Experimental evidence for a two-gap structure of superconducting NbSe$_2$: A specific-heat study in external magnetic fields


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To resolve the discrepancies of the superconducting order parameter in quasi-two-dimensional NbSe$_2$, comprehensive specific-heat measurements have been carried out. By analyzing both the zero-field and mixed-state data with magnetic fields perpendicular (H $\perp$ c) to and parallel (H$\parallel$ c) to the c axis of the crystal and using the two-gap model, we conclude that (1) more than one energy scale of the order parameter is required for superconducting NbSe$_2$ due to the thermodynamic consistency; (2) $\Delta_L = 1.26$ meV and $\Delta_S = 0.73$ meV are obtained; (3) $N_f(0)/N(0) = 11\% - 20\%$; (4) the observation of the kink in $\gamma(H)$ curve suggests that the two-gap scenario is more favorable than the anisotropic s-wave model to describe the gap structure of NbSe$_2$; and (5) $\Delta_S$ is more isotropic and has a three-dimensional-like feature and is located either on the Se or the bonding Nb Fermi sheets.

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NbSe$_2$ was one of the earliest layered materials known to be superconducting, with $T_c \sim 7$ K, and for 40 years had been thought to be a conventional type II superconductor. Moreover, the charge density wave (CDW) occurring at 33 K in NbSe$_2$ is also intriguing, and was once proposed to originate from a combination of the fractional nesting of Fermi surfaces (FSs) around K and the saddle band, and was related to the anomalies of FS attributed to a quasi-two-dimensional (quasi-2D) structure with hexagonal symmetry. Because the superconductivity and CDW compete with each other for FS, consequently, the interplay between superconductivity and CDW in NbSe$_2$ has been abundantly investigated, and the relation between Fermi surface nesting and CDW is still under debate in current literature. On the other hand, due to the recent discovery of new superconductors, new concepts of the superconducting order parameter have been well established, such as d-wave pairing in cuprates and two-gap superconductivity in MgB$_2$. Since then, interest has revived in the superconducting order parameter of NbSe$_2$. Recent studies of the superconducting order parameter in NbSe$_2$ generally agree that more than one energy scale is involved, and the relation between Fermi surface nesting and CDW is still under debate in current literature. Beyond that, research is inconsistent in terms of the magnitude of the superconducting gaps. In particular, there also remains an even more heated controversy on which Fermi sheets the large and small gaps are located, respectively. In this study, we have carried out comprehensive specific-heat measurements both at the zero magnetic field and in the mixed state to resolve these discrepancies. Being a bulk probe, low-temperature specific heat has been recognized as one powerful tool to determine the pairing state in superconductors and gives additional information on the vortex state. The previous specific-heat reports on NbSe$_2$, though showing part of the data in the present work, did not fully analyze the issue of multigap or anisotropic superconductivity. In this work, the magnetic field $H$ is applied both perpendicular ($H \perp c$) to and parallel ($H\parallel c$) to the $c$ axis of the crystal, respectively, to study the anisotropy of the order parameter. The present thermodynamic approach leads to a two-gap scenario with $\Delta_L = 1.26$ meV and $\Delta_S = 0.73$ meV in the two-gap model. The small gap $\Delta_S$ is somewhat isotropic and, therefore, is either on the Se or the bonding Nb Fermi sheets.

The single crystalline dichalcogenide NbSe$_2$ was grown by the standard iodine vapor transport method. Stoichiometric amounts of 99.9% pure Nb and 99.999% pure Se were sealed in a quartz ampoule and then heated in a temperature gradient for several weeks. The low-temperature specific heat $C(T, H)$ was measured with a $^3$He heat-pulsed thermal relaxation calorimeter in the temperature range from 0.6 to 10 K by applying different magnetic fields with $H \perp c$ and $H\parallel c$ to the $c$ axis of the single crystal. Details of the experiments are described in Refs. 10 and 24.

Figure 1 shows the result of the specific heat $C(T, H)$ of NbSe$_2$ plotted as $C/T$ vs $T^2$, with $H$ from 0 to 8 T. With decreasing $T$, the specific-heat jump starts at $T \sim 6.9$ K, consistent with that in another specific-heat study. The thermodynamic $T_c = 6.70$ K is determined by the local entropy balance around the phase transition anomaly. At zero field, $C(T)/T$ approaches a zero interception at low $T$, indicating a complete superconducting volume and the high sample quality. For $H\parallel c$, there is no observed superconducting transition anomaly at $H=5$ T. Thus, the normal-state specific heat $C_n(T)$ is extracted from $H=5$ T data between $T=0.6$ and 10 K with $H\parallel c$. $C_n(T)$ can be described as $C_n(T) = \gamma_c T + C_{\text{lattice}}(T)$, where $\gamma_c T$ is the normal electronic contribution and $C_{\text{lattice}}(T) = \beta T^3 + \alpha T^5$ represents the phonon contribution. The fit leads to $\gamma_c = 19.09 \pm 0.20$ mJ/mK$^2$, $\beta = 0.517 \pm 0.007$ mJ/mol K$^4$, and $\alpha = (2.7 \pm 0.6) \times 10^{-3}$ mJ/mol K$^6$.

