Magnetic-Field Effects in $NbSe_3$

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We have performed NMR studies on an aligned, multicrystalline $NbSe_3$ sample at various temperatures. We find conclusive evidence of field-induced Fermi-surface changes at low temperatures, and associate these changes with charge-density-wave (CDW) enhancement mainly localized on the yellow crystallographic site, contrary to expectations, since the low-temperature CDW is mainly localized on the orange site.

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Charge-density-wave (CDW) systems display fascinating static and dynamic properties, and the magnetic behavior of CDW systems has been a subject of growing attention. In niobium triselenide ($NbSe_3$), which has been extensively studied for the past decade [1,2], a number of magnetic-field-induced phenomena have been reported at temperatures below 59 K in a moderately high field. These magnetic anomalies have been related to the possibilities of CDW coupling with magnetic impurities, field-induced spin-density waves (SDW's), mixed density waves, and field-enhanced nesting of the Fermi surface due to the destruction of electron-hole pockets. So far, the nature of magnetic-field-induced phases in $NbSe_3$ has been open to question.

A large magnetoresistance enhancement was first observed in $NbSe_3$ by Coleman *et al.* [3] in a magnetic field perpendicular to the high-conductivity axis (*b* axis). They attributed the anomaly to field-induced reduction of the Fermi surface, and speculated on a SDW component in the ground state. A strong reduction of the threshold electric field, above which the conductivity due to CDW motion appears, was also reported at low temperatures [4,5]. Furthermore, a phase transition diagram related to these threshold-field changes has been suggested [4].

There has been much interest in field effects in low-dimensional materials and several models have been established to explain the magnetic-field-induced enhancement for CDW and SDW phases. Gor'kov and Lebed [6] proposed a simple quasiparticle spectrum to analyze the field-induced SDW in $(TMTSF)_2ClO_4$. For an anisotropic metal with two open Fermi-surface sheets, they showed that a SDW could be enhanced by a magnetic field applied parallel to the sheets. For $NbSe_3$, Balseiro and Falicov [7] developed a model which shows that the obliteration of the Fermi surface is related to field-enhanced CDW formation through an improvement of Fermi-surface nesting. Further work by Bjelis and Maki [8] suggests that the magnetic field can increase both static and dynamic CDW condensate densities at low temperatures, but with a much weaker effect on the dynamic density. However, Voit [9] suggested that CDWs can interact with magnetic fields through coupling with magnetic impurities, and can coexist with a SDW in a magnetic environment. In this mechanism, magnetic transport anomalies are not associated with Fermi-surface modifications. This would also be the case for field-induced Anderson localization in anisotropic conductors [10].

To understand the field effect, several experimental probes have been used, but the case has remained unclear. Narrow-band noise (NBN) measurements [11] on $NbSe_3$ in magnetic fields up to 7.5 T, indicated a 30% increase in the condensed carriers at 37 K and 7.5 T. Furthermore, a transverse-magnetic-field thermopower enhancement [12] was observed at low temperatures, and attributed to the conversion of normal carriers to CDW carriers by the field. However, Tritt *et al.* [13] found very little ($<6\%$) magnetic-field dependence of the CDW carrier concentration from a four-probe NBN measurement between 24 and 38 K, and no observable effect on CDW carrier concentrations above 40 K, in agreement with some previous NBN results of Monceau, Richard, and Laborde [14].

Hence, a direct probe of Fermi-surface changes is vital to understanding the origin of field-induced phases. Nuclear magnetic resonance (NMR) is such a microscopic probe, and in this Letter, we report an NMR measurement on $NbSe_3$ for each ^{93}Nb crystallographic site. Our previous NMR studies [15], which provided electronic structure details, had the magnetic field limited to the *b* axis, where no field effect has been observed. By extending the studies to other orientations, we now find conclusive evidence for a field-induced Fermi-surface change. We demonstrate these changes via Knight shifts below the 59-K transition, and measure them quantitatively via spin-lattice relaxation.

$NbSe_3$ contains three inequivalent structural chains referred to as "orange," "red," and "yellow" or columns I, II, and III, respectively. There are two incommensurate CDW's with onset temperatures of 59 and 144 K. In recent studies [15], we showed how spin-lattice relaxation could be used as a direct probe for changes of the Fermi surface. For a magnetic field applied parallel to the *b* axis, we showed that the most significant Fermi-surface changes occur for the yellow and orange sites at the high- and low-temperature phase transitions, respectively, but that none of these sites is insulating. We also observed a sudden linewidth change for the yellow site at 59 K, in

addition to the broadening at 145 K, which implies a changing yellow site in the low-temperature CDW transition, contrary to previous expectations.

