Evidence for Magnetism in the Low-Temperature Charge-Density-Wave Phase of $NbSe_3$

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Experimental data on the transverse magnetoresistance in $NbSe_3$, in the temperature range from 1 to 59 K, in magnetic fields of up to 227 kG, and for a variety of electrical currents are presented. They constitute clear evidence that (1) the observed behavior is caused neither exclusively by the normal galvanomagnetic properties of the conduction electrons nor by the conduction properties of the sliding charge-density wave and (2) the low-temperature phase of $NbSe_3$ is not, as it is ordinarily thought, a simple charge-density wave but exhibits a strong magnetic field dependence. The most probable structure of that phase is a mixed density wave, involving charge- and spin-density characteristics as well as a net magnetization.

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Niobium triselenide exhibits two independent charge-density-wave (CDW) transitions,[1,2] one with an onset temperature $T_1 = 144$ K and the second with an onset temperature $T_2 = 59$ K. Both transitions give rise to resistance anomalies which are estimated by Ong and Monceau[3] to represent the formation of gaps at the Fermi level with an attendant decrease in the area of the Fermi surface by 20% at T_1 and by 60% at T_2.

Measurements[4,5] in the lower-temperature CDW phase showed an unusually large magnetoresistance in the temperature range 20–40 K which was found to exhibit a strong electric field dependence above a given threshold electric field. The Hall effect[5] was also observed to show a strong electric field dependence above the same threshold electric field. The electric field dependence of both the magnetoresistance and the Hall effect has been shown[6] to be related to the sliding motion (Fröhlich mode[7]) of the CDW, leading to the conclusion that at low temperatures the threshold electric field is reduced by the application of the magnetic field.

Niobium triselenide remains semimetallic down to the lowest temperatures. Its Fermi surface is therefore not completely obliterated by the formation of the CDW. Electronic transport can thus be effected either by the normal electrons or by the CDW condenstate. In this Letter we report measurements of the transverse magnetoresistance over the complete temperature range 0–59 K at the low-temperature CDW phase. We conclude that the magnetic field modifies the electronic spectrum near the Fermi level and changes the ratio of condensed to normal electrons. This modification requires a fairly strong coupling of the magnetic field to the static density-wave structure. We discuss possible mechanisms for the coupling.

At low electric fields ($E \rightarrow 0$), the resistance anomaly associated with the low-temperature CDW phase shows a strong enhancement with the application of a magnetic field. At 227 kG this enhancement is by a factor of 2 to 4 over most of the temperature range, and decreases very rapidly as the temperature approaches T_2. Data recorded at $H = 0$ and $H = 227$ kG in a temperature range 1.2–80 K are shown in Fig. 1(a). The data were taken at a measuring current of 10 μA so that the electric fields were less than 1 mV/cm, except for those points near the resistance maximum at $H = 227$ kG, where the electric field reached 1.3 mV/cm. At these electric field values the CDW should remain pinned over the entire temperature range and the magnetoresistance behavior should be characteristic of the static CDW structure.

In a comparison of the data at $H = 0$ and at $H = 227$ kG in Fig. 1, it is evident that the magnetoresistance

$$[\rho(H) - \rho(0)]/\rho(0),$$

shown in Fig. 1(b), does not exhibit the usual dependence, i.e., a monotonically increasing function of only $\omega_c \tau$, where $\omega_c = eH/m^*c$ and τ is the electronic relaxation time. In the temperature range 10–48 K, τ decreases monotonically; in the same temperature range $\Delta\rho/\rho(0)$ increases and reaches a maximum value of 4.5 at 25 K. In the temperature range 0–10 K the magnetoresistance behaves more normally: With decreasing temperature the $H = 0$ resistance decreases, and both the relaxation time and the magnetoresistance increase. (The specimen used in this experiment[8] had a large residual resistance ratio RRR = 184; the data were essentially the same for both $\mathbf{H} \parallel \hat{\mathbf{c}}$ and $\mathbf{H} \perp \hat{\mathbf{c}}$.)

