Charge-Density-Wave Carrier Concentration in $NbSe_3$ as a Function of Magnetic Field and Temperature

T. M. Tritt, D. J. Gillespie, A. C. Ehrlich, and G. X. Tessema[(a)]
Naval Research Laboratory, Washington, D.C. 20375
(Received 27 May 1988)

We report measurements of the resistance and narrow-band noise in $NbSe_3$ for magnetic fields from 0 to 10 T and temperatures from 30 to 55 K. We find that a magnetic field effects a change of less than 5% on the charge-density-wave carrier concentration obtained from the slope of the current versus frequency curves. This disagrees with some previously reported measurements and resolves an existing controversy. Our work also implies that the increase in the resistance anomaly with magnetic field is not related to an increase in the carrier concentration.

PACS numbers: 71.45.Lr, 72.15.Gd, 72.15.Nj

There are two charge-density-wave (CDW) transitions which occur in $NbSe_3$, one at $T_1=145$ K and the other at $T_2=59$ K.[1] In most CDW materials, the formation of a CDW gap results in a complete destruction of the Fermi surface, resulting in a semiconducting ground state at temperatures below the transition. $NbSe_3$ is unique among CDW materials in that its low-temperature ground state is metallic or rather "semimetallic" and that its CDW can be made to slide. As estimated from resistivity measurements, 20% of the room-temperature Fermi surface is destroyed by the upper ($T_1=145$ K) transition and approximately 60% of the remaining Fermi surface by the lower ($T_2=59$ K) transition.[2] An extra contribution to the conductivity is observed in $NbSe_3$ (as in other sliding CDW materials) when the electric field exceeds a temperature-dependent threshold electric field E_T. According to the classical description for CDW motion, when $E>E_T$ the CDW is depinned from impurity centers and a nonlinear conduction is observed. When the CDW begins to slide a narrow-band noise (NBN) may be observed whose frequency F is linearly dependent on the current that is carried by the charge-density wave I_{CDW}. The slope of the I_{CDW} vs F curve is proportional to the CDW carrier concentration n_{CDW}.[3]

Coleman *et al.*[4] found that when a magnetic field was applied perpendicular to the high conductivity axis in $NbSe_3$, a very large magnetoresistance $\Delta\rho/\rho$ was observed at temperatures in the range $10\ K<T<50$ K. They found that at $B=22.7$ T, $\Delta\rho/\rho$ was on the order of 2-4 in the temperature range 20-45 K and that $\Delta\rho/\rho$ went to zero at the lower CDW transition temperature. They emphasized that the resistive anomaly is not caused by any dynamical motion of the CDW but by the effect of the magnetic field on either the number or the mobility of the normal electrons. They further stated that if the extra resistance is interpreted as being caused by a reduction of the Fermi surface area then, at $B=22.7$ T, approximately 92% of the remaining Fermi surface must be removed at T_2 compared to 60% at $B=0$. This would imply that the CDW carrier concentration had been increased by approximately 50% because of the application of the 22.7-T magnetic field. Stimulated by the work of Coleman *et al.*, Balseiro and Falicov[5,6] developed a theory in which it was shown that a magnetic field could enhance the CDW gap through an improvement of the Fermi surface nesting. This magnetic-field-enhanced gap would then lead to a direct conversion of carriers from the normal state to the CDW state though the degree to which this might happen cannot be readily obtained from the theory.

Recently, Parilla, Hundley, and Zettl[7] reported measurements of F as a function of I_{CDW} in $NbSe_3$ in the presence of an applied magnetic field and correlated this to the effect of the magnetic field on the CDW carrier concentration. They performed two-probe noise and resistance measurements on $NbSe_3$ in magnetic fields up to 7.5 T. From their noise data they concluded that at $T=37$ K and $B=7.5$ T a 30% increase in the CDW carriers can be observed. They related this to the increase in resistance and found reasonable agreement between the increase in CDW carriers derived from the noise and the resistance measurements. They also performed ac conductivity measurements[8] from which they concluded that at $T=30$ K and $B=7.5$ T a 20% increase in CDW carriers was observed, which was in qualitative agreement with their NBN results.

There has been some very limited preliminary data by Monceau, Richard, and Laborde,[9] which disagreed with the NBN results of Parilla, Hundley, and Zettl,[7] and a later inference by Richard, Monceau, and Renard,[10] that there was no dependence of the NBN slope on B. Nevertheless, the work described in Refs. 4-8 has provided a coherent and consistent picture of the effect of a magnetic field on the number of electrons in the CDW's of $NbSe_3$ that up to now has been widely accepted by most specialists and essentially all interested nonspecialists.

