

Unusual Magnetic-Field-Induced Phase Transition in the Mixed State of Superconducting NbSe₂

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The thermal conductivity κ in the basal plane of single-crystalline hexagonal NbSe₂ has been measured as a function of magnetic field H , oriented both along and perpendicular to the c axis, at several temperatures below T_c . With the magnetic field in the basal plane and oriented parallel to the heat flux we observed, in fields well below H_{c2} , an unexpected hysteretic behavior of $\kappa(H)$ with all the generic features of a first order phase transition. The transition is not manifest in the $\kappa(H)$ curves, if H is still in the basal plane but oriented perpendicularly to the heat-flux direction. The origin of the transition is not yet understood.

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The layered hexagonal compound NbSe₂ has been of interest to researchers for some time, mainly because of the relatively strong anisotropy of its superconducting properties. Pure samples exhibit a superconducting critical temperature $T_c \approx 7.2$ K, and the upper critical fields for H along and perpendicular to the hexagonal c axis are $H_{c2}^c = 40$ kOe and $H_{c2}^{ab} = 140$ kOe [1], respectively. The anisotropy of the electron system is also reflected in the charge density wave (CDW) transition at $T_{CDW} = 34$ K (in pure NbSe₂), interesting by itself and also in view of the competition between the CDW formation and superconductivity [2]. Another important feature of NbSe₂ is the existence of a variety of vortex matter related phenomena, such as a pronounced peak effect and various phase transitions and instabilities (see, e.g., Refs. [3–5] and references therein).

In this Letter, we present the observation of an unexpected hysteretic behavior of the thermal conductivity κ in external magnetic fields with the characteristic features of a first order phase transition. Several anomalies associated with the transition are yet to be explained.

The single crystal used in the experiments was grown by employing the standard iodine vapor transport method [6]. For the crystal growth, stoichiometric amounts of 99.9% pure Nb wire and 99.999% pure Se shots were sealed in a quartz ampoule, and then heated in a temperature gradient for a few weeks. Two bar-shaped samples with dimensions of $(4.4 \times 0.88 \times 0.42)$ mm³ and $(2.8 \times 0.51 \times 0.50)$ mm³ were cut from the crystal. Very detailed measurements of $\kappa(T, H)$ were done on one of the samples and the other specimen was used to ascertain that the observed effects described below are indeed sample independent. The thermal conductivity was measured by employing the standard uniaxial heat-flux method in an experimental setup that was also used in our recent study of $\kappa(T, H)$ in MgB₂ [7,8]. The heat flux \dot{Q}

was kept in the basal plane and along the longest lateral dimensions of the sample. The temperature difference ΔT along the specimen was kept to about 3%–5% of the average sample temperature. The zero-field superconducting transition temperature $T_c = 7.2$ K was determined via four-contact dc resistivity measurements and from the results of measurements of the magnetic susceptibility, employing a commercial Quantum Design SQUID magnetometer.

Figure 1 shows $\kappa(H)$ at $T = 0.85$ K for all three orientations of the magnetic field that we have explored. Similar results were obtained at other temperatures in the interval between 0.38 K and T_c . The data for $H \parallel c$ are in good agreement with the recent results presented by Boaknin *et al.* [9]. The main features of $\kappa(T, H)$ can readily be understood by considering that the total thermal conductivity consists of two components, namely, the phonon contribution κ_{ph} and the quasiparticle (electron) contribution κ_e . The normal electronic excitations in the cores of the vortices in the mixed state considerably reduce the phonon mean-free path, but they also add positively to the heat transport. Hence, when the external magnetic field is enhanced to above the lower critical field H_{c1} , $\kappa_{ph}(H)$ is efficiently reduced but, simultaneously, $\kappa_e(H)$ starts to increase. The result is a minimum in the $\kappa(H)$ curve in a magnetic field slightly exceeding H_{c1} . These features may be seen in Figs. 1 and 2(b). In the normal state, above the upper critical field H_{c2} , the thermal conductivity varies only weakly with H . It reflects the field induced positive variation of the electrical resistivity of NbSe₂ in the normal state, which also affects the electronic contribution κ_e to κ .

This general behavior of $\kappa(H)$ is observed for all orientations of the magnetic field, but, with $H \perp c$ and parallel to the heat-flux direction, a pronounced hysteretic behavior in $\kappa(H)$, as shown in Fig. 2, is observed.

