Low Field Anomaly in the Specific Heat of s-Wave Superconductors due to the Expansion of the Vortex Cores

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The magnetic field dependence of the electronic specific heat $C(H)$ in the s-wave superconductor NbSe$_2$ shows curvature at low fields, resembling the near $\sqrt{H}$ term in $C(H)$ which has been reported in high-T_c superconductors and attributed to a $d_{x^2-y^2}$-wave pairing state. In NbSe$_2$ we find that the low field behavior in $C(H)$ is described quantitatively by the expansion of vortex cores and the field dependence of the magnetic induction B above H_{c1}. The associated change in the density of quasiparticle states localized in the vortex cores provides a simple explanation for the "low field anomaly" in $C(H)$ observed in s-wave superconductors. [S0031-9007(99)09363-1]

In the vortex state of a type-II superconductor, an applied magnetic field penetrates the bulk in the form of quantized flux lines. The predictions of this state by Abrikosov [1] and of bound quasiparticle (QP) states in the normal vortex cores of a conventional superconductor by Caroli *et al.* [2] remain two great achievements in superconductivity theory. Although flux decoration experiments readily confirmed the existence of the vortex state, the electronic structure of the cores predicted by Caroli *et al.* was not established until the advent of scanning tunneling microscopy (STM). In particular, Hess *et al.* [3] observed tunneling spectra in the vortex cores of NbSe$_2$ consistent with localized QP states—thus seemingly completing the picture of the vortex state.

Interest in the vortex state was renewed with the discovery of the high-T_c superconductors (HTSCs). The general consensus is that the charge carriers in the HTSCs form pairs whose wave function (or order parameter) has a dominant $d_{x^2-y^2}$-wave symmetry, rather than the s-wave symmmetry characteristic of low-T_c conventional superconductors. Much theoretical work has focused on incorporating $d_{x^2-y^2}$-wave symmetry into a model for the vortex state of the HTSCs. Despite these efforts, experiments have yet to unambiguously confirm these predictions.

Measurements of the electronic specific heat $C(T, H)$ are one way of probing the QP excitation spectrum in the vortex state. In an s-wave superconductor, where there is an isotropic energy gap at the Fermi surface, there is a contribution to $C(H)$ which is proportional to the QP density of states (DOS) localized in the vortex cores. Since the density of vortices increases linearly as a function of magnetic field, this term is expected to be proportional to H [4]. On the other hand, in the vortex state of a $d_{x^2-y^2}$-wave superconductor, Volovik [5] predicted that the DOS varies as $\sqrt{H}$. This weaker field dependence of the DOS is mainly due to delocalized QPs which leak outside of the vortex cores along the nodal directions of the order parameter. Within this model, bound core states are at most a minor correction to the total DOS. Experiments per-

formed on the HTSCs, YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) [6,7] and La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) [8,9] showed that there is a contribution to $C(H)$ which is approximately proportional to $\sqrt{H}$—consistent with Volovik's prediction. Although this was one of the key early experiments providing evidence for $d_{x^2-y^2}$-wave symmetry in the HTSCs, the interpretation of such measurements has been plagued by puzzling reports of similar curvature in $C(H)$ at low magnetic fields in s-wave superconductors, such as NbSe$_2$ (Ref. [10]), V$_3$Si (Ref. [11]), and CeRu$_2$ (Ref. [12])—and in other unconventional superconductors, like the heavy fermion superconductor UPt$_3$ (Ref. [13]), the organic superconductor (BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (Ref. [14]) and the borocarbide superconductor LuNi$_2$B$_2$C (Ref. [15]). Ramirez [11] suggested that this behavior at low fields might be a general feature of all superconductors in the vortex state, independent of the order parameter symmetry, but somehow related to the strength of the vortex-vortex interactions. Clearly the $\sqrt{H}$ dependence of the specific heat in the HTSCs cannot be attributed to nodes in the energy gap function without a satisfactory explanation for similar behavior in fully gapped superconductors.

A long-standing general belief is that the superconducting coherence length ξ is independent of H. However, muon spin rotation (μSR) [16] and STM [17] measurements have shown that the radius r_0 of the vortex cores in NbSe$_2$ expand at low fields. In the μSR experiment, the field dependence of r_0 could be fit to a function dependent only on the intervortex spacing. These μSR and STM results have been met with some skepticism, however, since the change in r_0 implies that the superconducting coherence length ξ also varies with field. An obvious question raised by these observations is as follows: Could the low field anomaly in the specific heat be due to the expansion of the vortex cores?