Still, many of the most fundamental questions regarding sliding CDW's are not yet understood including the energy dissipation mechanisms, their I-V characteristics and their response to magnetic fields. Among the latter are a number of unexplained aspects regarding the Hall effect,[11,12,13] the remaining controversy over the magnetic field dependence of n_{CDW}, and therefore, by implication, the real origin of the unusually large magnetoresistance found below the lower CDW transition temperature.

We have performed NBN and resistance measurements over the magnetic field range 0–10 T and the temperature range 30–55 K in an effort to address the uncertainties surrounding the effect of the magnetic field on n_{CDW}.[7,9] We believe we have succeeded in this and in forcing a reexamination of the conceptually simple picture now widely held by identifying the source of an experimental error in the work of Parilla, Hundley, and Zettl.[7] We have observed a large magnetoresistance below the lower transition in agreement with others.[4,7,8] Nevertheless, over these parameter ranges the magnetic field has very little effect on the CDW carrier concentration as determined by the NBN measurements. The latter has implications for the magnitude of the effect calculated by Balseiro and Falicov[5,6] since it implies that the large increase in resistance is not primarily due to a decrease (increase) in normal carriers (CDW carriers).

We have carried out a large number of particularly careful measurements of F and J_{CDW}, and the sample resistance R_S as a function of magnetic field. Single crystals of $NbSe_3$ with a typical residual-resistivity ratio of ~ 80 were mounted perpendicular to the magnetic field in a four-probe resistance configuration. The electronics that were used allowed the current to be injected either through the outer current leads (labeled $I+$ and $I-$) resulting in a four-probe resistance measurement or through the inner potential leads (labeled $V+$ and $V-$) resulting in a two-probe resistance measurement. A possible problem with the two-probe method is the error introduced in the interpretation of the results because of an additional voltage from the contact resistance. The NBN was measured across the $V+$ and $V-$ leads on the sample with the current typically being injected into these same leads. Injecting the current into the $I+$ and $I-$ leads while measuring the NBN results in a number of problems, including the multiple frequencies discussed by Ong and Verma,[14] and greater background noise. Interpretation of the data was based on the following considerations. For $E > E_T$, we suppose that the total current in the sample I_T consists of two parts, the normal or Ohmic contribution I_Ω and the contribution from the motion of the charge-density wave I_{CDW}, i.e., $I_T = I_\Omega + I_{CDW}$, where $I_\Omega = V_S/R_\Omega$, R_Ω is the Ohmic sample resistance and V_S is the sample voltage. Thus $I_{CDW} = I_T - V_S/R_\Omega$. When we use the two-probe method, the existence of a significant contact resistance results in the apparent V_S and R_Ω becoming respectively: $V_S \rightarrow V_S + V_C$ and $R_\Omega \rightarrow R_\Omega + R_C$ and thus the apparent $I_{CDW} = I_T - (V_S + V_C)/R_\Omega + R_C)$, where R_C is the resistance of the contacts and $V_C = I_T R_C$ is the voltage across the contacts. With these additional two-probe contributions, the true CDW current cannot be calculated. One must instead measure the NBN frequency for a given total current I_T through the sample in a two-probe manner and then switch to a four-probe method for the same I_T (same NBN frequency) to measure V_S and thus calculate the correct CDW current. I_{CDW}^{2P} and I_{CDW}^{4P} will designate the CDW current derived for the two-probe and (correct) four-probe methods, respectively. The expressions for each of these, given above, can be solved simultaneously to eliminate $I_T R_\Omega - V_S$ and give the relationship

$$I_{CDW}^{2P} = I_{CDW}^{4P}\{1 + [R_C/R_\Omega(B,T)]\}^{-1}. \qquad (1)$$

Care was taken to achieve very stable contacts with contact resistance $R_C \leq 0.5 R_\Omega$. We held the temperature over the range of our data to within 50 mK for over 4–5 hrs. The dc current was passed through a standard resistor in series with the sample for determination of the total current with either the two-probe or the four-probe configuration. After obtaining the I_{CDW} vs F two-probe and four-probe data for $B=0$, the magnetic field was applied and the process repeated while maintaining a constant temperature. We found that the application of the magnetic field in no way affects the quality of the NBN spectrum. In Fig. 1. we show that data for both $B=0$ and 9.6 T in both the two- and four-probe configurations.

