## Heat Conduction in the Vortex State of NbSe<sub>2</sub>: Evidence for Multiband Superconductivity

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The thermal conductivity  $\kappa$  of the layered s-wave superconductor NbSe<sub>2</sub> was measured down to  $T_c/100$  throughout the vortex state. With increasing field, we identify two regimes: one with localized states at fields very near  $H_{c1}$  and one with highly delocalized quasiparticle excitations at higher fields. The two associated length scales are naturally explained as multiband superconductivity, with distinct small and large superconducting gaps on different sheets of the Fermi surface. This behavior is compared to that of the multiband superconductor MgB<sub>2</sub> and the conventional superconductor V<sub>3</sub>Si.

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Multiband superconductivity (MBSC) is the existence of a superconducting gap of significantly different magnitude on distinct parts (sheets) of the Fermi surface (FS). This unusual phenomenon has recently emerged as a possible explanation for the anomalous properties of some s-wave superconductors. Although first experimentally observed over 20 years ago [1], the possible existence of MBSC has not often been considered since then. The current interest in MBSC has been fueled by the peculiar properties of the 40-K superconductor MgB<sub>2</sub>, where the case for MBSC is now rather compelling [2]. In particular, a gap much smaller than the expected BCS gap has been resolved in tunneling experiments [3]. One consequence of a small gap is the ability to easily excite quasiparticles, which, for example, can make the properties of this s-wave superconductor similar to those of d-wave superconductors.

Based on angle-resolved photoemission (ARPES) measurements, it has recently been proposed that the 7-K layered superconductor NbSe<sub>2</sub> is also host to MBSC [4]. A sizable difference in the magnitude of the superconducting gap was found on two sets of Fermi surface sheets, with no detectable gap on the smallest sheet. However, these measurements were performed only at 5.3 K. It is clearly of interest to shed further light on this sheet-dependent superconductivity by performing bulk measurements down to low temperatures.

In this Letter, we report a study of heat transport in NbSe<sub>2</sub> down to  $T_c/100$  throughout the vortex state, providing further evidence for MBSC. By measuring the degree of delocalization of quasiparticle states in the vortex state, heat transport probes the overlap between core states on adjacent vortices, i.e., the size of the vortex core ( $\sim \xi$ ), and hence the magnitude of the gap ( $\sim 1/\xi$ ). We resolve two regimes of behavior: one limited to very low fields (up to  $\sim 5H_{c1}$ ), where delocalization is slow and activated as in conventional (single-gap) superconductors such as  $V_3Si$ , and one for all other fields up to  $H_{c2}$  where quasiparticles transport heat extremely well, as in unconventional superconductors with nodes in the gap.

NbSe<sub>2</sub>, a quasi-2D metal with hexagonal symmetry, displays a transition to a charge density wave state around  $T \simeq 35$  K. Measurements of its FS at low temperatures, by both de Haas-van Alphen (dHvA) [5] and ARPES measurements [4], agree with band structure calculations that predict a FS made of four or five sheets. These sheets divide into two groups: a small  $\Gamma$ -centered pocket derived from the Se 4p band (denoted as  $\Gamma$  band) and larger nearly two-dimensional sheets derived from Nb 4d bands. Scanning tunneling spectroscopy (STS) at 50 mK revealed a spectrum that is consistent with a distribution of gaps that range from 0.7 to 1.4 meV [6]. In the vortex state at very low fields (near  $H_{c1}$ ), a zero-bias conductance peak, characteristic of states localized in the vortex core, was observed at the vortex center [7].

The thermal conductivity  $\kappa$  of NbSe<sub>2</sub> was measured in a dilution refrigerator using a standard technique [8]. Measurements were made at temperatures increasing from 50 mK and in magnetic fields ranging from 0 to 6 T, applied parallel to the c axis and perpendicular to the in-plane heat current. The sample was cooled in field to ensure field homogeneity. Measurements as a function of field at fixed temperature resulted in nearly no difference as compared to the field-cooled data [see Fig. 2(a)].