The aligned multicrystalline $NbSe_3$ sample used here, the same as that used previously [15], contains nominally pure crystals exhibiting sharp CDW conduction thresholds. The fast-Fourier-transform (FFT) NMR spectrometer was operated in a fixed magnetic field of 8.97 T. Our measurements concern the central transitions, the $m=\frac{1}{2}$ to $m=-\frac{1}{2}$ lines for $I=\frac{9}{2}$ ^{93}Nb. For these transitions, the resonance frequencies are determined by Knight shifts due to spin and orbital moments of the conduction electrons and quadrupole shifts due to electric field gradients [16].

Spectra for 77 and 4.2 K, in a magnetic field perpendicular to the b and c axes, are exhibited in Fig. 1. Extensive measurements have already well established the identity of these NMR sites [17]. Frequency changes for the yellow and orange sites between these temperatures indicate considerable electronic structure modifications. The orange-site shift is associated with the 59-K CDW transition as already observed [15,17,18], and the line is broadened by the incommensurate CDW in the usual manner [17]. The linewidth and line shape are unchanged below 42 K for the orange site, indicating no further changes of the orange-site CDW modulation at low temperatures. On the other hand, the large yellow-site shift has a different temperature dependence, not seen with the field parallel to the b axis.

Figure 2 shows the temperature dependence of the orange- and yellow-site shifts with the same field orientation as Fig. 1. We see that the increase of the yellow-site resonance frequency begins at about 40 K and saturates near 15 K, and this is associated with partial destruction of the Fermi surface of that site. Note that this is the temperature region where a phase transition has been suggested [4]. On the other hand, no change of the orange-site resonance frequency is observed at low temperatures, just as the linewidth and line shape do not change.

Associating the resonance shift with specific electronic changes is complicated by possible quadrupole- as well as Knight-shift changes, and since for the Knight shift both orbital and core polarization terms contribute [16]. However, spin-lattice relaxation is comparatively simple, due to domination by core polarization, and thus provides a direct quantitative probe of Fermi-surface changes.

Based on band structure calculations [19,20], there is no s-contact contribution to T_1, and the orbital contribution also goes to zero since $|\langle k,m|L^{\pm}|k',m'\rangle|^2$ terms are negligible due to the absence of a d_{xz},d_{yz} mixture at the Fermi surface. Therefore core polarization dominates the relaxation, giving [16]

$$1/T_1=2\gamma_n^2hk[N(E_F)]^2H_{cp}^2T\,, \qquad (1)$$

where T_1 is spin-lattice relaxation time, H_{cp} is the hyperfine core-polarization field, $N(E_F)$ is the density of states, and γ_n is the gyromagnetic ratio. Interference terms [16] will not appear because there is essentially one orbital of importance, the d_{z^2} orbital. This has already given a good picture for measurements with the magnetic field along the b axis [15], where no field effect has been observed, and is confirmed by the field-orientation independence now observed above the 59-K transition (see below).

We applied a steady-state method in the T_1 measurements. An eight-echo Carr-Parcell-Meiboom-Gill pulse sequence was used, with each echo separately averaged, adding echo FFT's after multiplying by a weighting function, to optimize the signal-to-noise ratio. We determined signal strengths by integrating the echo FFT for each site. Finally, signals obtained at different tempera-

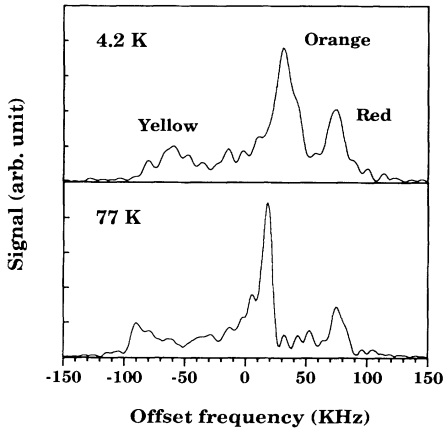

FIG. 1. Central-transition ^{93}Nb NMR line shapes measured at 77 and 4.2 K in $NbSe_3$. Measurements were taken at $H=8.966$ T, with field perpendicular to the b and c axes. Frequency denotes the offset from 93.350 MHz. Identification with the three crystallographic sites is as shown.

