Evidence for two-gap superconductivity in the non-centrosymmetric compound LaNiC$_2$

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New Journal of Physics 15 (2013) 053005 (16pp)
Received 20 October 2012
Published 7 May 2013
Online at http://www.njp.org/
doi:10.1088/1367-2630/15/5/053005

Abstract. We study the superconducting properties of the non-centrosymmetric compound LaNiC$_2$ by measuring the London penetration depth $\Delta \lambda(T)$, the specific heat $C(T, B)$ and the electrical resistivity $\rho(T, B)$. Both $\Delta \lambda(T)$ and the electronic specific heat $C_e(T)$ exhibit behavior at low temperatures that can be described in terms of a phenomenological two-gap Bardeen–Cooper–Schrieffer (BCS) model. The residual Sommerfeld coefficient in the superconducting state, $\gamma_0(B)$, shows a rapid increase at low fields and then an eventual saturation with increasing magnetic field. A pronounced upturn curvature is observed in the upper critical field $B_{c2}(T)$ near $T_c$. All these experimental observations support the existence of two-gap superconductivity in LaNiC$_2$.
1. Introduction

The spatial-inversion and time-reversal symmetries of a superconductor (SC) may impose important constraints on the pairing states. Among the SCs discovered in the past, most of them possess a center of inversion symmetry. In this case, the Cooper pairs are in either an even-parity spin-singlet or an odd-parity spin-triplet pairing state, constrained by the Pauli principle and parity conservation \[1, 2\]. However, the tie between spatial symmetry and the Cooper-pair spins is violated in SCs lacking spatial inversion symmetry \[3–7\]. In the non-centrosymmetric (NCS) SCs, an asymmetric electrical field gradient may yield an antisymmetric spin–orbit coupling (ASOC), which splits the Fermi surface into two subsurfaces of different spin helicities, with pairing allowed both across each one of the subsurfaces and between the two. The parity operator is then no longer a well-defined symmetry of the crystal, and allows the admixture of spin-singlet and spin-triplet pairing states within the same orbital channel.

NCS superconductivity has been intensively studied in a few heavy fermion compounds, e.g. CePt$_3$Si \[8–11\], CeRhSi$_3$ \[12\], CeIrSi$_3$ \[13\] and UIr \[14\]. In these systems, the nature of superconductivity is complicated by its coexistence with magnetism and the lack of inversion symmetry; both effects may give rise to unconventional superconductivity. It is, therefore, highly desirable to search for weakly correlated, non-magnetic NCS SCs to study the pure effect of ASOC on superconductivity. It has been demonstrated that, in Li$_2$(Pd$_{1-x}$Pt$_x$)$_3$B, the spin-singlet and spin-triplet order parameters can add constructively and destructively \[15\]. The mixing ratio in this compound appears to be tunable by the strength of ASOC \[15\]; Li$_2$Pd$_3$B behaves like a BCS SC, but Li$_2$Pt$_3$B shows evidence of a spin-triplet pairing state \[15–17\] attributed to an enhanced ASOC \[18\]. Recently, non-BCS-like superconductivity with a possible multi-gap structure at low temperatures was observed in Y$_2$C$_3$ \[19\], in spite of its relatively weak ASOC. On the other hand, evidence of multi-gap superconductivity was shown in La$_2$C$_3$ \[20\] and Mg$_{10}$Ir$_{19}$B$_{16}$ \[21\]. The diversity of the superconducting states in the NCS SCs requires more systematic investigations in order to reach a unified picture.

LaNiC$_2$, a simple metallic NCS SC \[22\], has recently attracted considerable attention. However, the order parameter of this compound remains highly controversial. Measurements of specific heat \[23\] and nuclear quadrupole relaxation (NQR)-1/T$_1$ \[24\] suggested that LaNiC$_2$ is a conventional BCS SC, which is further supported by theoretical calculations \[25\]. On
the other hand, evidence of possible nodal superconductivity was inferred from the recent penetration depth that follows $\Delta \lambda(T) \sim T^n$ ($n \geq 2$) [26] and also from the early measurements of specific heat by Lee et al [27]. Unconventional characteristics were also revealed from muon spin relaxation ($\mu$SR) experiments in which the absence of time-reversal symmetry was indicated [28, 29]. In order to elucidate the pairing state of LaNiC$_2$, here we present a systematic study of the penetration depth $\Delta \lambda(T)$, the electronic specific heat $C_e(T, B)$ and the electrical resistivity $\rho(T, B)$ on high-quality polycrystalline samples. We found that the temperature dependence of both $\Delta \lambda(T)$ and $C_e(T)$ can be well described by a phenomenological two-gap BCS model. The residual Sommerfeld coefficient, $\gamma_0(B)$, increases rapidly at low fields and eventually saturates with increasing magnetic field. Furthermore, the upper critical field $B_{c2}(T)$ shows an upward curvature near $T_c$. All these observations resemble those of MgB$_2$ [30–33], strongly supporting a two-gap SC in LaNiC$_2$.