The NBN frequency F is related to I_{CDW} through the following relationship[3]:

$$J_{CDW} = n_{CDW} e v = n_{CDW} e \lambda F, \qquad (2)$$

where $J_{CDW} = I_{CDW}/A$, I_{CDW} is given by $I_{CDW} = I_T - V_S/R_\Omega$, v is the CDW drift velocity, A is the sample

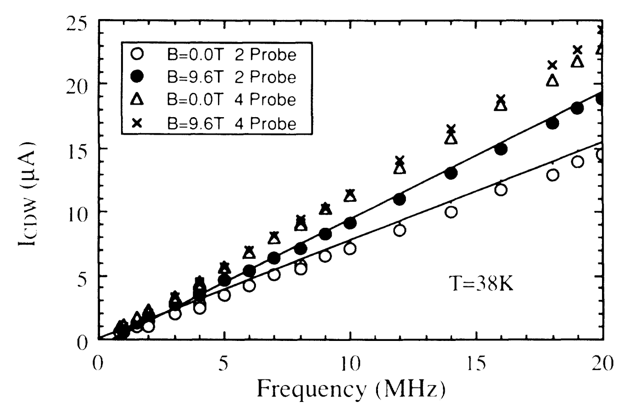

FIG. 1. I_{CDW} vs F at $T=38$ K. The sample parameters are: the sample length $l=0.51$ mm, $R_S(300\text{ K}) = 288\ \Omega$, and an estimated sample cross-sectional area $A = 4.4\ \mu m^2$. The data show the different magnetic field dependence for the two- and four-probe measurements. The straight lines are fits with Eq. (1) and the corresponding four-probe data.

cross sectional area, λ is the CDW wavelength, and n_{CDW} is the CDW carrier concentration. As stated in Ref. 7, the slope, Kn_{CDW} ($K=e\lambda A$), of I_{CDW} vs F is proportional to the CDW carrier concentration. Since e, λ, and A are essentially independent of the magnetic field then Kn_{CDW} as a function of B reflects the effect of the B on n_{CDW}. We have used the value for the room-temperature resistivity, $\rho(300\text{ K})=2.5\times10^{-4}$ Ω cm,[1a,1c] the room-temperature sample resistance $R_S(300\text{ K})$, and the sample length l to estimate the cross-sectional area of our samples. We find a value of 0.25 A/Hz m^2 for the slope of J_{CDW} vs F which is consistent for samples from different batches and in excellent agreement with other work.[1a,3] With a value of $\lambda=1.4$ nm,[1a,7] our estimates for n_{CDW} from the NBN measurements yield $n_{CDW}\approx1.2\times10^{21}$ carriers/cm^3.

From Eq. (1) we note that for $R_C \ll R_\Omega(B,T)$, $I^{2P}_{CDW}\approx I^{4P}_{CDW}$. We found that the effect of B was very different for the two- and the four-probe configurations. As seen in Fig. 1, with the use of I^{2P}_{CDW}, the effect of B yields a result that is in qualitative agreement with Ref. 7, i.e., at $T=38$ K and $B=9.6$ T an increase in n_{CDW} of approximately 23% is observed. However, if I^{4P}_{CDW} is used the effect of B yields a result that is in qualitative agreement with Ref. 9; i.e., at $T=38$ K and $B=9.6$ T the application of B has essentially no effect on n_{CDW} compared to the two-probe results. Of course, the difference between the correct I^{4P}_{CDW} and incorrect I^{2P}_{CDW} is due to the nonzero contact resistance. In fact, as shown in Fig. 1, we can use the value of our contact resistance and Eq. (1) to fit the two-probe data from the four-probe data.

We have carried out this experiment over the range $0<B<10$ T and $30<T<55$ K using a number of samples with a variety of contact resistances. The results are consistent—there is at most only a 5% effect of B on n_{CDW} (and this much only at the lowest temperatures) as derived from the NBN measurements with a $\pm1.5\%$ statistical fitting error. As a function of temperature n_{CDW} should go from essentially zero at T_2 to a saturated value as the temperature is decreased in a manner similar to a BCS superconductor.[15] From Fig. 2 it can be seen that the slope of J^{4P}_{CDW} vs F derived from a four-probe method displays exactly this behavior and most importantly the magnetic field does not change the magnitude (more than 5%) or the temperature dependence of the CDW carrier concentration.

