

MAGNETOTHERMOPOWER OF NbSe₃

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We report longitudinal thermopower measurements on the charge density wave (CDW) conductor NbSe₃ in transversely applied magnetic (H) fields up to 75 kG. In the lower CDW state, increasing H results in a positive increase in the thermopower, indicating that the magnetic field acts to destroy electron-like states on the Fermi surface. We interpret our results in terms of H-induced "one-dimensionalization" of the electronic band structure, and an associated normal-to-CDW carrier conversion.

Introduction

The inorganic linear chain material NbSe₃ exhibits unusual magnetotransport properties in the lower charge density wave (CDW) state ($T < 59$ K). For magnetic (H-) fields oriented transverse to the chain (b) axis of the crystal, an increase in H dramatically enhances the Ohmic resistance anomaly, and shifts the resistance maximum to lower temperature [1]. Measurements of the narrow band noise spectrum in the non linear conductivity regime suggest that the ratio I_{CDW}/f (where I_{CDW} is the excess current carried by the CDW and f is the fundamental noise frequency) is H-dependent and increases with increasing H, reflecting an increase in CDW carrier concentration [2]. Additional studies on the complex ac magnetoconductivity of NbSe₃ have indicated H-dependent characteristic pinning energies [3], different from those apparent in the dc limit.

Many of the observed magnetic properties of NbSe₃ have been attributed to novel interactions between the H- field and normal electrons and condensed electrons. In NbSe₃, the Fermi surface is not completely destroyed by either of the two Peierls transitions ($T_1=144$ K, $T_2=59$ K), resulting in (non-thermally excited) free carriers forming a conduction mechanism parallel to the CDW condensate. It has been suggested [4] that intense H fields in NbSe₃ improve the one dimensionality of the electronic structure, and increasing H effectively "converts" normal electrons to condensed (CDW) electrons. The high electric field dc conductivity [1], high frequency ac conductivity [3] and narrow band noise studies [2] appear consistent with such a simple interpretation. On the other hand, studies of low temperature Shubnikov de Haas oscillations [5], and narrow band noise oscillations in impure NbSe₃ specimens [6], have not borne out the expected changes in Fermi surface structure and condensate carrier concentration.

In this communication we report on careful magnetothermopower (TEP) measurements of NbSe₃ in the lower CDW state in magnetic fields up to 75 kG. At temperatures below the 59 K CDW transition, application of a large magnetic field transverse to the crystal chain axis causes the

longitudinal thermopower to become increasingly positive. At temperatures below 20 K, the thermopower appears to saturate at high magnetic field. These results indicate that the magnetic field causes NbSe₃ to become more hole-like. That is, the magnetic field removes normal electron-like states from the Fermi surface, leaving the holes less compensated and resulting in a positive increase in the thermopower. The "disappearing" electrons condense into the ground state CDW condensate where they give no contribution to the thermopower.

Experimental

Our experimental thermopower measurements were performed on single crystals of NbSe₃ grown by the usual vapor-transport method. The crystals were of reasonable quality as determined from dc electric threshold field measurements ($E_T=30$ mV/cm at 48 K). The thermopower was measured using a slow ac heating method [7]. Single-crystal samples with gold leads attached to the ends with silver paint were suspended (in vacuum) between a pair of crystalline quartz blocks. Both quartz blocks were wrapped with independent manganin heater wires which could be used to ramp a temperature gradient of varying magnitude and direction across the sample.

The temperature gradient was monitored with a chromel-constantan reference thermocouple, which was relatively insensitive to magnetic field [8]. For all the data presented in this communication, the magnetic field was directed perpendicularly to the chain (b) axis of the NbSe₃ crystals.

Figure 1 shows the thermopower of NbSe₃ at temperatures below 100 K, for selected values of applied magnetic field up to 75 kG. For H=0, our results are consistent with those of previous studies [9,10]. Above $T_2=59$ K, the TEP is independent of H. On the other hand, below T_2 application of H results in a positive increase in the TEP, with the effect becoming larger with decreasing temperature. At T=25 K, for example, a 75 kG H-field changes the TEP from zero to +60 μ V/K. Below 15 K the TEP at high H-field appears to saturate at a maximum value of roughly +80 μ V/K.