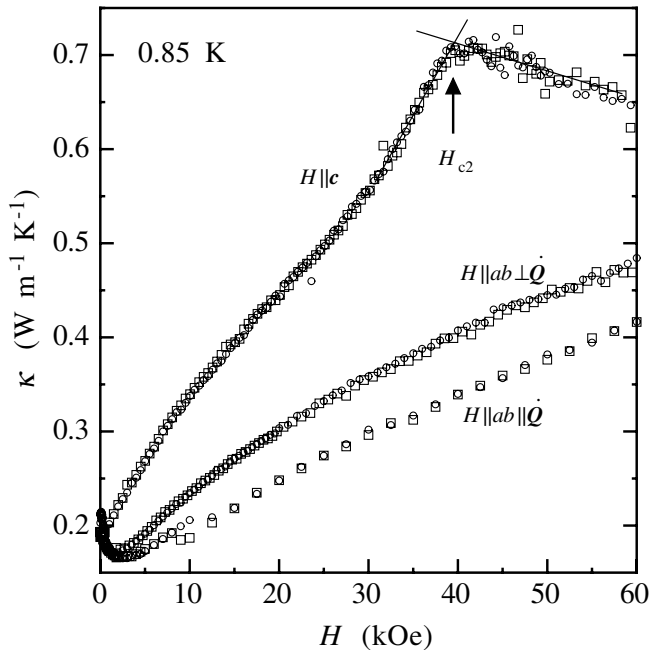


FIG. 1. The basal plane thermal conductivity of single crystalline NbSe₂ as a function of differently oriented magnetic fields at $T = 0.85$ K. The open circles and squares correspond to increasing and decreasing fields, respectively.

This feature, emphasized in Fig. 2(a), is a clear manifestation of some kind of phase transition, most likely of first order. As we discuss in detail below, some details are not compatible with a conventional first order transition, however. Inspecting the data presented in Fig. 2, it is clear that two different $\kappa(H)$ regimes have to be distinguished. They correspond to two different modifications or phases of the mixed state, one of which is stable in low fields (l phase) and the other (h phase) corresponds to the equilibrium state in high magnetic fields. In the following, we shall use $\kappa^{(l)}(H)$ and $\kappa^{(h)}(H)$ to denote the thermal conductivities of the l and h phases of the mixed state, respectively [see Fig. 2(a) for the definitions of $\kappa^{(l)}$, $\kappa^{(h)}$ and the corresponding characteristic fields]. While the l phase is stable up to $H = H_2$, the high-field modification remains stable down to $H = H_1 < H_2$. Also note that the transition from one modification to the other is rather narrow upon field reduction, whereas the transition in increasing field is more than twice as wide, with $\kappa(H)$ being almost constant in the transition region. All the features shown in Fig. 2 were confirmed to be reproducible and they were observed for both investigated samples.

The hysteresis is completely absent if the magnetic field, while still parallel to the basal plane, is rotated to be perpendicular to the heat-flux direction [see Fig. 2(b)]. This disappearance of the hysteresis is quite unexpected because, considering the hexagonal symmetry of the crystal structure of NbSe₂, no anisotropy is expected in the basal plane. It may also be seen that $\kappa(H)$ is notably