2. Experimental methods

Polycrystalline LaNiC$_2$ was synthesized by arc melting. A Ti button was used as an oxygen getter. Appropriate amounts of the constituent elements (3 N purity La, 2 N purity Ni and 3 N purity graphite) were pressed into a disc before arc-melting. The ingot was inverted and remelted several times to ensure sample homogeneity. The derived ingot, with a negligible weight loss, was annealed at 1050°C in a vacuum-sealed quartz tube for 7 days, and then quenched into water at room temperature.

A small portion of the ingot was ground into fine powder for x-ray diffraction (XRD) measurements on an X’Pert PRO diffractometer (Cu K$_\alpha$ radiation) in the Bragg–Brentano geometry. Measurements of the electrical resistivity, specific heat and magnetization were performed in a physical property measurement system (9T-PPMS) and a magnetic property measurement system (5T-MPMS) (Quantum Design), respectively. Precise measurements of the London penetration depth $\Delta \lambda(T)$ were performed utilizing a tunnel diode oscillator (TDO) technique [34] at a frequency of 7 MHz down to 0.37 K in a $^3$He cryostat.

3. Results and discussion

3.1. Sample characterizations

Figure 1 shows the XRD patterns of LaNiC$_2$, which identify it as a single phase. The Rietveld refinement confirmed an orthorhombic Amm2 structure (No. 38). The atoms of Ni (2b) and C (4e) are alternatively stacked on the NiC$_2$ plane but lose the inversion symmetry, as shown in the inset of figure 1. The derived lattice parameters are given as $a = 3.9599$ Å, $b = 4.5636$ Å and $c = 6.2031$ Å, in good agreement with those reported in the literature [22].

Figure 2(a) presents the temperature dependence of the electrical resistivity $\rho(T)$ between 2 and 300 K at $B = 0$, which shows simple metallic behavior above $T_c$. Observations of a large residual resistivity ratio (RRR = $\rho_{300 K}/\rho_{4 K} \simeq 26$) and a sharp superconducting transition ($T_c \rho \approx 3.5 \pm 0.1$ K) suggest a high quality of our samples. Figure 2(b) shows the temperature dependence of the specific heat $C(T)/T$ at $B = 0$ and the zero-field-cooling (ZFC) magnetization $M(T)$ ($B = 10$ Oe), respectively. A pronounced superconducting transition seen in both $C(T)/T$ and $M(T)$ confirms the bulk superconductivity in LaNiC$_2$. The bulk $T_c$ values, derived from the specific heat using an entropy balance method ($T_c^{S_p} = 2.75$ K) and the
Figure 1. XRD patterns and crystal structure of LaNiC$_2$. Short vertical bars indicate the calculated reflection positions.

Figure 2. Temperature dependence of the electrical resistivity $\rho(T)$ (a), specific heat $C(T)/T$ ((b), left axis) and dc magnetization $M(T)$ ((b), right axis) for LaNiC$_2$. The electrical resistivity and specific heat are measured at zero field, and the magnetization is measured at 10 Oe (ZFC).

magnetization ($T_c^M = 2.95 \pm 0.15$ K), are slightly lower than the resistive $T_c^\rho$, which is likely due to the residual sample inhomogeneity. It is noted that the magnetization $M(T)$ exhibits temperature-independent Pauli-paramagnetic behavior above $T_c$, ruling out any visible magnetic impurity in our samples. Furthermore, the above physical quantities were measured on different samples cut from the same batch; the consistent experimental results and fitting parameters, as shown below, again indicate a good sample quality. Based on the RRR value and the width of the superconducting transition, our samples have a quality better than or compatible with the best samples reported in the literature [26, 27].

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Figure 3. Temperature dependence of the penetration depth $\Delta \lambda(T)$ at low temperatures for LaNiC$_2$. The solid and dashed lines represent the fits of two-gap and one-gap BCS models to the experimental data, respectively. The dotted line shows a fit of $\Delta \lambda(T) \sim T^2$. Inset (a) plots $\Delta \lambda(T)$ in the full temperature range of our measurement. Inset (b) shows $\Delta \lambda(T)$ versus $T^{3.7}$ in the temperature range of $0.35 \, \text{K} \leq T \leq 1 \, \text{K}$.