To address this question we have carried out detailed measurements of the specific heat $C(T, H)$ in a 40 mg crystal of NbSe$_2$ from the same batch used in the μSR experiment of Ref. [16]. The crystal had a superconducting

transition temperature $T_c = 7.0(1)$ K, as determined previously [16] by resistivity and susceptibility measurements, and here from measurements of the specific heat in zero field (see Fig. 1). From magnetization and specific heat measurements, the upper and lower critical fields for this crystal were found to be $H_{c2} = 2.90(3)$ T and $H_{c1} = 0.025(2)$ T at $T = 2.3$ K, and $H_{c2} = 1.75(2)$ T and $H_{c1} = 0.015(1)$ T at $T = 4.2$ K. The specific heat was measured using a thermal relaxation calorimeter [18] with the magnetic field applied normal to the NbSe$_2$ layer direction. The data have been corrected for the small field-dependent background and addenda contributions.

Figure 2 shows the field dependence of $C(T,H)/T$ in NbSe$_2$ at $T = 2.3$ K and below H_{c2}. The downward curvature at low fields is similar to that reported in Ref. [10]. Measurements were taken four different ways: (i) The single crystal was zero-field cooled (ZFC) to $T = 2.3$ K, and measurements taken for increasing field up to $H = 2.5$ T, (ii) then taken for decreasing field down to $H = 0$ T. (iii) Starting with the crystal at $T = 2.3$ K and $H = 4$ T (i.e., in the normal state), the field was ramped down to 1 T and measurements taken for decreasing field down to $H = 0$ T. (iv) Measurements were also made after field cooling the crystal to $T = 2.3$ K, in different magnetic fields. No significant hysteresis is found in the specific heat measurements—consistent with the near reversibility of the magnetization (Fig. 2, inset).

In a conventional s-wave superconductor, the specific heat in the vortex state ($H > H_{c1}$) is greater than in the Meissner state ($H < H_{c1}$), due to a contribution from the localized QPs in the vortex cores. A precise calculation, from the Bogoliubov equations assuming noninteracting vortices, gives the density of states $N(E)$ per unit volume associated with the bound excitations as [4]

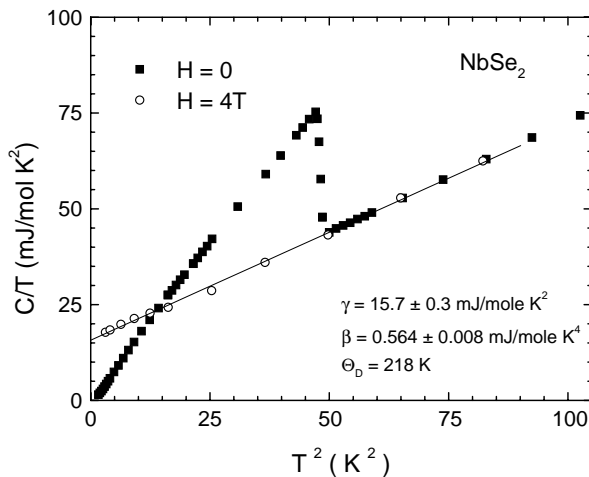$$N(E) = N(0)\pi\xi_0 \left[\frac{\pi I}{f'} \right] \frac{B(H)}{\Phi_0}, \qquad (1)$$

where ξ_0 is the coherence length, $N(0)$ is the density of normal electron states at the Fermi surface, f' is the slope of the order parameter at the vortex axis $r = 0$, I is a numerical constant, Φ_0 is the flux quantum, and $B(H)$ is the magnetic induction. The factor $B(H)/\Phi_0$ is the density of vortices. The coherence length in Eq. (1) is related to the value of the energy gap Δ_0 far outside the vortex cores, i.e., $\xi_0 = \hbar v_F/\pi\Delta_0$. In Ginzburg-Landau (GL) theory, $f \approx r/\xi$ at $r = 0$, so that $f' \approx 1/\xi$ [2,19]. The GL coherence length ξ is the characteristic length scale for spatial variations in the order parameter, and unlike ξ_0 depends on temperature and is proportional to the field-dependent vortex-core radius. Using Eq. (1), the contribution of the vortex cores to the specific heat when $k_B T \gg \Delta_0^2/E_F$ is

$$C_{\text{cores}}(T,H) = \frac{2}{3}\pi^2 N(E) k_B^2 T = \pi^2 \xi_0 \gamma_n T \left[\frac{B(H)}{\Phi_0} \right] \xi I, \qquad (2)$$

where $\gamma_n T = (2/3)\pi^2 N(0) k_B^2 T$ is the normal-state electronic specific heat and E_F is the Fermi energy. Thus, the specific heat in the vortex state may be written as

$$C(T,H) = C(T,0) + \pi^2 \xi_0 \gamma_n T \left[\frac{B(H)}{\Phi_0} \right] \xi I, \qquad (3)$$

where $C(T,0)$ is the specific heat at zero field in the Meissner state—with values from Fig. 1 given in Table I.

