Nodal gap structure in the noncentrosymmetric superconductor LaNiC$_2$ from magnetic-penetration-depth measurements

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Abstract. We report measurements of the temperature dependence of the magnetic penetration depth in different-quality polycrystalline samples of noncentrosymmetric LaNiC$_2$ down to 0.05 K. This compound has no magnetic phases and breaks time-reversal symmetry. In our highest-quality sample, we observe a $T^2$ dependence below 0.4$T_c$, indicative of nodes in the energy gap. We argue that previous results suggesting conventional s-wave behavior may have been affected by magnetic impurities.

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1. Introduction

Noncentrosymmetric superconductors have gained in interest since the discovery of superconductivity in CePt$_3$Si [1]. The absence of inversion symmetry leads to the indistinguishability of spin-singlet and spin-triplet states and to the appearance of an antisymmetric spin–orbit coupling (ASOC) that splits the electron bands by lifting the spin degeneracy. Thus unusual superconducting properties have been expected in all these materials, although to date such properties have been observed only in a small group: CePt$_3$Si [2, 3], Li$_2$Pt$_3$B [4, 5], CeIrSi$_3$, CeRhSi$_3$, CeCoGe$_3$ and CeIrGe$_3$ [6–8]. With the notable exception of Li$_2$Pt$_3$B, in this group superconductivity appears inside an antiferromagnetic order and mostly around a quantum critical point. This suggests that the unusual behavior may originate from the interplay of antiferromagnetic interaction and ASOC [9, 10].

Nonmagnetic LaNiC$_2$ is an intriguing noncentrosymmetric superconductor [11] in which both unconventional and conventional behavior has been uncovered. Unconventional characteristics were found in early specific-heat measurements [11] that showed a low-temperature $T^3$ dependence expected when the energy gap has nodes and in recent muon-spin-relaxation results [12] that suggested the lack of time-reversal symmetry (TRS). Nuclear quadrupole resonance (NQR)-1/T$_1$ [13] and recent specific-heat [14] data were interpreted in terms of conventional BCS superconductivity. On the other hand, theoretical approaches [9, 10, 15] imply that LaNiC$_2$ should behave like a conventional superconductor. The fact that LaNiC$_2$ is nonmagnetic and has a relatively strong ASOC [16] makes the determination of its pairing symmetry important for the understanding of the physics of noncentrosymmetric superconductors. Moreover, the symmetry of the order parameter of LaNiC$_2$ may be relevant for superconductivity in general, because (a) in the absence of inversion symmetry only some spin-triplet states are allowed [17], (b) in the absence of TRS spin-singlet states are forbidden and (c) TRS is required by the presence of ASOC [17].

The conflicting experimental results in LaNiC$_2$ may have been caused by the poor quality of the samples and the not-so-low temperatures of the experiments. It is known that in order to determine energy gap structures from thermodynamic and transport properties, temperatures below 0.3$T_c$ are needed. Here, we present measurements of the magnetic penetration depth $\lambda(T)$ in different quality samples of LaNiC$_2$ down to 50 mK ($\sim 0.017T_c$). Penetration depth is well recognized as a unique probe of the structure and symmetry of the superconducting order parameter. In our highest-quality sample, we found that $\lambda(T) \propto T^2$ as $T \rightarrow 0$, which suggests the existence of nodes in the energy gap.