3.2. London penetration depth

The London penetration depth is an important superconducting parameter. The TDO-based technique can accurately measure the temperature dependence of the resonant frequency shift $\Delta f(T)$, which is proportional to the changes of the penetration depth, i.e. $\Delta \lambda(T) = G \Delta f(T)$. Here the $G$ factor is a constant that is solely determined by the sample and coil geometries [34]. Figure 3 presents the temperature dependence of the penetration depth $\Delta \lambda(T)$ for LaNiC$_2$, where $G = 11 \, \text{Å Hz}^{-1}$. In the inset (a), $\Delta \lambda(T)$ is plotted over the full temperature range of our measurement, from which a sharp superconducting transition is observed at $T_c = 2.85 \pm 0.3 \, \text{K}$. In the main figure of figure 3, we show $\Delta \lambda(T)$ at low temperatures, along with the fits of quadratic temperature dependence (dotted line), one-gap (dashed line) and two-gap BCS models (solid line). For an isotropic one-gap BCS model, the penetration depth at $T \ll T_c$ is given by

$$\Delta \lambda(\Delta_0, T) \approx \lambda_0 \sqrt{\frac{\pi \Delta_0}{2T}} e^{-\frac{\Delta_0}{T}}$$  \hspace{1cm} (1)

where $\lambda_0$ and $\Delta_0$ are the penetration depth and energy gap at $T = 0$, respectively.

One can see from figure 3 that the penetration depth at low temperatures cannot be fitted by a quadratic temperature dependence which is expected for SCs with point nodes. Instead, it can be illustrated by either a power-law behavior with a large exponent $n$, i.e. $\Delta \lambda \sim T^n$ ($n \simeq 3.7$, inset(b)), or one-gap BCS-like exponential behavior with a small gap of $\Delta_0 \simeq 1.25T_c$.
(main figure) at temperatures below 0.95 K. It is noted that the values of \( n \) and \( \Delta_0 \) may depend on the fitting temperature region. Such behavior usually characterizes multiband superconductivity. In the following, we will analyze the penetration depth, \( \Delta \lambda(T) \), and its corresponding superfluid density, \( \rho_s(T) \), in terms of the phenomenological two-gap BCS model, which are further supported by the specific heat and the upper critical field (see below).

According to the phenomenological two-gap BCS model, which has been successfully applied to MgB\(_2\) [30], the superfluid density \( \rho_s(T) \) can be expressed as

\[
\tilde{\rho}_s(T) = x \rho_s(\Delta^1, T) + (1-x) \rho_s(\Delta^2, T),
\]

where \( x \) is the relative weight for \( \Delta^1 \). The normalized superfluid density for each band is given by

\[
\rho_s(\Delta, T) = 1 - \frac{2}{\pi} \int_{0}^{\infty} f(\epsilon, T) \cdot [1 - f(\epsilon, T)] \, d\epsilon,
\]

where \( f(\epsilon, T) = (1 + e^{\epsilon^2 + \Delta(T)/T})^{-1} \) is the Fermi distribution function. Here we adopt the following temperature dependence of the gap function [35]:

\[
\Delta(T) = \Delta_0 \tanh \left[ \frac{\pi T_c}{\Delta_0} \sqrt{\frac{\Delta_C}{\epsilon_c} \left( \frac{T_c}{T} - 1 \right)} \right],
\]

where \( \Delta_C \) denotes the specific heat jump at \( T_c \) and \( a = 2/3 \).

In the low-temperature limit (\( T \ll T_c \)), one can derive the expression of the penetration depth for a two-gap BCS SC from equation (2) provided that the two energy bands possess the same value of \( \lambda_0 \), which can be written as

\[
\tilde{\Delta} \lambda(T) = x \Delta \lambda(\Delta^1_0, T) + (1 - x) \Delta \lambda(\Delta^2_0, T).
\]

In NCS SCs, the spin degenerate band may be split by the ASOC effect, and the resulting bands have the same penetration depth at zero temperature. Thus, one may fit the experimental data with the above expression if this is the case. In figure 3(c), one can see that the experimental penetration depth, \( \Delta \lambda(T) \), can be well described by the two-gap BCS model. The so-derived parameters of \( \Delta_0^1, \Delta_0^2 \) and \( x \) are highly consistent with those obtained from the superfluid density, \( \rho_s(T) \), and specific heat, \( C_c(T) \) (see below). This indicates that the low-temperature penetration depth is indeed compatible with the scenario of two-gap superconductivity originating from the ASOC effect. It is pointed out that, at sufficiently low temperatures, the small gap of a two-gap BCS SC becomes dominant on the penetration depth. A fit of the low-temperature penetration depth by the one-gap BCS model may provide a good estimation of the small gap. Indeed, the so-derived gap value of \( \Delta_0 = 1.25 \, T_c \) at \( T < 0.95 \, K \) is close to the small gap \( \Delta^2_0 \) as shown in table 1. The slightly enhanced gap is due to the non-negligible contributions of the large gap in this temperature range.