The sample, a rectangular parallelepiped with dimensions  $1.2 \times 0.5$  mm in the plane and 0.1 mm along the c axis, is from the same batch as the sample used by Sonier et al. [10,11] and has a superconducting transition temperature  $T_c = 7.0 \text{ K}$  with a width  $\delta T_c = 0.1 \text{ K}$ . It was cleaved to provide six fresh surfaces for silver paint contacts with resistances at low temperatures of roughly 20 m $\Omega$ . The residual resistivity ratio is 40 ( $\rho_0 \simeq$ 

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3  $\mu\Omega$  cm), and the upper and lower critical fields are, respectively,  $H_{c2}=4.5~\mathrm{T}$  and  $H_{c1}=20~\mathrm{mT}$  for  $H\parallel c$ . The coherence length estimated from  $H_{c2}$  is  $\xi(0)=85~\mathrm{Å}$ .

The thermal conductivity of NbSe<sub>2</sub> is plotted in Fig. 1, as  $\kappa/T$  against  $T^2$ . This enables a separation of the electronic and the phononic thermal conductivities, since the asymptotic T dependence of the former as  $T \rightarrow 0$  is linear while that of the latter is cubic. The electronic thermal conductivity  $\kappa_0/T$  is thus obtained as the extrapolated  $T \rightarrow 0$  value. In zero field,  $\kappa_0/T = 0.000 \pm$  $0.005 \text{ mW K}^{-2} \text{ cm}^{-1}$ , a clear indication that NbSe<sub>2</sub> is an s-wave superconductor with a fully gapped excitation spectrum. However, by applying a small magnetic field  $(H \ge H_{c1})$ , an electronic contribution develops as a rigid shift from the H=0 curve in Fig. 1. At higher fields  $(H \ge 1.5 \text{ T})$ , the electronic contribution dominates the conduction over the entire temperature range and  $\kappa/T$  is constant in temperature within our experimental resolution. Above  $H_{c2}$ , the Wiedemann-Franz (WF) law is satisfied and the thermal conductivity saturates.

The  $\kappa_0/T$  values are plotted as a function of H on a reduced scale in Fig. 2. Also plotted is a field sweep at T=130 mK from which the zero-field value (the phononic contribution) has been subtracted. As seen in

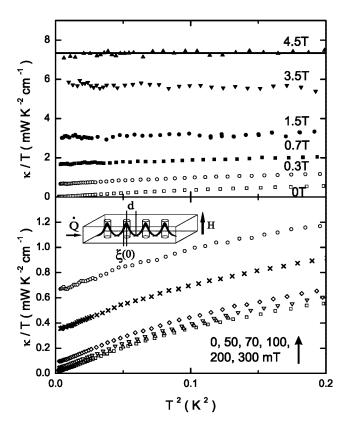


FIG. 1. Thermal conductivity of NbSe<sub>2</sub> at several applied fields, plotted as  $\kappa/T$  vs  $T^2$ . The solid line indicates the value expected from the Wiedemann-Franz law as obtained from resistivity measurements at H=4.5 T. The field is applied parallel to the c axis and perpendicular to the heat current  $\dot{Q}$ .

Fig. 2(c), heat conduction starts to increase right at  $H_{c1}$  in what could be qualified as an activated behavior, although in a very limited range of fields:  $H_{c1} \le H \le 0.03H_{c2}$ . (The value of  $H_{c1}$  is determined in situ as the drop in the phonon  $\kappa$  due to vortex scattering.) At higher fields,  $\kappa_0/T$  increases rapidly, i.e., faster than  $(H/H_{c2})$   $\kappa_N/T$ , where  $\kappa_N/T$  is the normal state value. This shows the presence of highly delocalized quasiparticle states almost throughout the vortex state of NbSe<sub>2</sub>.