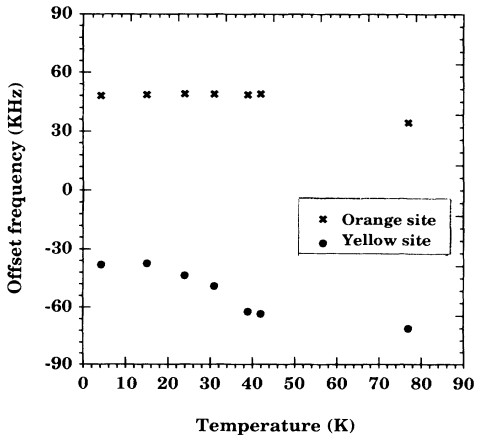

FIG. 2. Yellow- and orange-site resonance frequency as a function of temperature. Frequency represents the peak of resonance line shape and denotes the offset from 93.250 MHz.

TABLE I. ^{93}Nb NMR spin-lattice relaxation time (T_1) measured for each site in $NbSe_3$, at different temperatures, at $H=8.966$ T with the field perpendicular to the b and c axes. Data with field parallel to the b axis, from previous results [15], are also shown.

	Red site (II)		Orange site (I)		Yellow site (III)	
Temp. (K)	**H⊥(b,c)**	**H∥b**	**H⊥(b,c)**	**H∥b**	**H⊥(b,c)**	**H∥b**
4.2	40.5 ± 1.4 s	26.6 ± 1.8 s	25.5 ± 1.1 s	23.5 ± 1.4 s	50.1 ± 1.4 s	18.7 ± 1.2 s
77	430 ± 18 ms	410 ± 22 ms	165 ± 4 ms	165 ± 9 ms	340 ± 10 ms	330 ± 16 ms
292	72 ± 6 ms	67.3 ± 2.4 ms	24 ± 3 ms	21 ± 1 ms	14 ± 2 ms	12.6 ± 0.7 ms

tures were χ^2 fitted to the theoretical recovery curve. While spin-lattice relaxation is a multiexponential expression for the steady state [15], only two parameters were adjusted in the fit: T_1 and the asymptote.

The final T_1 figures for the three sites at three temperatures are given in Table I. The uncertainties correspond to the 90%-confidence level obtained from the fit. Compared with our previous data with field parallel to the b axis, we can see that T_1 for all three sites remains unchanged at 292 and 77 K, consistent with the core-polarization model. However, there is a large increase in T_1 for the yellow site at 4.2 K with the field perpendicular to the b axis, while T_1 for the orange site remains unchanged, consistent with the unchanged Knight shift, linewidth, and line shapes at low temperatures for that site.

To verify the Korringa form of relaxation, we measured T_1 at 2 K with the magnetic field parallel to the b axis. The T_1 for all these sites is consistent with the Korringa relation between 4.2 and 2 K, characteristic of metallic electrons. Thus mechanisms such as quadrupole relaxation are excluded for NMR. On the other hand, we note that for nuclear-quadrupole-resonance (NQR) measurements of the yellow site at 4.55 MHz, we have observed somewhat faster relaxation at 4.2 K than for high-field NMR, with a distinctly non-Korringa temperature dependence. This can be attributed to quadrupole effects, for which the NMR and NQR recovery curves are rather different. This may account for the generally shorter average T_1 in an earlier study [21]. Details of the NQR measurements will be reported separately. In addition, we neglected the oribtal T_1 contribution based on the lack of d_{xz},d_{yz} mixture at the Fermi surface [19,20]. But even if a strong d_{xz} or d_{yz} mixture were found at the Fermi surface, a simple calculation shows that the observed factor of 3 change in T_1 for the yellow site cannot correspond to a field-independent density of states.

While several other mechanisms may enhance the relaxation, we show that these are not important at the temperatures and fields used here, so that T_1 can indeed provide a direct probe of the Fermi-surface electrons in this system. Coherence effects below CDW transitions can cause non-Korringa relaxation, much as in superconductors [22]. This has been observed in SDW studies [23] and may also account for NQR observations [24] in $NbSe_3$ near 145 K. This term appears near the transition and falls exponentially with decreasing temperature, and the Korringa temperature dependence we observed between 2 and 4.2 K indicates that any such term is unimportant at these temperatures.