The large magnetoresistance at higher temperatures is correlated with the ordering of the CDW and falls

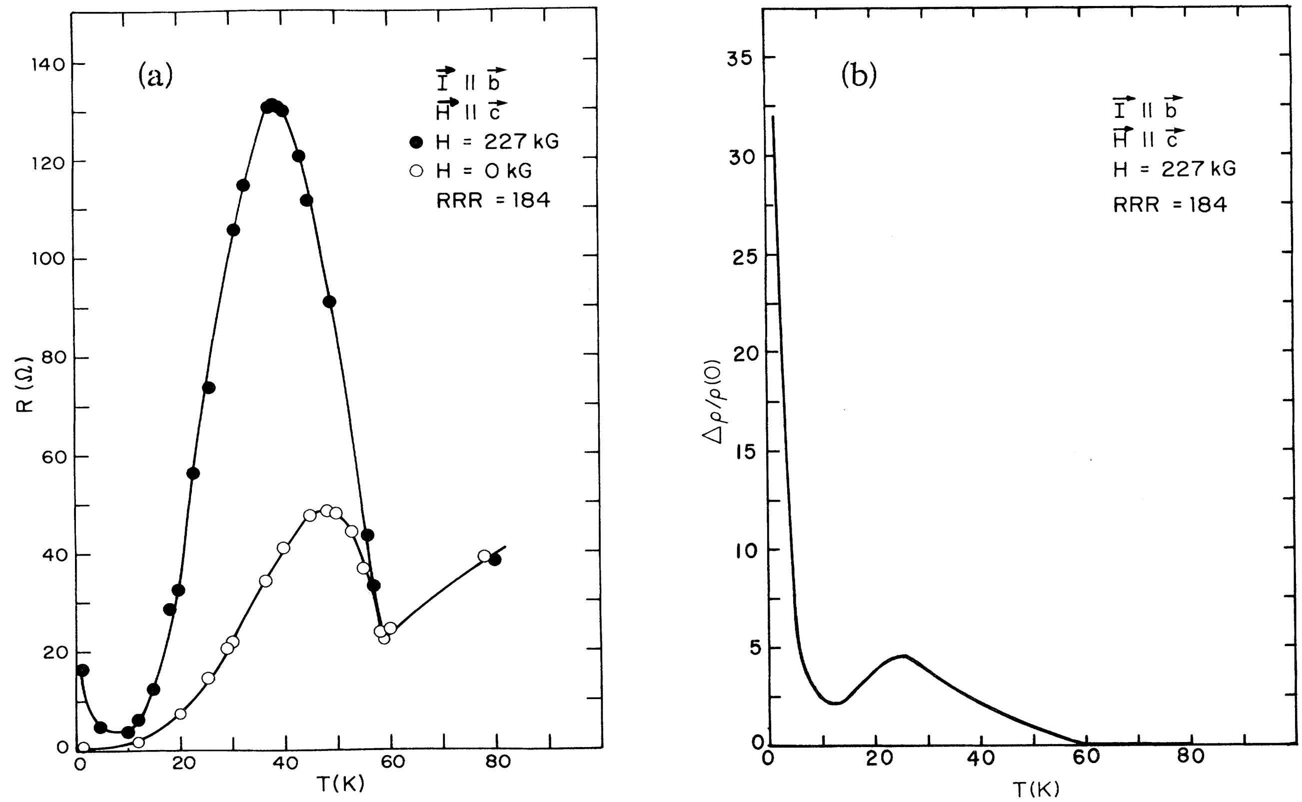

FIG. 1. (a) The resistance of $NbSe_3$ as a function of temperature, measured at $H=0$ (open circles) and at $H=227$ kG (solid circles) with $I=10$ μA. The resistance anomaly due to the low-temperature CDW is enhanced by the magnetic field and the maximum is shifted from 48 to 38 K while the transition temperature remains unchanged. As the temperature increases from 1 K the magnetoresistance at 227 kG decreases to a minimum at 10 K, increases to maximum at 25 K, and decreases to zero at T_2. (b) The magnetoresistance $\Delta\rho/\rho$ for the same sample in the same temperature range.

rapidly to zero[9] at approximately 59 K, in agreement with the value of T_2 observed at $H=0$. The maximum in the resistance at 227 kG is shifted to 38 K from the 48 K value observed at $H=0$. This shift may be associated with enhanced fluctuations which may also play a role in depinning the CDW when higher electric fields are applied.

Figure 2 shows the effect of increasing electric field on the resistance at $H=0$ and $H=227$ kG at a temperature of 30 K. At $H=0$ the threshold electric field for CDW motion is approximately 75 mV/cm. The decrease in resistance at higher electric fields is associated[6,7] with the extra current carried by the moving CDW. At $H=227$ kG the extra magnetoresistance also decreases rapidly as the electric field increases above roughly 70 mV/cm. This rapid decrease approximately removes all the extra magnetoresistance as the electric field increases to a range beteween 150 and 200 mV/cm. At sufficiently high electric fields the resistance at 227 kG approaches that observed at $H=0$. The dc experiments are limited by power dissipation; higher electric field experiments can only be carried out with pulsed current sources.