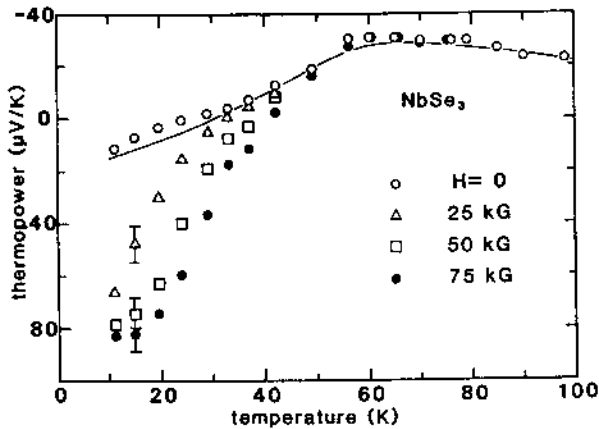


Fig. 1 Magnetothermopower versus temperature in NbSe₃. The lower CDW state is for $T < 59$ K. The solid line is $H=0$ data from ref. 9.

Figure 2 shows the thermopower plotted as a function of H in the temperatures range 11 K to 56 K. Just below the Peierls transition temperature T_2 , the magnetic field affects the TEP by only a small amount ($\Delta S = 3 \mu\text{V/K}$ at $H = 75$ kG). As the temperature is lowered the H -induced change in the thermopower becomes larger, and follows a roughly quadratic dependence on H . The dashed lines in Fig 2, drawn for the 42 K, 33 K, and 29 K data, are quadratic fits normalized to the high and low H -field values. The sensitivity of the thermopower on H increases by roughly one order of magnitude between 49 K and 29 K (d^2S/dH^2 (49 K) = $7.1 \times 10^{-4} \mu\text{V/K}$, d^2S/dH^2 (29 K) = $6.9 \times 10^{-3} \mu\text{V/K}$). Below 30 K the thermopower appears to lose its quadratic dependence on H , becoming approximately linear in field strength.

Finally, at temperatures below 20 K the TEP appears to saturate at high H , to roughly +80 $\mu\text{V/K}$. The saturation value is approached approximately as $1/H^2$. The general trend we thus observe is that at low magnetic fields and high temperatures the TEP is quadratic in H , while at high magnetic fields and low temperatures the TEP saturates in an inverse quadratic manner. At moderate temperatures and H -fields there is a crossover between these two behaviors; this is well illustrated by the $T = 24$ K data of Fig 2.

Discussion

In analyzing our results we consider two possible mechanisms for the magnetic field thermopower enhancement. The strong magnetothermopower effect could be due to novel magnetic field interactions with the imperfectly nested remnants of the Fermi surface, or the effect could be a result of more conventional magnetic field interactions with the conduction electrons, as occurs in noble metals. Before examining this question in detail a few comments on thermopower in general are in order. The thermopower of a conductor is due to two contributions. First is the contribution of charge carriers (electrons, or electrons and holes if we consi-

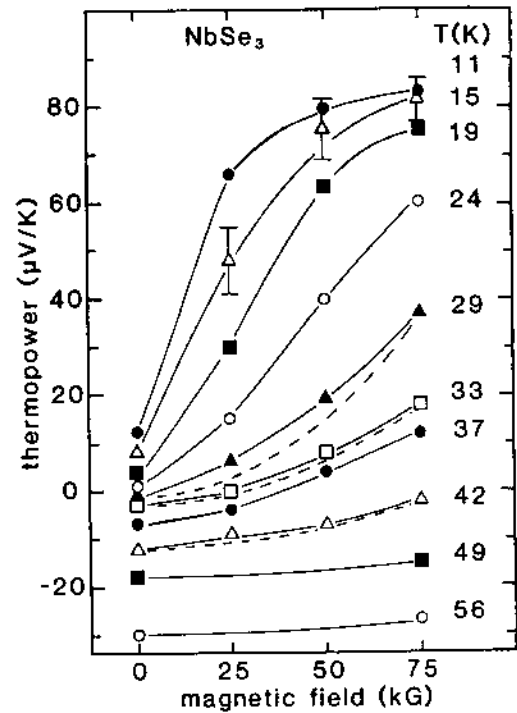


Fig. 2 Magnetothermopower versus magnetic field strength up to 75 kG at temperatures below the 59 K Peierls transition. The solid lines are guides to the eye. The dashed lines are quadratic fits to the 29 K, 33 K, and 42 K data.