Another enhancement mechanism is electron diffusion in quasi-one-dimensional conductors, with sufficient anisotropy [25] so that the impurity scattering time (τ) exceeds the interchain tunneling time ($\tau_\perp$). For $NbSe_3$, where dipolar relaxation can be neglected [15], T_1^{-1} would have a $H^{-1/2}$ field dependence only for $\omega_e\tau \leq 1 \leq \omega_e\tau_\perp$ (ω_e is the electron spin frequency). However, based on the observed resistance anisotropy in $NbSe_3$ (a factor of 30), $\tau_\perp$ would be on the order of $\sqrt{30}(b/v_F) \approx 6 \times 10^{-15}$ s [1]. On the other hand, for our nominally pure sample, $\tau \approx 4\times 10^{-13}$ s at low temperatures [5,26]. Thus we expect no enhancement since $NbSe_3$ is not sufficiently anisotropic. This is borne out by the above-mentioned NQR results, in which a small enhancement of T_1^{-1} at zero field and 4.2 K (a factor of 2 above the NMR) can be attributed to quadrupole effects, consistent with a field-independent magnetic T_1.

We used a core-polarization hyperfine field (H_{cp}) equal to -0.18×10^6 G, the experimental value for $NbSe_2$ [27] to calculate for the density of states from Eq. (1). Theoretical H_{cp} values for Nb metal range from -0.14×10^6 to -0.21×10^6 G [15]; choosing values in this range will scale $N(E_F)$ accordingly, but relative $N(E_F)$ changes reported here will not be affected. For 292 and 77 K, it is apparent from Table I that $N(E_F)$ is the same for both orientations, which agrees with the fact that no magnetic-field-induced effect has been observed at these temperatures.

For 4.2 K, $N(E_F)$ for all sites and both orientations is shown in Table II. Comparing [15], we can see that the yellow site exhibits a large $N(E_F)$ change, a 39% reduction, due to the 8.97-T transverse field. There is also an

TABLE II. Densities of states at the Fermi surface, in states/[eV(Nb atom)], for each Nb site at 4.2 K with the field perpendicular to the b and c axes. Data with field parallel to the b axis, from previous results [15], are also shown.

Orientations	Red site (II)	Orange site (I)	Yellow site (III)
H⊥(b,c)	0.49	0.64	0.43
H∥b	0.60	0.64	0.71

18% further reduction of $N(E_F)$ for the red site at 4.2 K, indicating some red-site involvement in the magnetic-induced phase. [Note that the red-site $N(E_F)$ has been observed to change in both CDW transitions.] On the other hand, there is no field-induced $N(E_F)$ change for the orange site at 4.2 K, again consistent with the Knight shift and line shapes observed. The natural assumption has been that field-induced Fermi-surface changes below 59 K are connected to the orange site, since the 59-K CDW is apparently located mainly on that site [15, 18,28]. We have seen that other sites remain conducting and participate in this CDW transition [15], and we now demonstrate that the yellow and red sites dominate the magnetic effect.

Hence, summing the contributions in Table II, there is 20% further reduction of the density of states at the Fermi surface at 4.2 K in 8.97 T, when the orientation changes from parallel to the b axis to perpendicular to the b and c axes. This is in qualitative agreement with rough estimates from magnetoresistivity changes showing Fermi-surface modification in a transverse magnetic field similar to ours [11,13]. However, our line shapes suggest that if a SDW component exists at low temperature, it will be less than $10^{-4}\mu_B$ in Nb d orbitals, given the Nb hyperfine field. We conclude that the Fermi-surface changes must be associated with a CDW enhancement, which is consistent with the Balseiro and Falicov model [7].

Our results indicate that the yellow-site CDW is enhanced by the magnetic field below 59 K, since we find that the CDW-broadened orange line is completed unchanged at low temperatures, while we see large frequency shifts as well as a large T_1 change for the yellow site. This can happen since the formation of the 59-K CDW modifies the band structures: Bands associated with the yellow and red sites become modified so that they are susceptible to field-induced CDW enhancement. Involvement of all sites in the low-temperature CDW transition has already been observed [15]. The fact that the field-induced enhancement is mainly on the yellow-site (144-K) CDW can explain the small magnetic-field effect on narrow-band noise at low temperatures [13].

In conclusion, we provide a quantitative picture of magnetic-field-induced changes at the Fermi surface below the 59-K transition in NbS_3. We measured line shifts and T_1's, and demonstrated that T_1 provides a direct probe of the Fermi-surface changes. We associated these Fermi-surface changes with field-induced CDW enhancement. We also showed that field-induced CDW enhancement is mainly localized on the yellow site through electronic structure modifications of the low-temperature CDW transition. Note that NMR has been instrumental in studying the materials that exhibit field-induced SDW's [29], but this study is the first to measure field-induced Fermi-surface changes directly.

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