In figure 4, we plot the superfluid density \( \rho_s(T) \) converted from the penetration depth by \( \rho_s(T) = [\lambda_0/\lambda(T)]^2 \), where \( \lambda(T) = \lambda_0 + \Delta \lambda(T) \). The parameter, \( \lambda_0 \approx 3940 \, \text{Å} \), is estimated from \( \lambda_0 = \frac{1}{\Delta T_c} \sqrt{\frac{\Phi_0 B_{c2}^{c}(0)}{24 \gamma_n}} \), as derived from both the BCS and Ginzburg–Landau theories for a type-II SC [35]. Here we take the experimental values of \( T_c = 2.75 \, K \), \( B_{c2}^{c}(0) \approx 0.48 \, T \) and \( \gamma_n = 7.7 \, \text{mJ} \, \text{mol}^{-1} \, \text{K}^{-2} \) directly from our specific heat measurements (see below), and \( \Phi_0 \) is the flux quantum. Indeed, the superfluid density \( \rho_s(T) \) can be well fitted by the two-gap BCS model (solid line); the fitting parameters are listed in table 1. The individual contribution to

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Table 1. Fitting parameters of the two-gap BCS model obtained from the penetration depth $\Delta \lambda(T)$, the superfluid density $\rho_s(T)$ and the electronic specific heat $C_e(T)$ data.

| $\Delta \lambda(T)$ | $\Delta_1/\Delta_2$ | $\rho_s$ | $C_e$ |
|---------------------|---------------------|----------|-------|
| 2.0                 | 1.1                 | 0.72     | 2.0   |
| 2.0                 | 1.2                 | 0.70     | 2.2   |
| 2.2                 | 1.2                 | 0.76     |       |

Figure 4. Temperature dependence of the superfluid density $\rho_s(T) = [\lambda_0/\lambda(T)]^2$. The solid line represents the fit of a two-gap BCS model. The dashed-dotted lines present the respective contributions to $\rho_s(T)$ from the two superconducting gaps of $\Delta_1$ and $\Delta_2$. The inset shows $\rho_s(T)$ from [26] with $\lambda_0 = 1230$ and 3940 Å, together with a fit of a two-gap BCS model (solid line).

the total superfluid density $\rho_s(T)$ from the respective order parameters $\Delta_1$ and $\Delta_2$ is shown in figure 4; the large gap has a dominant contribution. For comparison, we replot $\rho_s(T)$ from [26] in the inset of figure 4 which are converted from the penetration depth data by using $\lambda_0 = 1230$ and 3940 Å. It is noted that $\lambda_0 = 1230$ Å, derived in [26], is largely underestimated due to the use of an inaccurate upper critical field of $B_{c2}(0) = 0.125$ T in their calculations. The superfluid density $\rho_s(T)$ from [26] is in reasonable agreement with our data if $\lambda_0 = 3940$ Å is applied. Furthermore, one can also fit its superfluid density $\rho_s(T)$ by the two-gap BCS model at temperatures above 0.5 K. The derived parameters of $\Delta_1 = 1.9 \ T_c$, $\Delta_2 = 0.72 \ T_c$ and $x = 0.73$ are again compatible with our results. As a first approximation, two-gap-like superconductivity is expected in NCS SCs with a moderate ASOC strength, in which the spin degenerate bands are split by the ASOC, but the triplet component is not yet dominant. Nevertheless, it is still possible that a weak linear term of $\Delta \lambda(T)$ may develop at very low temperatures as seen in $Y_2C_3$ [19]. At present, we cannot exclude such a possibility in LaNiC$_2$ as argued in [26]. It is noted that the discrepancy between our TDO data and those reported in [26] at low temperatures.
Figure 5. Temperature dependence of the specific heat at zero field for LaNiC$_2$. The upper inset shows the total specific heat $C(T)/T$ and its polynomial fit of $C(T) = \gamma_n T + B_3 T^3 + B_5 T^5 + B_7 T^7$. The main figure plots the electronic specific heat $C_e(T)/T$ after subtracting the phonon contributions. The lower inset expands the low-$T$ section. The solid, dotted and dashed lines present fits of the two-gap BCS model, the conventional BCS model and the quadratic temperature dependence, respectively.

is unlikely to be caused by the impurity scattering because all the studied samples bear similar qualities. Furthermore, a coherence length of $\xi_0 \approx 26$ nm and a mean free path of $l \approx 200$ nm are estimated from our experimental data of $\rho_0 = 6 \mu \Omega \text{cm}$, $T_c = 2.75$ K, $B_{c2}(0) = 0.48$ T and $\gamma_n = 7.7$ mJ mol$^{-1}$ K$^{-2}$, indicating that our samples are in the clean limit. Thus, more precise measurements of the penetration depth at lower temperatures are desired to resolve this issue.