At temperatures below a CDW transition and when $E\gg E_T$, the resistance drops to a value which is approximately the value the resistance would have if no CDW anomaly had occurred. Ong and Monceau[2] used the Ohmic change in resistance at the CDW transition as a rough estimate of the fraction of Fermi surface which is destroyed by the CDW transition. This derives from a two-fluid model in which the total number of carriers, n_T, is equal to the number of CDW carriers, n_{CDW}, plus the number of normal or Ohmic carriers, n_Ω. They defined a quantity α which yields essentially n_{CDW}/n_T. Parilla, Hundley, and Zettl[7] assumed that in the temperature range near the CDW-associated resistivity peaks, the major contribution to the magnetoresistance is the B dependence of n_{CDW} and so introduced the B dependence of the conductivity into α. Thus,

$$\alpha(B,T)=\sigma_{CDW}(B,T)/[\sigma_\Omega(B,T)+\sigma_{CDW}(B,T)], \quad (3)$$

where

$$\sigma_\Omega(B,T)\approx[R_\Omega(B,T)]^{-1}, \quad (4)$$

and

$$\sigma_{CDW}(B,T)\approx[R_{E\gg E_T}(B,T)]^{-1}-\sigma_\Omega(B,T), \quad (5)$$

where R_Ω is proportional to $1/n_\Omega$ and $R(E\gg E_T)$ is proportional to $1/n_T$, where $n_T=n_\Omega+n_{CDW}$. Then α is pro-

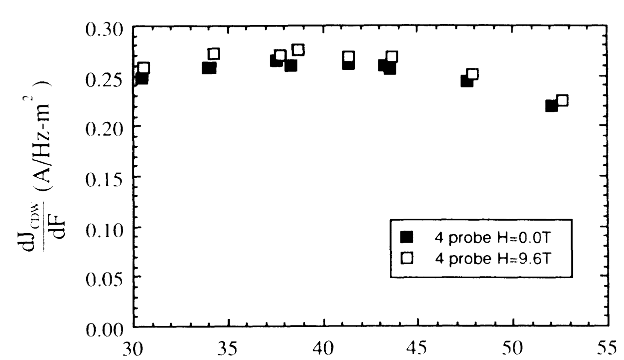

FIG. 2. Temperature dependence of $dJ_{CDW}/dF \sim n_{CDW}$ with and without an applied magnetic field. The magnetic field has little or no effect on either the magnitude or the temperature dependence of n_{CDW} derived from the NBN measurements.

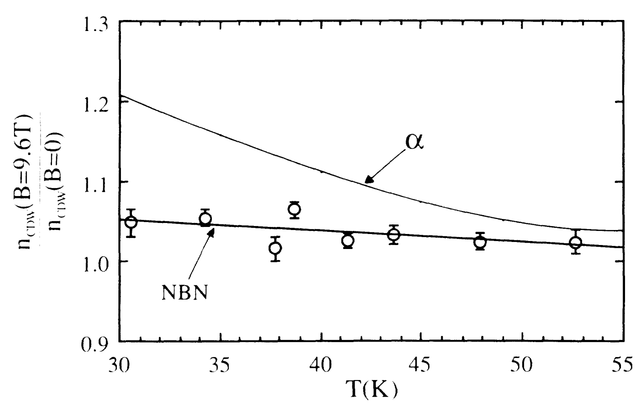

FIG. 3. Temperature dependence of the relative increase from $B=0$ in the CDW carrier concentration at $B=9.6$ T as determined from the two methods: the magnetoresistivity (α) and the NBN (I_{CDW} vs F). According to the previous models, both curves should yield essentially n_{CDW} ($B=9.6$ T)/$n_{CDW}(B=0)$ as a function of temperature.

portional to n_{CDW}/n_T. From this quantity at $B=0$, Ong and Monceau[2] proposed that at the lower (T_2) transition 60% of the Fermi surface remaining from T_1 was removed. Since at high electric fields, $E \gg E_T$, $R(B) \approx R(B=0)$, n_T appears to be independent of magnetic field and the increase in resistance and therefore α should be due to an increase in n_{CDW}. This is the model mentioned above wherein 92% of the Fermi surface would be removed at $B=22.7$ T (Ref. 4) instead of the 60% at $B=0$. By the hypothesis of the model, $\alpha(B)/\alpha(B=0)=n_{CDW}(B)/n_{CDW}(B=0)$. Figure 3 is a plot of $n_{CDW}(B)/n_{CDW}(B=0)$ derived from both the resistance and the NBN measurements. The α (resistivity) results suggest that the magnetic field increases n_{CDW} and that the effect increases as the temperature is decreased, i.e., at $T=30$ K and $B=9.6$ T the CDW carrier concentration increases by approximately 20%. On the other hand, the NBN results indicate that the magnetic field has little if any effect on the CDW carrier concentration over the entire temperature range of 30–55 K. From this comparison it is obvious that the magnetoresistivity and the NBN are not measuring the same effect.