This is in stark contrast to the behavior expected of a type-II s-wave superconductor. Indeed, when a field in excess of  $H_{c1}$  is applied, and vortices enter the sample, the conventional picture is that the induced electronic states are localized within the vortex cores. As one increases the field, the intervortex spacing  $d \simeq \sqrt{\Phi_0/B}$  decreases. The localized states in adjacent vortices will have an increasing overlap leading to enhanced tunneling between vortices and the formation of conduction bands. Strictly speaking, the electronic states are actually

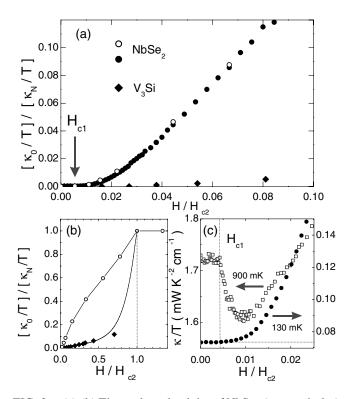


FIG. 2. (a),(b) Thermal conductivity of NbSe<sub>2</sub> (empty circles) and V<sub>3</sub>Si (diamonds) at  $T \rightarrow 0$  vs H, normalized to values at  $H_{c2}$ . Filled circles come from a sweep in field at T=130 mK from which the H=0 thermal conductivity (phononic contribution) has been subtracted. The thick solid line in (b) is a theoretical curve for the thermal conductivity of V<sub>3</sub>Si [9]. The thin line is a guide to the eye. (c)  $\kappa/T$  vs H for NbSe<sub>2</sub> at T=130 mK (circles) and T=900 mK (squares). The latter shows a typical drop in the phononic thermal conductivity at  $H_{c1}=20$  mT. The former shows that the electronic thermal conductivity starts to increase right at  $H_{c1}$  but has a slow activated-like behavior for fields below  $0.03H_{c2}$ .

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always delocalized but with extremely flat bands at low fields [12]. As these gradually become more dispersive, the thermal conductivity should increase accordingly and grow exponentially with the ratio  $d/\xi$ , as is indeed observed in Nb [13].

A better point of comparison for NbSe<sub>2</sub> is V<sub>3</sub>Si, an extreme type-II superconductor with comparable superconducting parameters ( $T_c = 17 \text{ K}$ ,  $\xi = 50 \text{ Å}$ ). This is done in Fig. 2, where the thermal conductivity of V<sub>3</sub>Si is seen to grow much more slowly with H than that of NbSe<sub>2</sub>, as described by theory [9]. Quantitatively, at  $H = H_{c2}/20$ ,  $\kappa_0/T = \frac{1}{20} \times \kappa_N/T$  for NbSe<sub>2</sub> and  $\frac{1}{400} \times \kappa_N/T$  for V<sub>3</sub>Si [14]. Note that the samples compared in Fig. 2 are in the same regime of purity. From the standard relation  $\xi(0) = 0.74\xi_0[\chi(0.88\xi_0/l)]^{1/2}$ , we obtain for V<sub>3</sub>Si  $\xi_0/l = 0.13$ , with  $\xi(0) = 50 \text{ Å}$  from  $H_{c2}$  and l = 1500 Å from dHvA [15]. This is similar to the value of 0.15 for NbSe<sub>2</sub> [16].

The high level of delocalization in NbSe<sub>2</sub> is a clear indication of either a gap with nodes (e.g., d wave) or a nodeless gap which is either highly anisotropic or small on one FS and large on another. A gap with nodes is ruled out by the absence of a residual term in the thermal conductivity in zero field [17].