der a two-band system) as they diffuse across the sample in response to the applied temperature gradient. This portion of the thermoelectric power is expected to be roughly linear in temperature, and to have a sign that reflects the sign of the majority carrier. In tandem with carrier diffusion is the diffusion of phonons across the sample. At high temperatures such phonons give no contribution to the thermopower, because they cannot effectively couple to the charge carriers. At low temperatures, well below the Debye temperature, phonons can effectively scatter off holes or electrons, thereby imparting momentum to them; in essence the stream of phonons drag the charge carriers along, resulting in a "phonon drag" contribution to the TEP. At moderate to low temperatures, such phonon drag contributions can dominate the TEP.

Experimental and theoretical work has demonstrated that both charge diffusion and phonon drag components of the TEP can be affected by magnetic fields. In Al alloys, for example, the drift contribution has been observed to change sign with increasing H and saturate at high H [11]. Using a simple model of electron diffusion magnetothermopower, Blatt et al. [12] suggest that the TEP always saturates at high H fields, irrespective of the H -dependence of the magneto-resistance. In noble metals, the phonon drag contribution to the TEP can be substantially enhanced by H [13]; similar results are obtained in Al and In [14].

Although magnetothermopower effects such as those just described cannot be entirely ruled out for NbSe₃, they do not appear to form a significant contribution to the behavior observed in Figs 1 and 2. Even with H=0, NbSe₃ shows no substantial phonon drag behavior, and the H-induced changes in the TEP shown in Figs 1 and 2 are much larger than those normally associated with H-field phonon drag enhancement. In the diffusion magneto thermopower theory of Blatt et al. [12], the TEP can be expressed as

$$\Delta S = \frac{\pi^2 K_B^2 T}{3|e|} \left[\frac{\Delta\rho/\rho}{1+\Delta\rho/\rho} \right] D \quad (1)$$

where $\Delta\rho/\rho$ is the magnetoresistance and D is a fitting parameter. From Eq. (1), $\Delta S(H)$ saturates at high H-field for $\Delta\rho/\rho \gg 1$. This expression is in strong disagreement with our TEP results for NbSe₃. For example, in Fig 2 the low temperature saturation of the TEP near H = 75 kG occurs for $\Delta\rho/\rho \approx 2.2$, in contrast to the expected condition $\Delta\rho/\rho \gg 1$. Detailed fits of Eq. (1) to the data of Fig 2 also indicate $D \approx 300 \text{ eV}^{-1}$ near 17 K, an unreasonably large value [12]. Hence neither conventional phonon drag nor diffusion thermopower can account for the observed magnetothermopower in NbSe₃.

We now consider the special CDW properties of NbSe₃ and the associated TEP. The usual interpretation of the H=0 TEP of NbSe₃ is that the lower Peierls transition at T₂ takes place on predominantly electron-like portions of the Fermi surface [9]. As a result, the material becomes hole-like with decreasing T below T₂, resulting in an increasingly positive TEP. From Fig 1 it appears that the effect of a magnetic field is to further enhance the process of electron state destruction, resulting in a positive enhancement of the (normal carrier) TEP.

The electron-like carriers removed from the conduction band probably condense into the CDW, thereby enhancing the CDW carrier concentration and order parameter, as has been suggested by other transport studies [1-3]. The condensed CDW carriers carry no entropy, and hence the CDW contributes nothing to the TEP [15]. Our magnetothermopower data is thus at least qualitatively consistent with the view that transverse H-fields in NbSe₃ essentially improve the one-dimensionality of the system, and convert normal carriers left over from the imperfectly nested Fermi surface and higher bands to condensed carriers.

