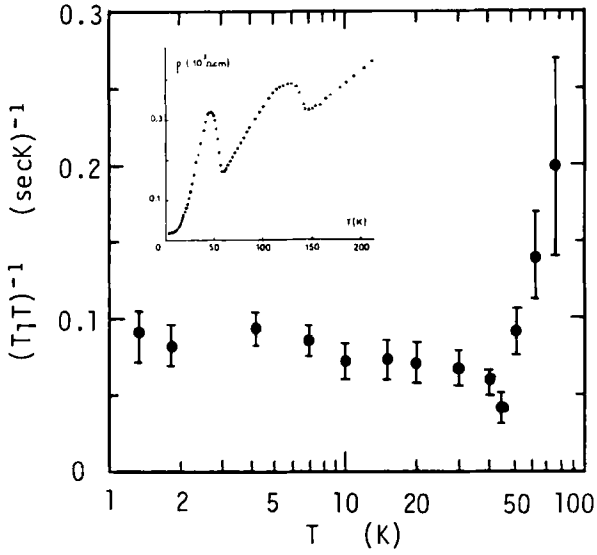

FIGURE 3 Variation of $[T_1T]^{-1}$ of ^{93}Nb in $NbSe_3$ polycrystalline as a function of the temperature T at 10.5 MHz. The characteristic of the resistivity is shown in the insert.[3]

The most striking result is the increase of the $[T_1T]^{-1}$ with lowering T after providing the minimum at $\sim$ 45 K. Then, it approaches to the metallic relation, $T_1T = const$. This increase of $[T_1T]^{-1}$ gives an estimate of $N(E_F)$ recovery to about 70 % of the value at 77 K. This recovery can not be explained by the knots model since, if it is the case, the $N(E_F)$ should be constant after the significant reduction just below the T_c. Though the origin of this $N(E_F)$ recovery effect is unclear at present, it might be worthwhile to point out that this may relates to the strong recovery of the conductivity below the second resistive peak at 49 K. At this point, more experimental and theoretical works are necessary to obtain a full understanding.

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