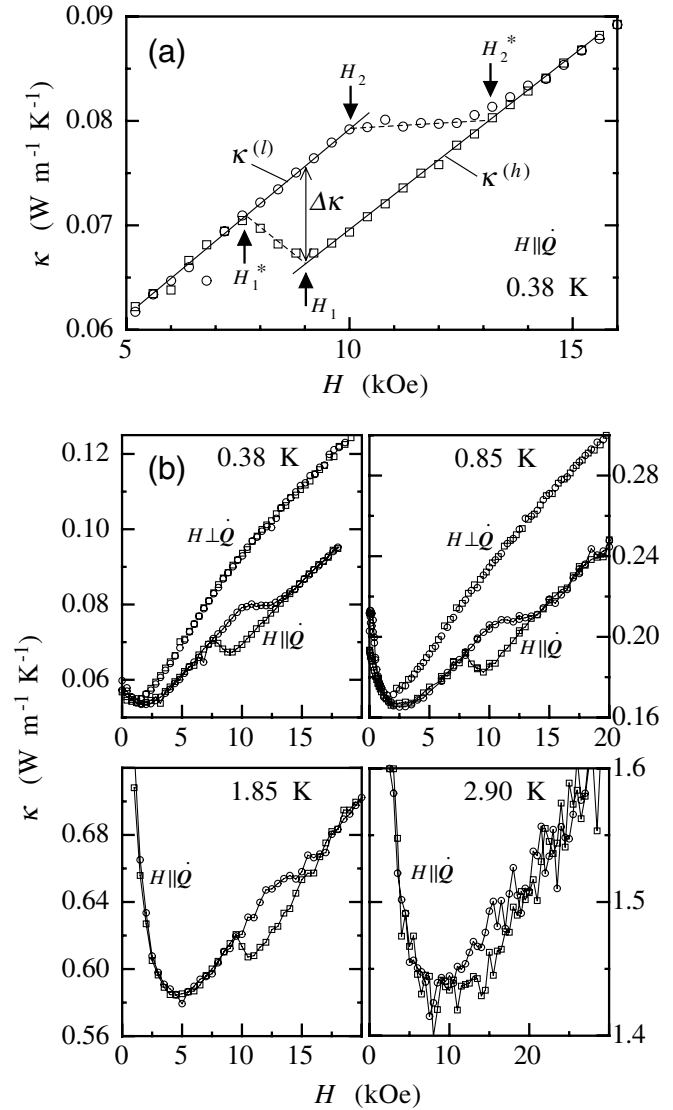


FIG. 2. (a) Characteristic features of the hysteresis exemplified by $\kappa(H)$ at $T = 0.38$ K. The open circles and squares correspond to increasing and decreasing field, respectively. (b) The thermal conductivity as a function of magnetic field oriented perpendicularly to the c axis at several temperatures. Note the difference for different field orientations.

higher if the magnetic field is oriented perpendicularly to the heat flux.

Another unusual feature of this transition is the considerable width of the hysteresis loop with $H_2^*/H_1^* \approx 1.7$. It turns out that both H_1^* and H_2^* increase with increasing temperature [see Fig. 3(a)]. Considering that all critical fields of a superconductor usually decrease with increasing temperature, this is again an unexpected observation.

The magnetic field ranges $H_2 < H < H_2^*$ in increasing and $H_1^* < H < H_1$ in decreasing fields, respectively, correspond to transition regions where the l and the h phases coexist. Because both $\kappa^{(l)}(H)$ and $\kappa^{(h)}(H)$ may quite well be approximated by parallel straight lines, the volume

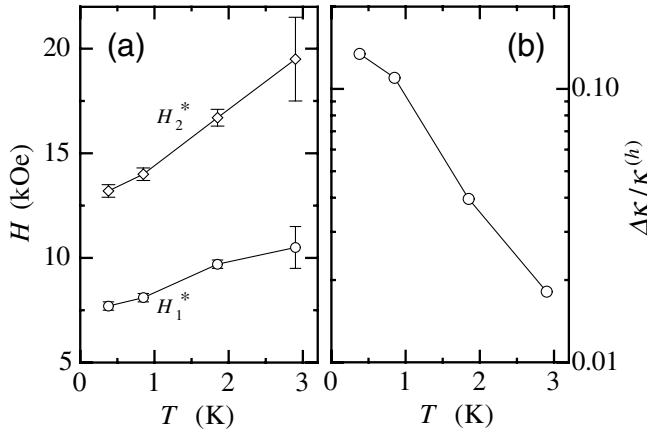


FIG. 3. (a) Temperature dependencies for the fields H_1^* and H_2^* . (b) Temperature dependence of the normalized difference $\Delta\kappa = \kappa^{(l)} - \kappa^{(h)}$. For definitions, see Fig. 2(a).

ratio between the two phases for each point in the transition regions can easily be evaluated from the experimental data.

Partial hysteresis loops, as shown in Fig. 4, are also unusual. If a reduction of the magnetic field is started from the transition region between H_2 and H_2^* [Fig. 4(a)], the measured $\kappa(H)$ curve is practically parallel to $\kappa^{(l)}(H)$ and $\kappa^{(h)}(H)$ until H_1 is reached. Roughly the same feature emerges if the magnetic field is enhanced from the transition region $H_1 > H > H_1^*$ [see Fig. 4(b)]. These observations imply that, in the limited field range between the vertical broken lines in Fig. 4, the volume ratio between the l and the h phases in the sample is independent of the applied magnetic field and can be changed only if the