A more quantitative analysis of our data is complicated by the nature of the thermoelectric effect. In a two band model, the thermopower becomes a weighted average given by [16]

$$S = \frac{\sigma_e S_e + \sigma_h S_h}{\sigma_e + \sigma_h} \quad (2)$$

where $\sigma_{e(h)}$ is the electron (hole) contribution to the dc electrical conductivity, and $S_{e(h)}$ is the electron (hole) diffusion thermopower neglecting the other band in the material. In the semi-classical model, the diffusion thermopower can be expressed in terms of the conductivity as [17]

$$S = -\frac{\pi^2}{3} \frac{K_B^2 T}{|e|} \left. \frac{\sigma'}{\sigma} \right|_{\epsilon_F} \quad (3)$$

where the derivative is made with respect to energy and is evaluated at the Fermi energy ϵ_F . The dc electrical conductivity may be expressed in terms of Fermi surface parameters by [18]

$$\sigma = \frac{1}{3} e^2 \tau_F \bar{v}_F^2 N(\epsilon_F) \quad (4)$$

where τ_F is the relaxation time, \bar{v}_F is the mean Fermi velocity averaged over the Fermi surface, and $N(\epsilon_F)$ is the density of states at the Fermi energy. In combining Eqns. (3) and (4) we see that the TEP depends on the density of states, carrier velocity and relaxation time, and energy derivatives of these quantities, evaluated at ϵ_F . Together with Eq. (2), the two-band TEP is a highly convoluted function of six Fermi surface parameters and their derivatives. Hence, to obtain semi-quantitative information from our TEP data necessitates some approximations.

Of specific interest is the H-dependent concentration of normal electronic states in the lower CDW state of NbSe₃. We may estimate this quantity by assuming that the dominant effect of H is to change σ_e ; σ_h , S_h , and S_e are to first order taken as independent of H. This leads to an H-dependent (normal) electron concentration

$$\frac{n_e(H)}{n_e(0)} = \frac{S(0) - S_e}{S(H) - S_e} \cdot \frac{S_h - S(H)}{S_h - S(0)} \quad (5)$$

Figure 3 shows, as a function of temperature, $n_e(H)/n_e(0)$ determined from Eq. (5), using estimated values for S_h and S_e of 80 $\mu\text{V/K}$ and -30 $\mu\text{V/K}$, respectively, and the experimentally determined values of $S(H)$. Figure 3 indicates that the effect of an H field in the lower CDW

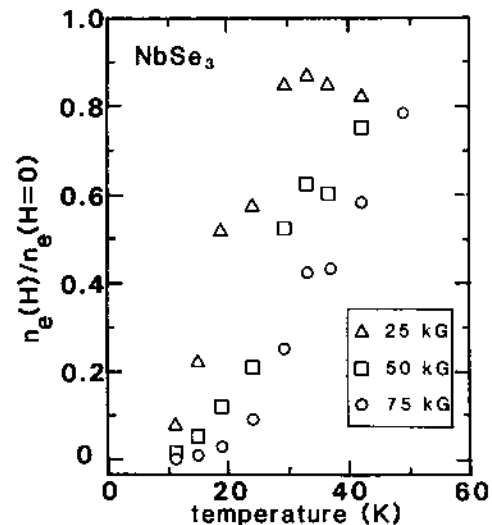


Fig. 3 Normalized conduction electron concentration versus temperature in the lower CDW state, as determined from Eq. (5).

state of NbSe₃ is to reduce the free electron carrier concentration n_e . We emphasize, however, that the results of Fig 3 are only qualitatively correct owing to the limited validity of Eq. (5). An obvious difficulty with Fig 3 is that it indicates that at $H = 75$ kG and below $T \approx 20$ K, virtually all free electron states have been eliminated. This would appear inconsistent with the nearly linear increase in CDW carrier concentration with H up to $H = 75$ kG [2]. This effect appears related to the saturation in the magnetothermopower at low T and large H , despite the

nearly quadratic increase in magnetoresistance.

In summary, the strong H -dependence of the TEP of NbSe₃ in the lower CDW state is suggestive of an H -induced destruction of electron states at the Fermi level, resulting in a more hole-like TEP and more electrically insulating state.

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