3.3. Specific heat

In the upper inset of figure 5, we plot the total specific heat $C(T)$ as a function of temperature for LaNiC$_2$, which was obtained after subtracting the addenda contributions from the raw data. At temperatures above $T_c$ ($3.5 \text{ K} \leq T \leq 20 \text{ K}$), $C(T)$ follows a polynomial expansion of $C(T) = \gamma_n T + B_3 T^3 + B_5 T^5 + B_7 T^7$, in which $C_e = \gamma_n T$ and $C_{ph} = B_3 T^3 + B_5 T^5 + B_7 T^7$ represent the electronic and phonon contributions, respectively. This yields the Sommerfeld coefficient in the normal state, $\gamma_n = 7.7$ mJ mol$^{-1}$ K$^{-2}$, and the Debye temperature $\Theta_D = 450$ K, the latter being derived from $B_3 = N \pi^4 R \Theta_D^{-3} 12/5$, where $R = 8.314$ J mol$^{-1}$ K$^{-1}$, $N = 4$ and $B_3 = 0.085$ mJ mol$^{-1}$ K$^{-4}$. The small value of $\gamma_n$ indicates the weak electronic correlations in LaNiC$_2$. The specific heat jump at $T_c$, i.e. $\Delta C/\gamma_n T_c = 1.05$, is lower than the BCS value of 1.43, which might arise from the multi-gap structure as seen in MgB$_2$ or the gap anisotropy [32].

In the superconducting state, the total heat capacity $C$ is the sum of a $B$-dependent electronic contribution $C_e$, a $B$-independent lattice contribution $C_{ph}$ and a small $B$-dependent Schottky contribution $C_{Sch}$. We obtained the electronic specific heat $C_e$ by subtracting the
B-independent phonon contribution $C_{\text{ph}}$ and the $B$-dependent $C_{\text{Sch}}$ using the following two methods. The first one is to directly subtract the phonon contribution of $C_{\text{ph}}$ from the total heat capacity by

$$C_e(B, T) = C(B, T) - C_{\text{ph}}(T).$$

In the second method, we calculate the electronic specific heat $C_e$ in the superconducting state by using the reference value at $B = 1$ T where superconductivity is suppressed [32], i.e.

$$C_e(B, T) = C(B, T) - C(1 \ T, T) + \gamma_n(1 \ T) T.$$  

Indeed, both methods give nearly identical results of $C_e$ at $T < T_c$, indicating that the $B$-dependent $C_{\text{Sch}}$ is negligible in the temperature and magnetic field ranges of our measurements. In the following, we will present the electronic specific heat $C_e(T)$ derived from equation (6).

For a system of independent fermion quasiparticles, the entropy can be calculated by [31]

$$\frac{S(\Delta, T)}{\gamma_n T_c} = -\frac{6}{\pi^2} \int_0^\infty f(\epsilon, T) \times \ln f(\epsilon, T) + [1 - f(\epsilon, T)] \times [\ln[1 - f(\epsilon, T)] \ d\epsilon.$$  

In the case of a two-gap SC, the entropy expression can be generalized as follows [31]:

$$S(T) = x S(\Delta^1, T) + (1 - x) S(\Delta^2, T).$$  

Differentiation of equation (8) gives the total electronic specific heat $C_e$ in the superconducting state, i.e., $C_e(T) = T dS(T)/dT$. In figure 5, we plot the electronic specific heat $C_e(T)/T$ of LaNiC$_2$ at zero field, together with the fits of the conventional BCS model, the two-gap BCS model and the quadratic temperature dependence for the case of point nodes. One can see that the two-gap BCS model can well describe the experimental data over a wide range from the base temperature up to $T_c$. On the other hand, either the conventional BCS model or the quadratic temperature dependence shows significant deviations from the experimental data at low temperatures. Fits of the two-gap BCS model to the specific heat data give the following parameters: $\Delta_1^0 = 2.2 T_c$, $\Delta_2^0 = 1.2 T_c$ and $x = 0.76$ for $\Delta_0^0$, which are remarkably consistent with those obtained from the penetration depth $\Delta\lambda(T)$ and the superfluid density $\rho_s(T)$ (see table 1). It is noted that the specific heat $C_e(T)$ digitalized from [27] overlaps perfectly with our data in the entire temperature range (not shown). However, the experimental data clearly deviate from the fit of $C_e \sim T^3$ at $T < 0.6 \ K$ (see the lower inset), which was previously shown in [27]. For a two-gap SC, the interband coupling ensures that the two gaps open at the same $T_c$. Usually, the main contributions to both the electronic specific heat $C_e$ and the superfluid density $\rho_s$ stem from the larger gap $\Delta^1$ at temperatures just below $T_c$, but the physical behavior can be modified at lower temperatures attributed to the opening of a smaller gap $\Delta^2$.