It is far more likely that the NBN measurements are giving the correct effect of B on n_{CDW} than is the magnetoresistance. The former have a rather direct relation to n_{CDW} through I_{CDW}. The latter, having in general a very complicated dependence on various aspects of Fermiology and scattering anisotropy, could easily manifest the behavior seen without change of carrier concentration. It is of interest to note that effects analogous to the magnetoresistance have been very recently reported in the piezoresistance of $NbSe_3$. Lear *et al.*[16] have found that stress increases the resistance substantially but Stillwell and Skove[17] have reported that n_{CDW}, as determined by NBN measurements under strain, shows no change with stress. Rapid variations of resistivity with stress,[18] however, is a familiar phenomena in semimetals, as is large magnetoresistance.

In conclusion, we find that the magnetic field has little if any effect on the CDW carrier concentration over the temperature and magnetic field ranges that we have reported. We believe that the conclusions of Ref. 7 are incorrect by virtue of their neglect of contact resistance. Our results confirm and extend the range of validity of the preliminary results of Ref. 9. Since, on the other hand, there is good agreement among the various groups on the effect of the magnetic field on the resistivity this current work compels a reexamination of the apparently coherent picture of the effect of magnetic fields on n_{CDW} in $NbSe_3$.

We would like to thank N. P. Ong for useful comments during the course of this work and for the kind use of his spectrum analyzer. We would like to thank E. P. Stillwell and M. J. Skove for informing us of their results prior to publication and for many helpful and enlightening discussions. We are also grateful to G. N. Kamm for the technical help he provided us. One of us (T.M.T.) acknowledges support from the Office of Naval Technology-American Society for Engineering Education NRL Research Associateship program.

[a]On assignment from: Sachs Freeman and Assoc., Landover, MD 20785.

[1a]For a review see *Electronic Properties of Inorganic Quasi-One-Dimensional Compounds,* edited by P. Monceau (Reidel, Boston, 1985).

[1b]Also see A. Zettl and G. Gruner, Phys. Rep. **119**, 117 (1985).

[1c]Also see N. P. Ong, Can. J. Phys. **60**, 757 (1981).

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

[3]P. Monceau, J. Richard, and M. Renard, Phys. Rev. Lett. **45**, 43 (1980), and Phys. Rev. B **25**, 931 (1982).

[4]R. V. Coleman, G. Eiserman, M. P. Everson, A. Johnson, and L. M. Falicov, Phys. Rev. Lett. **55**, 863 (1985).

[5]C. A. Balseiro and L. M. Falicov, Phys. Rev. Lett. **55**, 2336 (1985).

[6]C. A. Balseiro and L. M. Falicov, Phys. Rev. B **34**, 863 (1986).

[7]P. Parilla, M. F. Hundley, and A. Zettl, Phys. Rev. Lett. **57**, 619 (1986).

[8]M. F. Hundley, P. Parilla, and A. Zettl, Phys. Rev. B **34**, 5970 (1986).

[9]P. Monceau, J. Richard, and O. Laborde, Synth. Met. **19**, 801 (1987).

[10]J. Richard, P. Monceau, and M. Renard, Phys. Rev. B **35**, 4533 (1987).

[11]N. P. Ong and P. Monceau, Solid State Commun. **26**, 487 (1978).

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

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

[14]N. P. Ong and G. Verma, Phys. Rev. B **27**, 4495 (1983).

[15]J. Bardeen, E. Ben-Jacob, A. Zettl, and G. Gruner, Phys. Rev. Lett. **49**, 493 (1982); A. Zettl and G. Gruner, Phys. Rev. B **29**, 755 (1984).

[16]R. S. Lear, M. J. Skove, E. P. Stillwell, and J. W. Brill, Phys. Rev. B **29**, 5656 (1984).

[17]E. P. Stillwell and M. J. Skove, Bull. Am. Phys. Soc. **33**, 391 (1988).

[18]T. M. Tritt, E. P. Stillwell, and M. J. Skove, Phys. Rev. B **34**, 6799 (1986).