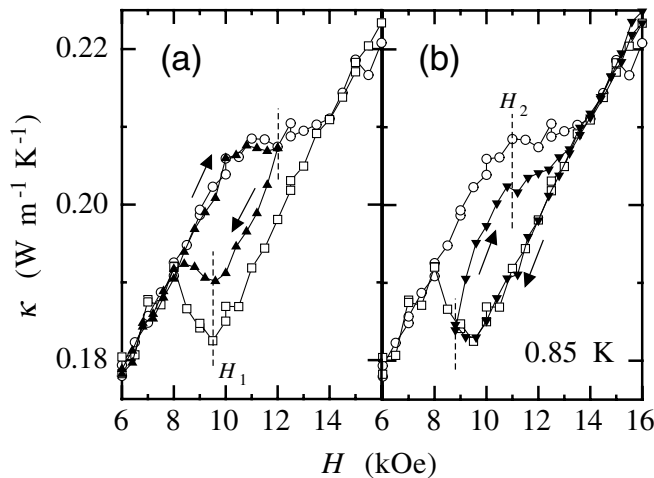


FIG. 4. Partial hysteresis loops of $\kappa(H)$ at $T = 0.85 \text{ K}$. The open circles and squares represent the full loop and are the same as in Fig. 2(b). (a) H is first increasing from 0 to 12 kOe and then decreasing. (b) H is first enhanced from 30 to 8.8 kOe and then reduced. The broken vertical lines mark the special fields values.

magnetic field exceeds H_2 (in increasing field) or is reduced to below H_1 (in decreasing field). This behavior is rather difficult to understand in terms of a common first order phase transition. Indeed, in conventional first order transitions, the main reason for a hysteresis is the inertia toward generating a sufficiently large nucleus of a new phase. Once the nucleus exists, the transition usually happens in a rather narrow range of fields or temperatures. Here we have a completely different situation. Two different phases coexist in fixed amounts over an extended field region, and it needs to be understood why the transformation from one phase to the other does not happen upon varying the applied magnetic field within the limits mentioned above.

We also tested the stability of κ at fixed values of the magnetic field in the transition regions and at constant temperature. As may be seen in Fig. 5, there are no observable changes of κ with time. This observation provides again clear evidence that the transformation of one phase into the other cannot happen as easily as it usually does in the case of common first order phase transitions. In an extended range of the magnetic field, both the l and the h phases are present and stable in the sample. Taking into account that near the edges of the hysteresis loop only one of them represents the equilibrium, the stability of the described situation implies that some potential barrier seems to prevent the completion of the transition from one equilibrium phase to the other.

Before we discuss the situation further, we note that, at temperatures as low as 0.38 K, the phonon contribution κ_{ph} to the thermal conductivity in the mixed state is small compared to κ_e , certainly in fields beyond the $\kappa(H)$ minima (see Figs. 1 and 2). Because we are mainly interested in low magnetic fields $H \leq 0.1H_{c2}$, no overlap of vortex cores needs to be considered and each vortex line is expected to contribute to the heat transport individually. If the magnetic field is perpendicular to the heat flux, the vortex motion along the heat flux, induced by a

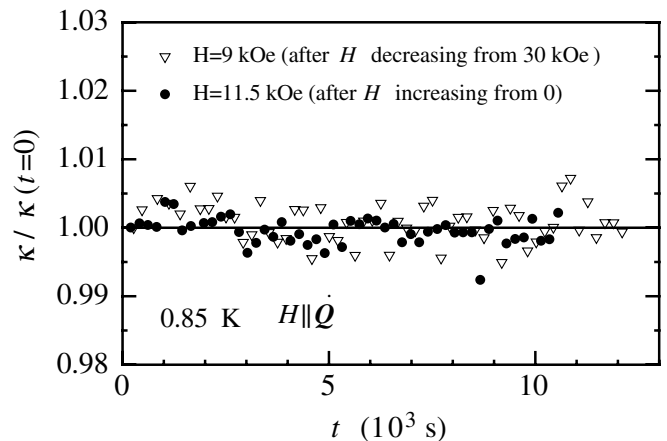


FIG. 5. κ vs time for two values of the external magnetic field at $T = 0.85 \text{ K}$.

temperature gradient ∇T , also contributes to κ , but this contribution is not expected to be significant (see Ref. [10] and references therein).

The results presented above clearly imply the existence of a phase transition in the mixed state of our NbSe₂ samples with the following main features: (i) a very large difference $\Delta\kappa = \kappa^{(l)} - \kappa^{(h)}$ between the thermal conductivities in the low and the high-field phase. If we assume that $\Delta\kappa$ is only due to a change of the vortex density, we have to assume an unrealistically large variation of the magnetic induction $\Delta B \approx 3$ kG [see Fig. 2(a)]; (ii) a very large width of the hysteresis loop with $H_2^*/H_1^* = 1.7$; (iii) the coexistence of the l and the h phases of the mixed state in an extended range of magnetic fields. The adopted volume ratio is practically independent of H in this range (Fig. 3). This particular feature is incompatible with a conventional first order transition; (iv) a completely different behavior of $\kappa(H)$, if the magnetic field is oriented perpendicularly to the heat flux, exhibiting no visible signs of a phase transition [Fig. 2(b)]; (v) a shift of the transition to higher fields with increasing temperature [Figs. 2(b) and 3(a)].