In figure 6, the temperature dependence of the electronic specific heat $C_e(T)/T$ is shown at various magnetic fields for LaNiC$_2$. Obviously, the superconducting transition is shifted to lower temperatures, and becomes broadened with increasing magnetic field, resembling that of the two-gap SC, MgB$_2$ [32]. The inset in figure 6 describes the specific heat near the upper critical field in detail. One can see that the superconducting transition still exists at $B = 0.4$ T but vanishes at $B = 0.55$ T. This suggests a bulk upper critical field of $B_c^c(0) < 0.55$ T, which is much lower than the resistive upper critical field ($B_c^r(0) \approx 1.67$ T, see below). The underlying reason for such a discrepancy remains unclear. Similar observations were also made for other unconventional SCs. For instance, the heavy fermion CeIrIn$_5$ shows a much larger resistive
Temperature dependence of the electronic specific heat $C_e(T)/T$ at various magnetic fields for LaNiC$_2$. The dashed horizontal line represents $\gamma_n$. The magnetic field increases along the arrow direction. The inset shows the electronic specific heat $C_e(T)/T$ at magnetic fields near $B_{c2}(0)$.

$T_c$ ($\approx 1.3$ K) than the bulk $T_c$ ($\approx 0.4$ K), resulting in a large difference in the corresponding upper critical fields [36].

The residual Sommerfeld coefficient in the superconducting state, $\gamma(0)(B)$, which describes the low-energy quasiparticle excitations, provides important insights into the superconducting pairing symmetry. In fully gapped BCS SCs, the low-lying excitations are usually confined to the vortex cores and the specific heat is, therefore, proportional to the vortex density which increases linearly with increasing magnetic field, i.e. $\gamma(0)(B) \propto B$ [38]. On the other hand, for a highly anisotropic or gapless SC, the quasiparticle excitations can spread outside the vortex cores, which can, in fact, significantly contribute to the specific heat at low temperatures. The local supercurrent flow may give rise to a shift on the excitation energy (Doppler shift), resulting in a distinct magnetic field dependence of the density of state, $N(E_F)$, at the Fermi energy. In SCs with line nodes, Vologik showed that $N(E_F) \propto B^{1/2}$, leading to a square-root field dependence of the residual Sommerfeld coefficient, i.e. $\gamma(0)(B) \propto B^{1/2}$ [39]. In figure 7, we present the normalized Sommerfeld coefficient, $\gamma(0)(B)/\gamma_n$, as a function of $B/B_{c2}(0)$ for LaNiC$_2$ ($B_{c2}(0) = 0.48$ T from our specific heat data, see below). Here the values of $\gamma(0)(B)$ are determined at $T = 0.35$ K after subtracting the small non-zero fraction at zero magnetic field. One can see that $\gamma(0)(B)$ of LaNiC$_2$ shows a fast increase at low fields and then saturates with increasing magnetic field, clearly deviating from the linear field dependence expected for a conventional BCS SC-like Nb$_{77}$Zr$_{23}$ (squares) [37], and also from the square-root field dependence expected for a nodal SC (solid line). The curvature of $\gamma(0)(B)$ is rather similar to that of the prototypical two-gap SC, MgB$_2$ [32], and also the residual thermal conductivity $\kappa_0/T$ of the multiband SC, PrRu$_4$Sb$_{12}$ [40], providing another important evidence of two-gap superconductivity for LaNiC$_2$. 
3.4. Electrical resistivity and upper critical field

Figure 8 shows the temperature dependence of the electrical resistivity $\rho(T)$ at various magnetic fields ($B = 0$–1.5 T) for LaNiC$_2$. The superconducting transition is eventually suppressed, and the transition width is slightly broadened upon applying a magnetic field. The temperature dependence of the upper critical field $B_{c2}(T)$ is plotted in the inset of figure 9, in which $T_c$ is
For comparison, in figure 9 we show the normalized upper critical field, $B_{c2}/[T_c(dB_{c2}/dT)_T]$, versus $T/T_c$ for several representative SCs, i.e. LaNiC$_2$ (this study), MgB$_2$ [33] and Li$_2$Pt$_3$B [41]. One can see that the upper critical fields $B_{c2}(T)$ of LaNiC$_2$, derived from both the specific heat (stars) and the resistivity (squares), follow the same scaling behavior even though the corresponding $T_c$ is different. The dotted line shows the fits of the $B_{c2}(T)$ data to the Werthamer–Helfand–Hohenberg (WHH) theory for LaNiC$_2$ [42]. A clear deviation is observed at low temperatures, and the experimental value of $B_{c2}(0)$ exceeds that of the WHH predictions. A positive curvature of $B_{c2}(T)$ near $T_c$ and the enhancement of $B_{c2}(0)$ are typical features of multi-gap SCs, arising from the contributions of the small gap at low temperatures. Indeed, the upper critical field $B_{c2}(T)$ of LaNiC$_2$ remarkably resembles that of the prototype two-band SC MgB$_2$ [33]. The upper critical field value is estimated to be $B_{c2}^P(0) \approx 1.67$ T from the electrical resistivity and $B_{c2}^{C_p}(0) \approx 0.48$ T from the specific heat. In any case, $B_{c2}(0)$ for LaNiC$_2$ is well below the Pauli paramagnetic limit of $B_{c2}^P(0) = 1.86T_c \approx 6$ T, indicating an orbital pair-breaking mechanism for LaNiC$_2$.