It is revealing to compare NbSe<sub>2</sub> to MgB<sub>2</sub>, for which the thermal conductivity has a similar field dependence. Strikingly,  $\kappa$  follows roughly the same field dependence as the specific heat C for both NbSe<sub>2</sub> and MgB<sub>2</sub>. This is shown in Fig. 3 where  $\kappa(H)$  and C(H) are plotted on a reduced field scale for single crystals of NbSe<sub>2</sub> [10,18], MgB<sub>2</sub> [19,20], and V<sub>3</sub>Si [21,22], with  $H \parallel c$  for hexagonal NbSe<sub>2</sub> and MgB<sub>2</sub>, and  $H \parallel a$  for cubic V<sub>3</sub>Si. In conventional superconductors such as V<sub>3</sub>Si,  $\kappa(H)$  and C(H) are very different [see Fig. 3(c)] because the excited electronic states are largely localized.

 $MgB_2$  is a well-established case of MBSC with a small gap on one FS ( $\Delta_{\pi} = 1.8$  meV) and a large gap on the

other ( $\Delta_{\sigma} = 6.8 \text{ meV}$ ). The field dependence of its heat capacity is well understood in this context [20], with a distinctive shoulder at a field of  $H_{c2}/10$  [see Fig. 3(b)] [23]. A similar shoulder is also manifest in NbSe<sub>2</sub> around  $H_{c2}/9$  [see Fig. 3(a)]. Empirically, the striking fact that heat transport and heat capacity have the same field dependence in both materials points to a common explanation and hence suggests that  $NbSe_2$  is host to multiband superconductivity [24]. This is consistent with recent ARPES measurements at  $T = 0.8T_c$  [4].

In conventional superconductors, the delocalization of vortex core bound states occurs gradually on the scale of  $H_{c2}$ , and the characteristic length scale is  $\xi(0) \simeq \sqrt{\Phi_0/2\pi H_{c2}}$ . It appears that in NbSe<sub>2</sub> (and MgB<sub>2</sub>), there are two characteristic length scales for delocalization:  $\xi^*$  and  $\xi(0)$ . To see this, we focus on the low-field region. For NbSe<sub>2</sub>, both  $\kappa/T$  and C/T have been measured with high precision on the same crystals, thereby making a detailed comparison possible. Figure 4(a) shows the comparison for fields below  $H_{c2}/10$ , where the two do not coincide: C/T increases abruptly above  $H_{c1}$  while  $\kappa/T$  grows slowly, in an activated way. This is consistent with the presence of localized states at very low fields as imaged by STS [6,7]. Then this behavior gives way to a rapid increase of the thermal conductivity at fields above  $0.03H_{c2}$ . This is a clear indication that the field scale associated with delocalization in NbSe<sub>2</sub> is much smaller than  $H_{c2}$ .

In fact, we can scale the behavior of the low-field thermal conductivity of NbSe<sub>2</sub> to that of V<sub>3</sub>Si using  $H^* = H_{c2}/9$  [Fig. 4(b)]. This is also seen clearly if we plot the ratio of the thermal conductivity to the specific heat [Fig. 4(c)] which measures the degree of delocalization. The ratio is seen to have two regimes: a rapid increase below  $H^* \simeq H_{c2}/10$  and a slow one above. In summary, the second length scale associated with delocalization in NbSe<sub>2</sub> is  $\xi^* \simeq \xi(0)/\sqrt{9} = \xi(0)/3$ . This is consistent and