The superconducting electronic contribution $\delta C(T)$ can be obtained by $\delta C(T) = C(T, H) - C_n(T)$, and $\delta C(T)/T$ vs $T$ for $H=0$ is shown in Fig. 2. The entropy conservation required for a second order phase transition is fulfilled, as shown in...
he elucidation of the superconducting order parameter, thus, indicates a moderate or strong coupling scenario in $s$ and emphasized in a study by Sanchez et al. Inset: (a) The determination of $\gamma(H)$ from the linear extrapolation of data for $T^2 \approx 2 \, \text{K}^2$ and (b) entropy conservation for superconducting phase transition.

The inset of Fig. 1(b). This check verifies the thermodynamic consistency of the measured data. By the balance of entropy around the transition, the dimensionless specific-heat jump $\delta C/\gamma_n T_c = 2.12$ at $T_c$ is determined, which was also observed and emphasized in a study by Sanchez et al. This value is much larger than the weak coupling limit value 1.43 and, thus, indicates a moderate or strong coupling scenario in NbSe$_2$. To elucidate the superconducting order parameter, $\delta C(T)/T$ is analyzed by the isotropic $s$ wave, line node order parameter, anisotropic $s$ wave, and the two-gap model. The order parameters used to fit the data are $\Delta = \Delta_0$ for isotropic $s$ wave, $\Delta = \Delta_0 \cos 3\phi$ for line nodes, and $\Delta = \Delta_0 (1 + \alpha \cos 6\phi)$ (where $\alpha$ denotes the gap anisotropy) for anisotropic $s$ wave. In the two-gap model, two (assumed) isotropic order parameters $\Delta_1$ and $\Delta_2$ are introduced as in the previous works. It is clear that neither isotropic $s$ wave nor line node order parameter is consistent with the experimental data. On the other hand, both anisotropic $s$ wave and the two-gap model could result in satisfactory descriptions of the data. To achieve optimal fitting, the anisotropic $s$-wave model requires that $\alpha = 0.35$ and $2\Delta_0/kT_c = 4.2$. The two-gap model with $2\Delta_0/kT_c = 4.2$, $2\Delta_2/kT_c = 2.6$, and $\gamma_{\Delta L}/\gamma_{\Delta S} = 80\% : 20\%$ also leads to an accurate description of experimental data. In order to further distinguish between the anisotropic and two-gap model for the present case, magnetic field dependent data in the mixed state are analyzed and the Fermi surfaces of NbSe$_2$ are discussed.

In Fig. 3, $\gamma(H)$, obtained from the linear extrapolation of the low-$T$ data in Fig. 1 to $T = 0$, is shown for $H\parallel c$ and $H \perp c$, respectively. The fitting temperature range is $T^2 \approx 2 \, \text{K}^2$ for

**FIG. 1.** (Color online) Temperature ($T$) dependence of specific heat ($C$) plotted as $C/T$ vs $T^2$ at various magnetic fields for NbSe$_2$ in (a) $H \perp c$ (from right to left: $H=0, 0.3, 0.5, 1, 1.5, 2, 3, 4, 6$, and 8 T) and (b) $H\parallel c$ (from right to left: $H=0, 0.1, 0.2, 0.3, 0.5, 0.75, 1, 2, 3, 4$, and 5 T). Insets: (a) The determination of $\gamma(H)$ from the linear extrapolation of data for $T^2 \approx 2 \, \text{K}^2$ and (b) entropy conservation for superconducting phase transition.

**FIG. 2.** (Color online) Various fitting of $\delta C(T)/T$ vs $T$ using (a) isotropic $s$-wave, (b) line node, (c) anisotropic $s$-wave, and (d) two-gap models. The deviation of each fitting from data is shown in the respective inset, where DF represents the difference between the fitting values and actual data.
that the anisotropic s-wave model fits \( \gamma(H) \) reasonably, and is consistent with the results in Ref. 30, yet the obtained anisotropy value of \( \alpha = 0.5 \) is larger than \( \alpha = 0.35 \) from the zero-field data. Third, the fit of the two-gap model (standard deviation, SD = 0.112, where \( \text{SD} = \sqrt{\sum (\gamma_{\text{exp}} - \gamma_{\text{mod}})^2 / n} \)) actually leads to a better fit, with a smaller standard deviation than that by the anisotropic s-wave model (SD = 0.322). To more clearly show the difference, we have plotted DF in the inset of Fig. 3(a). The fit of the two-gap model even reproduces the small kink (or say, change in slope) around \( H = 0.75 \) T, which is attributed to the upper critical field \( H_{\text{c}2} = 0.62 \pm 0.06 \) T associated with the small gap \( \Delta_S \). The fit also leads to \( \gamma_{\text{lin}} / \gamma_{\text{exp}} = 92\% \pm 18\% \), almost identical to the ratio from the zero-field data. This makes sense, the two-gap model is better than the anisotropic s-wave model in describing the in-field data. In Fig. 3(b), \( \gamma(H) \) is shown for \( H \parallel c \) and \( H \perp c \). Note that \( \gamma(H) \) for \( H \perp c \) also shows a kink around \( H = 0.75 \) T. Indeed, the \( H \perp c \) data can be described well by \( H_{\text{c}2} = 0.73 \pm 0.10 \) T and \( H_{\text{c}2L} = 15.2 \pm 0.3 \) T. It is interesting to note that \( H_{\text{c}2L} \) is almost the same for both \( H \parallel c \) and \( H \perp c \). This points to \( \Delta_S \) more isotropic and rather three-dimensional. Moreover, the anisotropy parameter \( \Gamma = H_{\text{c}2L} / H_{\text{c}2} = 15.2 / 0.73 = 20.7 \), which may be related to the origin of the kink and which of those are possibly due to gapless FS. Therefore, the kink structure probably reflects the nature of the low \( T \) data.