4. Discussion

As described above, two-gap BCS superconductivity in LaNiC$_2$ has been evidenced from the penetration depth $\Delta \lambda(T)$, the electronic specific heat $C_e(T)$, the residual Sommerfeld

Figure 9. Normalized upper critical field, $B_{c2}/[T_c(dB_{c2}/dT)_T]$, versus $T/T_c$ for LaNiC$_2$ (this work), MgB$_2$ [33] and Li$_2$Pt$_3$B [41]. Here the upper critical fields for LaNiC$_2$ are taken from the middle point of the resistive drops (■) and the specific heat jumps (★) at $T_c$. The dotted line shows the fittings of the WHH method. Inset: the resistive upper critical field $B_{c2}$ versus $T$ for LaNiC$_2$.
coefficient $\gamma_0(B)$ and the upper critical field $B_{c2}(T)$. Such a pairing state can be qualitatively interpreted in terms of the ASOC effect as argued in many NCS SCs. In LaNiC$_2$, calculations of the electronic structure based on the first-principles full-potential linearized augmented plane-wave method gave a band splitting of 3.1 mRyd [43], which is small in comparison with the heavy fermion NCS SCs and also Li$_2$Pt$_3$B (see table 2). Then the ASOC only has a moderate effect on the pairing state; both the spin-singlet and spin-triplet components may have comparable contributions to the pairing state, naturally leading to the behavior of two-gap-like superconductivity. On the other hand, analyses of the recent $\mu$SR experiments indicate that only the spin-triplet state with a non-unitary character is compatible with the observation of time-reversal symmetry breaking in LaNiC$_2$ [28, 29]. In this case, the spin-up and spin-down bands may develop different pairing potentials at $T_c$ spontaneously, leading to distinct superconducting gaps and, thus, giving rise to two-gap behavior. However, a pure triplet pairing state would be contradictory to the observation of a coherence peak below $T_c$ in the NQR-measurements [24], and further experiments are still needed to clarify this scenario. Furthermore, we also cannot exclude the possibility that LaNiC$_2$ may share the same mechanism of two-gap superconductivity as MgB$_2$. To confirm this, one needs to identify two distinct types of bands in LaNiC$_2$ which are not very obvious but cannot be ruled out from the band structures shown in [25, 43]. Also, a model with an anisotropic energy gap might fit the temperature dependence of the penetration depth, superfluid density and even specific heat data. However, with such a model it is difficult to describe the field dependence of $\gamma_0(B)$.

In the following, we will present a brief overview on the properties of NCS SCs (see table 2). The heavy fermion systems typically possess a sizeable spin–orbit coupling which results in a large band splitting too. In these compounds, an extremely large upper critical field $B_{c2}(0)$, well exceeding the paramagnetic limit, and evidence of a dominant spin-triplet pairing state with line nodes in the superconducting energy gap have been observed in the Ce-based materials [8–10, 12, 13]. These unconventional superconducting properties can be qualitatively described in terms of the ASOC effect [3–7], even though the strong electronic correlations and magnetism existing in these compounds may complicate the interpretation. Li$_3$(Pd$_{1-x}$Pt$_x$)$_3$B provides a model system to study the ASOC effect on superconductivity in the absence of inversion symmetry [15]. In Li$_2$Pd$_3$B, various measurements have demonstrated BCS-like superconductivity [15–18]. With increasing Pt concentration, which corresponds to an increase of the ASOC strength, the spin-triplet component eventually grows, showing spin-triplet superconductivity in Li$_2$Pt$_3$B [15–17].

In recent years, a growing number of NCS SCs have been discovered, showing more diverse properties. For example, BaPtSi$_3$ [51], Re$_3$W [52] and Ir$_2$Ga$_9$ [53], in which a strong ASOC is expected from their large atomic numbers, demonstrate conventional s-wave superconductivity. On the other hand, two-gap superconductivity has been shown in Y$_2$C$_3$ [19], La$_2$C$_3$ [20], Mg$_{10}$Ir$_{10}$B$_{16}$ [21], BiPd [49, 50] and LaNiC$_2$ (this work). In Y$_2$C$_3$, evidence of line nodes was noticed in the low-temperature limit, even though the ASOC is weak in this compound [19]. According to the available experiments, we are, besides Li$_2$Pt$_3$B, still short of examples showing spin-triplet superconductivity in NCS compounds with weak electron correlations. The ASOC may enhance the upper critical field which can nicely explain the extremely large value of $B_{c2}(0)$ and its anisotropy in the heavy fermion NCS SCs [12, 13, 54]. However, in the weakly correlated NCS SCs like Li$_2$Pt$_3$B [41] and BaPtSi$_3$ [51], $B_{c2}(0)$ is rather small even though the ASOC is strong in these compounds. Moreover, the upper critical field $B_{c2}(T)$ of Li$_2$(Pd$_{1-x}$Pt$_x$)$_3$B behaves similarly at different doping concentrations.
Table 2. Superconducting parameters in some major NCS SCs. Since the ASOC strength is expected to be proportional to the square of the atomic numbers for atoms on the NCS crystalline sites, we assign the band splitting $E_{\text{ASOC}}$ with ‘large’ or ‘small’ by their atomic numbers in case no band structure calculations are available.