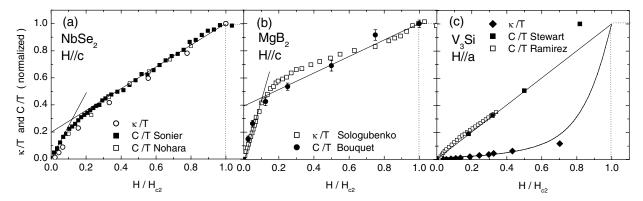


FIG. 3. (a) Thermal conductivity and heat capacity of NbSe<sub>2</sub> normalized to the normal state value vs  $H/H_{c2}$ . The heat capacity was measured in two different ways: (i) at T=2.4 K on the same crystals as used in this study [10], and (ii) extrapolated to  $T\to 0$  from various temperature sweeps on different crystals [18]. (b) Equivalent data for MgB<sub>2</sub> single crystals [19,20]. (c) Equivalent data for V<sub>3</sub>Si, with a theoretical curve for  $\kappa/T$  [9]. The specific heat is measured at T=3.5 K [21] and extrapolated to T=0 [22]. The straight line is a linear fit. The thermal conductivity is seen to follow the specific heat very closely for both NbSe<sub>2</sub> and the multiband superconductor MgB<sub>2</sub>. It does not, however, for the conventional s-wave superconductor V<sub>3</sub>Si.

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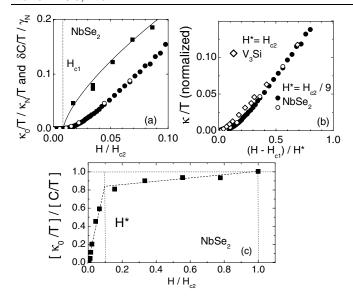


FIG. 4. (a) Thermal conductivity (circles) and the field evolution of the heat capacity  $\delta C/T = [C(T,H) - C(T,H=0)]/T$  (squares) [10] of NbSe<sub>2</sub> normalized to the normal state values vs  $H/H_{c2}$  at very low fields. The line is a guide to the eye. (b) Normalized thermal conductivity vs  $(H - H_{c1})/H^*$  for NbSe<sub>2</sub> and V<sub>3</sub>Si with  $H^* = H_{c2}/9$  and  $H_{c2}$ , respectively. (c) Ratio of heat transport to heat capacity in NbSe<sub>2</sub>.

may explain naturally the shrinking of the vortex cores observed with muon spin rotation [11].

Considering the fact that the upper critical field is related to the superconducting gap by  $H_{c2} \simeq \Delta^2/v_F^2$  where  $v_F$  is the Fermi velocity, we estimate the gap to vary over the FS by a factor of 3 ( $\Delta^* \simeq \Delta_0/3$ ). (Note that we assume  $v_F$  to be constant, within the direction of the ab plane, as found by band structure calculations [5].) A variation of this order was reported earlier from STS measurements [6], where the spread in  $\Delta$  was measured to be between 0.7 and 1.4 meV. Moreover, theoretical modeling of STS features associated with the vortex cores [25] and efforts to model C(T) [26] were found to require an anisotropy in the gap of a factor of 3 and 2.5, respectively.

Our results are consistent with dHvA measurements [15]: while extended quasiparticles are seen deep into the vortex state in both NbSe<sub>2</sub> and V<sub>3</sub>Si, the additional damping attributed to the superconducting gap below  $H_{c2}$  increases more slowly in NbSe<sub>2</sub>. Corcoran *et al.* measured the electron-phonon constant  $\lambda_{e-ph}=0.3$  for the  $\Gamma$  band whereas they extract an average value of  $\lambda_{e-ph}=1.8$  from specific heat [5]. The origin of MBSC may lie in the fact that  $\lambda_{e-ph}$  is smaller for the  $\Gamma$  band. This suggests that superconductivity originates in the Nb 4d bands and is induced onto the Se dp $\Gamma$  pocket.

In summary, measurements of heat transport in the vortex state of NbSe<sub>2</sub> at low temperatures reveal the existence of highly delocalized quasiparticles down to fields close to  $H_{c1}$ . This is in striking contrast with what is

expected in a s-wave superconductor where well-separated vortices should support only localized states, as is observed in V<sub>3</sub>Si. We identify two characteristic length scales that govern the destruction of superconductivity in NbSe<sub>2</sub>: the usual one associated with  $H_{c2}$  and another associated with a much smaller field  $H^* \simeq H_{c2}/9$ . We attribute this to multiband superconductivity, whereby the gap on the pocketlike  $\Gamma$  band is approximately 3 times smaller than the gap on the other two Fermi surfaces.

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