The above data and analysis establish that more than one energy scale is needed to explain the specific-heat data. Moreover, the small energy gap is three-dimensional-like. The issue remains on the assignment of the two simplified energy gaps to various Fermi sheets in NbSe2. This point can be further illustrated with the help of a basic picture of the Fermi surfaces as shown in Fig. 4.17 It denotes two Nb-derived bands and one Se-derived band crossing the Fermi energy. In total, there are five distinct Fermi sheets. The four Nb-derived Fermi sheets are quasi-2D, and the Se-derived Fermi surface is in the shape of a three-dimensional (3D) pancake. It seems natural to assign \( \Delta_S \) to the Se-derived Fermi sheet, and \( \Delta_L \) to the other four Nb-derived quasi-2D Fermi sheets. Actually, \( \Delta_S = 1.26 \) meV is consistent with the observed energy gap value of 1.13 – 1.22 meV on the Nb-derived sheets by angle resolved photoemission spectroscopy.
However, the low energy scale of the gap \( \Delta_s \) =0.73 meV (0.7 meV by scanning tunneling spectroscopy\(^\text{16}\) and 0.6 meV by the de Hass–van Alphen experiments\(^\text{12}\)) was not observed by ARPES (partly due to the energy resolution and the low \( T \) limit of ARPES). The derived gap values are fairly consistent with tunneling spectroscopy results,\(^\text{20,21}\) where a highly anisotropic (or multiband) gap with \( \Delta_{\text{max}} =1.4 \) meV and \( \Delta_{\text{min}} =0.4–0.7 \) meV was revealed. Related to \( \Delta_s \), the present specific-heat data require that the Fermi surface density of states (DOS) \( N_s(0) \) should be 11\%–20\% of the total DOS \( N(0) \). Density functional theory (DFT) calculations suggest \( N_{Se}(0)/N(0) \approx 5\% \) in Ref. 7. Nevertheless, \( N_{Se}(0) \) can be effectively enhanced to the observed values by only a minor charge transfer (=0.04 electrons) from the Nb bands to the Se band in DFT calculations, due to the large effective mass of the latter.\(^\text{7}\) However, if the renormalization factor in \( \gamma \) is considered, a larger number of the charge transfer is required. On the other hand, it is noted that de Haas–van Alphen measurements suggest a Se pancake which is considerably smaller than the local density approximation estimates.\(^\text{12}\) A recent work based on the penetration depth study also reported anisotropic or two-gap superconductivity in NbSe\(_2\).\(^\text{19}\) That work suggests that the energy gap on the Se-derived sheet is at least as large as that on the Nb-derived sheets, and the small energy gap is on some portion of the Nb-derived sheets. This is not consistent with the relatively uniform energy gap on the Nb-derived sheets observed by ARPES.\(^\text{16}\) However, the penetration depth study’s results might find some agreement in the present study. The bonding

Nb (BN) Fermi sheets have strong warping along \( k_z \), and are estimated to have \( \sim 40\% \) of \( N(0) \). Actually, the average \( v_Fz/v_Fs (=2) \) implies that BN sheets are not extremely anisotropic.\(^\text{7}\) Following the context of Ref. 19, \( \Delta_s \) is likely on some portion of the BN sheets or the superconducting energy gap on BN sheets is anisotropic. To further clarify this issue, the more comprehensive ARPES works on NbSe\(_2\) are necessary.

To summarize, the comprehensive magnetic field dependence of specific-heat measurements has been performed to study the superconducting order parameter of NbSe\(_2\). The two-gap model with \( \Delta_s =1.26 \) meV, \( \Delta_s =0.73 \) meV, and \( N_s(0)/N(0) =11\%–20\% \) can accurately describe the gap structure. By analyzing the in-field data with \( H \parallel c \) and \( H \perp c \), respectively, we argue that the two-gap scenario is more favorable than the anisotropic \( s \)-wave model in describing the gap structure of NbSe\(_2\). Also, the small gap \( \Delta_s \) is more isotropic and has a 3D-like feature, and is located either on the Se-derived Fermi surface or on the bonding Nb Fermi sheets. The present two-gap scenario largely clarifies the controversies and debates over the order parameter of superconducting NbSe\(_2\) in the previous literature.

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