| Material      | Space group | $T_c$ (K) | $B_{c2}(0)$ (T) | $\gamma_0$ (mJ mol$^{-1}$ K$^{-2}$) | $E_{\text{ASOC}}$ | Pairing state |
|---------------|-------------|-----------|-----------------|------------------------------------|-------------------|---------------|
| CePt$_3$Si    | $P4mm$      | 0.75      | 3.2($||c$), 2.7($\perp c$) | 390                                | 200 meV           | $s + p$       |
| CeIrSi$_3$    | $I4mm$      | 1.6       | 45($||c$), 11($\perp c$) | 100                                | 4 meV             | Triplet       |
| CeRhSi$_3$    | $I4mm$      | 1.05      | 30($||c$), 7($\perp c$)  | 110                                | 10 meV            | Triplet       |
| Li$_2$Pt$_3$B | $P4_132$    | 2.6       | 1.9             | 7                                  | 200 meV           | Triplet       |
| Li$_2$Pd$_3$B | $P4_132$    | 7.6       | 6.2             | 9                                  | 30 meV            | s-wave        |
| LaNiC$_2$     | $Amm2$      | 2.75      | 1.67            | 7.7                                | 42 meV            | Two-gap       |
| Y$_2$C$_3$    | $I4_3d$     | 16        | 29              | 6.3                                | 15 meV            | Two-gap       |
| La$_2$C$_3$   | $I4_3d$     | 13.2      | 19              | 10.6                               | 30 meV            | s-wave        |
| Mg$_{10}$Ir$_{10}$B$_{16}$ | $I4_3m$ | 5         | 0.77            | 52.6                               | Large             | Two-gap       |
| BiPd          | $P2_1$      | 3.8       | 0.8($||b$)      | 4                                  | Large             | Two-gap       |
| BaPtSi$_3$    | $I4mm$      | 2.25      | 0.05            | 5.7                                | Large             | s-wave        |
| Re$_3$W       | $I4_3m$     | 7.8       | 12.5            | 15.9                               | Large             | s-wave        |
| Ir$_2$Ga$_9$  | $Pc$        | 2.25      | 0.025           | 6.9                                | Large             | s-wave        |
| Rh$_2$Ga$_9$  | $Pc$        | 1.95      | type-I          | 7.9                                | Small             | s-wave        |
| Mo$_3$Al$_2$C | $P4_132$    | 3.3       | 1.7($||c$), 1.6($\perp c$) | 43.7                                | Small             | s-wave        |
| Ru$_7$B$_3$   | $P6_3mc$    | 3.3       | 1.7($||c$), 1.6($\perp c$) | 43.7                                | Nodal SC          |

and can be scaled by the corresponding $T_c$ [41]. In contrast, a large upper critical field $B_{c2}(0)$ is observed in Y$_2$C$_3$ [19], La$_2$C$_3$ [20] and Mo$_3$Al$_2$C [55]. In order to elucidate the nature of superconductivity in NCS compounds, a systematic study, both experimental and theoretical, remains highly desirable.

5. Conclusion

In summary, we have systematically measured the low-temperature London penetration depth, specific heat and electrical resistivity in order to probe the superconducting order parameter in the weakly correlated, NCS SC LaNiC$_2$. It was found that both the penetration depth $\Delta \lambda(T)$ and the electronic specific heat $C_e(T)$ show behavior at low temperatures that can be best fitted by a two-gap BCS model. The upper critical field $B_{c2}(T)$ is enhanced at low temperatures, as a result of the contributions from the small superconducting gap. The residual Sommerfeld coefficient, $\gamma_0(B)$, increases rapidly at low fields, and eventually gets saturated with further increasing magnetic field. All these experimental facts provide unambiguous evidence of two-gap superconductivity for LaNiC$_2$. We argue that such a superconducting state might arise from the moderate ASOC strength as a result of lacking inversion symmetry in LaNiC$_2$, even though other possibilities cannot be completely ruled out for the moment.
Acknowledgments

We acknowledge valuable discussions with M Sigrist, D F Agterberg, E Bauer and M B Salamon. This work was supported by the National Basic Research Program of China (grant numbers 2009CB929104 and 2011CBA00103), the Natural Science Foundation of China (grant number 10934005), Zhejiang Provincial Natural Science Foundation of China, the Fundamental Research Funds for the Central Universities and the Max-Planck Society under the auspices of the Max-Planck partner group of the MPI for Chemical Physics of Solids, Dresden.

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New Journal of Physics 15 (2013) 053005 (http://www.njp.org/)