Maki [20] was the first to consider the effect of vortex-vortex interactions on the specific heat—deriving the following relation from London theory, just above H_{c1} in the high-κ limit

$$C(T,H) = C(T,0) - \frac{TB}{4\pi}\frac{d^2 H_{c1}}{dT^2}$$
$$+ \frac{TB^{3/2}\lambda}{H - H_{c1}}\left(\frac{dH_{c1}}{dT}\right)^2 \left(\frac{\sqrt{3}}{8\pi^2\Phi_0}\right)^{1/2}$$
$$+ \text{ terms in } \frac{1}{\lambda}\frac{d\lambda}{dT}, \qquad (4)$$

FIG. 1. The specific heat of NbSe$_2$ in zero field and $H = 4$ T (i.e., the normal state) plotted as $C(T,0)/T$ vs T^2. The solid line is a fit to $C_n/T = \gamma_n + \beta T^2$, where $\Theta_D = (12\pi^4 N k_B/5\beta)^{1/3}$ is the Debye temperature.

γ = 15.7 ± 0.3 mJ/mole K^2

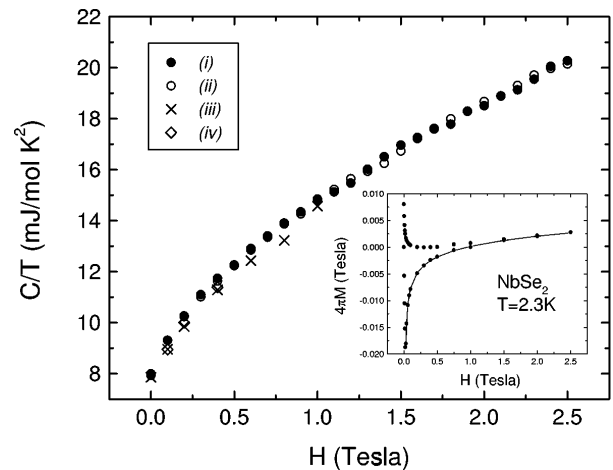β = 0.564 ± 0.008 mJ/mole K^4

Θ$_D$ = 218 K

FIG. 2. The specific heat of NbSe$_2$ at $T = 2.3$ K plotted as $C(T,H)/T$ vs H. The data were taken four different ways, as described in the text. The inset shows the dc magnetization-hysteresis loop for the ZFC crystal.

TABLE I. Results from fitting the specific heat for NbSe$_2$ to Eq. (6). Only $C(T,0)$ and $a(T)$ were free to vary.

T	$C(T,0)/T$		a	b_1 [a]	b_2 [a]
	($\frac{\text{mJ}}{\text{mol K}^2}$)		($\frac{\text{mJ}}{\text{mol K}^2 \text{T}}$)		
(K)	Fig. 1	Eq. (6)		(T^{-1})	(T^{-1})
2.3	7.7(1)	7.78(4)	12.7(1)	0.555	2.48
4.2	29.6(1)	29.26(9)	15.0(5)	0.891	4.68

[a]Reference [16].

where λ is the magnetic penetration depth. Strictly speaking, B and λ are functions of both T and H. The second term in Eq. (4) has the same form as Eq. (2), whereas the third term describes the perturbation due to vortex-vortex interactions. In Ref. [11] it was suggested that this latter term may explain the downward curvature in $C(H)$ observed at low fields in V$_3$Si. However, Eq. (4) has never been quantitatively verified. Furthermore, it was noted in earlier measurements of $C(T,H)$ in V$_3$Si (Ref. [21]) that Eq. (4) does not yield a term $\sim HT^3$ which is observed experimentally.