The electric field dependence of the magnetoresistance at 30 K demonstrated above is characteristic of the magnetoresistance at all temperatures in the range of the CDW anomaly, including the lowest temperatures. The threshold electric field E_T is a function of magnetic field strength: E_T decreases with H. The decrease is small at 30 K but becomes sizable—a factor of 2—at 20 K. This reduction in E_T makes it possible to observe the CDW sliding motion[6] even at temperatures as low as 1.2 K. The important point to emphasize is that *the large enhancement of the resistance anomaly is caused not by the sliding CDW but by the effect of the magnetic field on either the number or the mobility of the normal electrons.*

The large enhancement by the magnetic field of the resistance anomaly associated with the static CDW structure requires a mechanism for coupling of the magnetic field to the electronic structure and the Fermi surface of the density-wave state. If the extra resistance is interpreted as caused by a reduction of the Fermi surface area, then at $H=227$ kG approximately

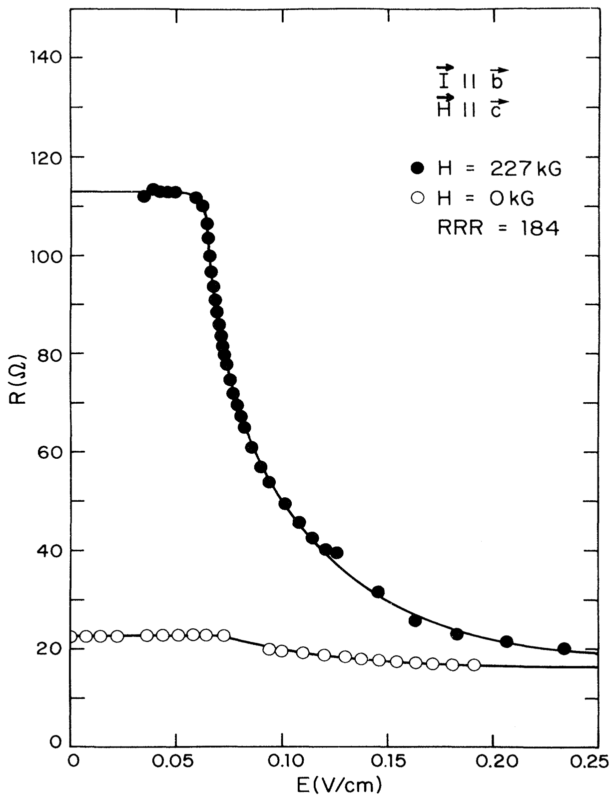

FIG. 2. The resistance of $NbSe_3$ at 30 K as a function of electric field, measured at $H=0$ (open circles) and $H=227$ kG (solid circles). At high electric field the resistances measured at $H=0$ and $H=227$ kG approach the same value because of the onset of CDW motion above $E=70$ mV/cm.

92% of the Fermi surface must be removed at T_2, as opposed to 60% for $H=0$.

Gor'kov and Dolgov[10] have pointed out that the three-dimensional character of the CDW in $NbSe_3$, caused by the interchain tunneling and the imperfect "nesting" of the normal Fermi surface, make the transport properties more complex. Within the framework of their model, the size of the resistivity anomaly when the CDW condensate is pinned is very sensitive to the deviations of the normal Fermi surface from nesting. Modifications of both the Fermi-surface area and the density of states at the Fermi level must be taken into account. Gor'kov and Dolgov[10] also show that as the ordinary electron conductivity is reduced, the mobility of the Fröhlich mode and its contribution to the conductivity increase, in agreement with the electric field dependence of the magnetoresistance as shown in Fig. 2.

The magnetic field dependence of the Fermi surface suggests the coexistence of the CDW with both a spin-density wave (SDW) and a net magnetization (ferrimagnetism). The presence of two of these effects ordinarily requires the third one. Such a mixed-density-wave (MDW) ground state has been considered by several authors.[11,12] Denley and Falicov[11] showed that a MDW ground state was stable in a model system calculated for layer structures for a given range of interaction parameters when the repulsive electron-electron interaction dominates. Balseiro, Schlottmann, and Ynduráin[12] looked at the competition of electron-phonon and Coulomb interactions and found regions of parameter space where a MDW is the stable ground state. Overhauser[13] has argued that in the case of metals with a CDW ground state, a SDW component may develop if the CDW amplitude is sufficiently large and if the elastic stiffness constants are sufficiently anharmonic. Gor'kov and Lebed[14] have shown that for a simple anisotropic metal with two open nesting Fermi-surface sheets, the tendency to SDW formation is enhanced by the application of a magnetic field. All these models suggest well-defined mechanisms by which the magnetic field can readily couple to the density-wave structure and thus modify the final Fermi surface, as required by our magnetoresistance data.