Although the phase transition manifests itself by a rather prominent feature in the $\kappa(H)$ curves, we could not find a reasonable scenario which would explain all the different features of the transition. Below, we briefly consider several possible phase transitions in the mixed state of type-II superconductors and discuss their relevance for our experimental observations.

1. The well-known vortex-lattice melting transition explains neither the magnitude of the observed difference $\Delta\kappa = \kappa^{(l)} - \kappa^{(h)}$ nor the vanishing of the transition for $H \perp \mathbf{Q}$. Quite unlikely are other vortex ordering transitions considered in the literature, because all of them invoke only small changes of the vortex density. We also recall that the vortex-lattice melting is a typical first order transition and therefore it is incompatible with the partial hysteresis loops shown in Fig. 4 [11].

2. It was pointed out that, in superconductors with other ordering phenomena, a first order phase transition may occur due to the competition between superconductivity and the additional ordering phenomenon [12]. As an example of additional ordering, the authors of Ref. [12] considered a charge density wave formation. This matches exactly the case for NbSe₂ but, because the assumed transition is of first order, it is not clear how the coexistence of two mixed state phases and the dependence of the $\kappa(H)$ feature on the orientation of the magnetic field can be explained.

3. The first order transition discussed in Ref. [5] was observed for $H \parallel c$ and therefore seems not to be relevant to our case. The same applies to other reports of instabilities of the mixed state of NbSe₂ which were observed either close to H_{c2} or for other field orientations [3,4,13].

4. The possible phase transition discussed in Ref. [14] is expected to occur in fields rather close to H_{c2} and therefore is *a priori* considered as unlikely to be the reason for our observation.

In conclusion, measurements of the thermal conductivity in external magnetic fields revealed an unusual phase transition in the mixed state of NbSe₂. The origin and the nature of this transition are not yet understood and further experiments are needed to clarify the situation.

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- [1] J. A. Woollam and R. B. Somoano, Phys. Rev. B **13**, 3843 (1976).
 - [2] R. Sooryakumar and M.V. Klein, Phys. Rev. Lett. **45**, 660 (1980).
 - [3] S.S. Banerjee, N.G. Patil, S. Ramakrishnan, A.K. Grover, S. Bhattacharya, P.K. Mishra, G. Ravikumar, T.V. Chandrasekhar Rao, V.C. Sahni, M. J. Higgins, C.V. Tomy, G. Balakrishnan, and D. McK. Paul, Phys. Rev. B **59**, 6043 (1999).
 - [4] M. Marchevsky, M.J. Higgins, and S. Bhattacharya, Nature (London) **409**, 591 (2001).
 - [5] Y. Paltiel, E. Zeldov, Y. Myasoedov, M.L. Rappaport, G. Jung, S. Bhattacharya, M. J. Higgins, Z. L. Xiao, E.Y. Andrei, P.L. Gammel, and D. J. Bishop, Phys. Rev. Lett. **85**, 3712 (2000).
 - [6] F. Levy and H. Berger, J. Cryst. Growth **61**, 61 (1983).
 - [7] A.V. Sologubenko, J. Jun, S. M. Kazakov, J. Karpinski, and H. R. Ott, Phys. Rev. B **65**, 180505(R) (2002).
 - [8] A.V. Sologubenko, J. Jun, S. M. Kazakov, J. Karpinski, and H. R. Ott, Phys. Rev. B **66**, 014504 (2002).
 - [9] E. Boaknin, M. A. Tanatar, J. Paglione, D. Hawthorn, F. Ronning, R.W. Hill, M. Sutherland, L. Taillefer, J. Sonier, S. M. Hayden, and J.W. Brill, Phys. Rev. Lett. **90**, 117003 (2003).
 - [10] A. Freimuth and B. Zeini, Phys. Rev. B **67**, 052504 (2003).
 - [11] In principle, the entanglement of vortices, accompanying the vortex-lattice melting transition, may influence the thermal conductivity. However, such an entanglement is likely to affect the thermal conductivity for any orientation of the magnetic field and thus cannot explain the absence of the anomaly for the field orientation perpendicular to the heat flow direction.
 - [12] V.V. Kurin and A.I. Panfilov, Physica (Amsterdam) **224C**, 277 (1994).
 - [13] S. Bhattacharya and M. J. Higgins, Phys. Rev. Lett. **70**, 2617 (1993).
 - [14] I. L. Landau and H. R. Ott, J. Phys. Condens. Matter **14**, L313 (2002).