Recently, Ichioka *et al.* [22] used the quasiclassical Eilenberger equations to calculate the DOS in an *s*-wave superconductor with interacting vortices. At $T = 0$ K the DOS is found to vary as $H^{0.67}$ due to a change in the slope of the order parameter in the vortex cores. Fitting the increasing field ZFC data for $C(T,H)/T$ in the inset of Figs. 3 and 4 (the fit is not shown) to a function of the form $C(T,0)/T + \beta H^n$ using the values of $C(T,0)/T$ from Fig. 1 gives $\beta = 5.36(4)$ mJ/mol K^2 T^n and $n = 0.75(1)$ at $T = 2.3$ K, and $\beta = 4.70(2)$ mJ/mol K^2 T^n and $n = 0.826(8)$ at $T = 4.2$ K. Using these two values of the exponent n, a linear extrapolation to $T = 0$ K gives $n = 0.66$—which is close to the result predicted
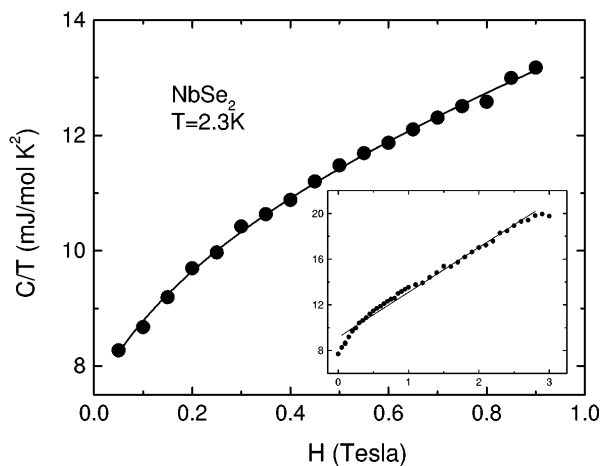
in Ref. [22]. Thus within this theoretical picture, vortex-vortex interactions affect the specific heat by decreasing both the size of the vortex cores and the corresponding density of bound QP states.

A direct test of this idea can be made using the precise field dependence of the vortex-core radius determined from μSR. We first note that for a fixed value of the temperature, the radius of a coherence length ξ in Eq. (2) is usually assumed to be independent of H, so that $\xi \approx \xi_0$—in which case the relation $\Phi_0 = 2\pi\xi^2 H_{c2}$ can be used to give the familiar result: $C_{\text{cores}} \sim \gamma_n TB/H_{c2}$. More generally, however, the density of core states $N(E)$ in Eq. (1) will have two sources of magnetic field dependence. First, the vortex density $B(H)/\Phi_0$ increases rapidly just above H_{c1} approaching H/Φ_0 as $H \rightarrow H_{c2}$. Second, due to vortex-vortex interactions, $r_0 \approx \xi$ decreases rapidly just above H_{c1} approaching a constant value near H_{c2}. In Ref. [16], the fitted value of the GL coherence length for NbSe$_2$ is well approximated by the relation $\xi(H) = 46(2) + 28.9(9)/(H - H_{c1})^{1/2}$ and $\xi(H) = 47(5) + 46(3)/(H - H_{c1})^{1/2}$ at $T = 2.3$ and 4.2 K, respectively. Substituting these relations into Eq. (3) gives an equation of the form

$$C(T,H) = C(T,0) + c_1 TB(H) + \frac{c_2 TB(H)}{(H - H_{c1})^{1/2}}, \quad (5)$$

where c_1 and c_2 are numerical constants. The form of Eq. (5) is similar to Maki's macroscopic specific heat equation, since $d^2 H_{c1}/dT^2 < 0$ in Eq. (4). The main difference is that the second term in Eq. (5) was derived from data at fields $4H_{c1} < H < 0.3 H_{c2}$, whereas Eq. (4) is valid near H_{c1} only.

The form of $B(H)$ in NbSe$_2$ was determined from the ZFC magnetization measurements with increasing magnetic field, where $B(H) = H + 4\pi M$. A phenomenological equation was chosen to fit the magnetization data (e.g., solid curve in Fig. 2, inset) since there is no analytical equation from theory which is valid over the entire
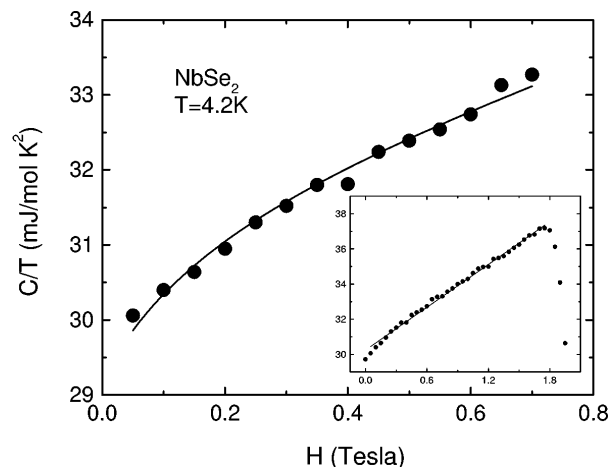

FIG. 3. The specific heat of NbSe$_2$ at $T = 2.3$ K over the field range of the μSR experiment [16] plotted as $C(T,H)/T$ vs H. The solid curve is a fit to Eq. (6). Inset: The specific heat over an extended field range. The solid curve is a fit to Eq. (3).