The presence of a SDW component in the low-temperature phase could also explain the measurements of the paramagnetic susceptibility by Kulick and Scott.[15] They observed a sharp increased at the 59-K transition, and pointed out that the magnitude of the paramagnetic susceptibility in the low-temperature phase was too large to be consistent with known Fermi surface data.[16,17]

Below 59 K the Hall effect of $NbSe_3$ exhibits a change in sign with magnetic field strength.[5,18] The value H_Z of the Hall-effect zero decreases as the temperature decreases: Either increasing magnetic field or decreasing temperature results in more positive Hall resistances. It has also been found[5] that increasing the current (i.e., the longitudinal electric field) displaces H_Z to higher values. Dolgov[19] has argued that, at finite temperatures, excitation and relaxation of elecfrom the condensate induce changes which result in a contribution of the CDW condensate to the Hall effect. This change can partially compensate, at least near the transition temperature, the loss in number of carriers caused by Fermi-surface annihilation.

The high-magnetic-field Hall data are not inconsistent with such an interpretation. Above 50 kG the data of Ref. 5 cannot be explained simply by a change in longitudinal conductivity σ_{xx}. Below 20 kG the product $R_H \tau_{xx}$ is a constant[5,18]; in the high-field range it is not. The constancy of the product $R_H \sigma_{xx}$ would require a constancy of H_Z with current, since only the magnitude (and not the sign) of the Hall resistance would change. Although the Hall voltage requires a more detailed interpretation, the data indicate that its behavior is also affected by a change in the electronic structure at the Fermi level induced by the applied magnetic field.

In summary, we have demonstrated that an applied magnetic field couples strongly to the static density-wave structure of the low-temperature phase of $NbSe_3$. High fields must induce a substantial decrease in the free Fermi-surface area and an increase in the number of electrons in the condensate. Although possible models and mechanisms have been discussed, a specific extension of the theoretical models to $NbSe_3$ and additional experimental data will be required to determine accurately the nature and properties of this unusual phase.

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[1]P. Monceau, N. P. Ong, A. M. Portis, A. Meerschaut, and J. Rouxel, Phys. Rev. Lett. **37**, 602 (1976).

[2]R. M. Fleming, D. E. Moncton, and D. W. McWhan, Phys. Rev. B **18**, 5560 (1978); R. M. Fleming, Phys. Rev. B **22**, 5606 (1980).

[3]N. P. Ong and P. Monceau, Phys. Rev. B **16**, 3443 (1977).

[4]M. P. Everson, G. Eiserman, A. Johnson, and R. V. Coleman, Phys. Rev. Lett. **52**, 1721 (1984).

[5]M. P. Everson, G. Eiserman, A. Johnson, and R. V. Coleman, Phys. Rev. B **30**, 3582 (1984).

[6]R. V. Coleman, M. P. Everson, G. Eiserman, and A. Johnson, Phys. Rev. B **32**, 537 (1985).

[7]H. Fröhlich, Proc. Roy. Soc. London, Ser. A **223**, 296 (1954).

[8]Although the data shown in Fig. 1(a) correspond to a sample with a high residual resistance ratio, the effect reported here is independent of RRR in the measured range $20 < \mathrm{RRR} < 200$. For the dirtier samples the magnetoresistance is reduced in the He temperature range, but is unaffected in the range of interest, $10\ \mathrm{K} < T < T_2$.

[9]No magnetoresistance was observed in the high-temperature phase for temperatures $T_2 < T < 80$ K.

[10]L. P. Gor'kov and E. N. Dolgov, J. Low Temp. Phys. **42**, 101 (1981).

[11]D. Denley and L. M. Falicov, Phys. Rev. B **17**, 1289 (1978).

[12]C. A. Balseiro, P. Schlottmann, and F. Yndurâin, Phys. Rev. B **21**, 5267 (1980).

[13]A. W. Overhauser, Phys. Rev. B **29**, 7023 (1984).

[14]L. P. Gor'kov and A. G. Lebed, J. Phys. (Paris), Lett. **45**, L-433, (1984).

[15]J. D. Kulick and J. C. Scott, Solid State Commun. **32**, 217 (1979).

[16]R. M. Fleming, J. A. Polo, Jr., and R. V. Coleman, Phys. Rev. B **17**, 1634 (1978).

[17]P. Monceau and A. Briggs, J. Phys. C **11**, L465 (1978).

[18]G. X. Tessema and N. P. Ong, Phys. Rev. B **23**, 5607 (1981).

[19]E. N. Dolgov, Solid State Commun. **50**, 405 (1984).