FIG. 4. Same as Fig. 3, but with the sample at $T = 4.2$ K.

field range. We find that

$$B(H) \approx H - 0.00009(2)H^{-1.32(7)}$$
$$- 0.0062(2)\ln[0.91(6)/H],$$

$$B(H) \approx H - 0.00063(2)H^{-0.65(7)}$$
$$- 0.00105(12)\ln[0.87(8)/H]$$

at $T = 2.3$ and 4.2 K, respectively. The contribution of $B(H)$ to the field dependence of $C(H)$ is observed by assuming ξ is independent of field and equal to ξ_0, and substituting the relation for $B(H)$ into Eq. (3). The solid curve in the inset of Figs. 3 and 4 is the corresponding fit which gives $C(T,0)/T = 9.2(1)$ mJ/mol K^2 and 30.25(5) mJ/mol K^2 at $T = 2.3$ and 4.2 K, respectively. It is clear that the field dependence of the magnetic induction above H_{c1} does not alone account for the low field curvature in $C(H)$. We note that the fitted value of $C(T,0)/T$ at $T = 2.3$ K, is nearly 20% larger than that measured in zero field.

To account for the effect of vortex-vortex interactions, we substitute the precise expression for $\xi(T,H)$ measured by μSR [16] into Eq. (3) to give

$$\frac{C(T,H)}{T} = \frac{C(T,0)}{T} + a(T)B(T,H)\frac{[1 + b_1(T)H]}{[1 + b_2(T)H]},$$
(6)

where $a(T) = \pi^2\xi_0\gamma_n\xi(T,0)I/\Phi_0$, and $b_1(T)$ and $b_2(T)$ are temperature dependent coefficients. The values for $b_1(T)$ and $b_2(T)$ were determined in the work of Ref. [16] and are given in Table I. Note that $\xi(T,0)$ is merely an extrapolation of $\xi(T,H)$ from the vortex state to $H = 0$ T, and should not be confused with the coherence length in the Meissner state. The unusual form of the μSR term has the following interpretation: (i) the numerator is the field dependence of the fitted magnetic penetration depth λ_{ab}, whereas (ii) the denominator is the field dependence of the GL parameter $\kappa = \lambda_{ab}/\xi_{ab}$.

In the main panel of Figs. 3 and 4, the data are plotted over the field range of the μSR experiment. The solid curve is a fit to Eq. (6), with the fitted values of $a(T)$ and $C(T,0)/T$ given in Table I. The quality of these fits lend strong support to the assertion that the downward curvature of $C(H)$ at low fields is partially due to the expansion of the vortex cores. Using the fitted values of $a(T)$, $\gamma_n = 15.7(3)$ mJ/mol K^2 from Fig. 1, the GL value $I = 1.92$ [2], $\xi(2.3,0) = 157(4)$ Å and $\xi(4.2,0) = 252(10)$ Å from Ref. [16], we find that $\xi_0 = 56(4)$ Å and $\xi_0 = 42(8)$ Å at $T = 2.3$ and 4.2 K, respectively.

As discussed earlier, in a pure $d_{x^2-y^2}$-wave superconductor the DOS comes predominantly from the QP spectrum outside of the vortex cores, since the presence of the gap nodes inhibit the formation of localized states within the cores. In this case the low field expansion of the vortex cores recently measured by μSR in YBCO [23,24] should have little effect on $C(H)$. However, the vortex-

vortex interactions which are responsible for the changing core size should play some role in the behavior of $C(H)$. For instance, in Ref. [22] it was shown that due to nearest neighbor vortex-vortex interactions, the density of the extended QP states in a $d_{x^2-y^2}$-wave superconductor will be proportional to $H^{0.41}$, rather than $\sim\sqrt{H}$, as predicted by Volovik [5]. Thus far, measurements of $C(H)$ in the HTSCs have not been performed with sufficient accuracy to verify this prediction.

In conclusion, we have shown that the field dependence of the electronic specific heat measured in the s-wave superconductor NbSe$_2$ is due to both the field dependence of the magnetic induction and the vortex-core size. We attribute the latter contribution to vortex-vortex interactions. Our findings provide a simple explanation for the downward curvature of $C(H)$ reported in superconductors which do not have nodes in the energy gap function.

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