2. Experimental methods

LaNiC$_2$ crystallizes in the orthorhombic CeNiC$_2$-type structure with space group Amm2 [11]. We studied four different polycrystalline samples (labeled A, B, C and D) prepared by arc melting suitable amounts of La (99.9%, Ames Lab), C (99.9995%, Alpha Aesar) and Ni in two degrees of purity. Samples A and B were prepared with 99.9% Ni (40 ppm of Fe, Alpha Aesar) and samples C and D with 99.995% Ni (13 ppm of Fe, Alpha Aesar). Samples B and D were then sealed under argon in quartz tubes and annealed at 1273 °C for 10 days and finally water quenched to room temperature. To check for impurity phases in the samples, we carried out powder x-ray diffraction measurements using a microcomputer-controlled MXP3 diffractometer.
Figure 1. Room-temperature powder x-ray diffraction patterns for our LaNiC$_2$ samples prepared with (a) 99.9% Ni and (b) 99.995% Ni.

with graphite monochromated Cu Kα radiation. Annealed samples B and D displayed sharp diffraction lines and no additional reflections (see the upper spectra in figure 1), which is taken as evidence of single phases. In contrast, as-cast samples A and C showed additional reflection lines (see the lower spectra in figure 1) corresponding to the secondary phases LaC$_2$ and La$_2$Ni$_5$C$_3$. In samples A, B and C the transition temperature $T_c \approx 3.6$ K, whereas in sample D $T_c \approx 3$ K.

Penetration-depth measurements were carried out utilizing a 14 MHz tunnel diode oscillator. The deviation of the penetration depth $\lambda(T)$ from its value at the lowest measured temperature, $\Delta \lambda(T) = \lambda(T) - \lambda(0.05 \text{ K})$, was obtained up to $T \sim 0.99T_c$ from the corresponding change in the measured resonance frequency $\Delta f(T) = G \Delta \lambda(T)$. Here $G$ is a constant factor that depends on the sample and coil geometries and that includes the demagnetizing factor of the sample. We estimated $G$ by measuring a sample of known behavior and of the same dimensions as the test sample [18]. To within this calibration factor, $\Delta \lambda(T)$ is raw data.

We note here that the low-temperature dependence of $\lambda(T)$ does not seem to be affected by the sample type (single crystal, polycrystal, etc) [3, 19]. In any case, intergrain or proximity effects are not expected to be relevant in the present results, because the measuring magnetic field is very small (about 5 mOe) [20]. For comparison, we measured a pure (99.999%) polycrystalline sample of the s-wave superconductor In ($T_c = 3.4$ K). Intergranular susceptibility normally saturates at low temperatures.
Figure 2. Low-temperature $\Delta \lambda(T)$ of samples A and B. The upturns below $0.2T_c$ are due to a contribution coming from Fe impurities in the samples. Inset: EPR spectra at different temperatures for sample B that clearly indicate the presence of interstitial $\text{Fe}^{3+}$. $g_{\parallel}$ and $g_{\perp}$ are the parallel and perpendicular components of the $g$-factor, respectively.

3. Results and discussion

Figure 2 displays the low-temperature region of $\Delta \lambda(T)$ of samples A and B. Both curves have an upturn below $0.2T_c$ that in polycrystalline samples is usually caused by the competition between the superconducting screening effect and the magnetic permeability (whose thermal response is due to magnetic-impurity effects) [21]. To check for the presence of magnetic impurities in samples A and B, we performed EPR spectroscopy at 100 and 300 K. In both samples the spectra indicate the presence of interstitial $\text{Fe}^{3+}$ in the orthorhombic structure of LaNiC$_2$ (see the spectra of sample B in the inset of figure 2). Thus, the upturns in the penetration-depth data of these samples could indeed be produced by magnetic impurities. Previous measurements in LaNiC$_2$ samples prepared with 99.9% Ni, i.e. similar to samples A and B, were carried out with probes sensitive to magnetic impurities and were thus most probably affected by the $\text{Fe}^{3+}$ impurities. Notably, the results of all these measurements—$1/T_1$-NQR [13], magnetization and heat capacity [14]—point to conventional BCS behavior.

Figure 3(a) shows $\Delta \lambda(T)/\Delta \lambda_0$ of sample C, sample D and indium. The data were scaled by the corresponding total penetration depth shift $\Delta \lambda_0$ so as to compare them. The superconducting transitions in these LaNiC$_2$ samples are quite broad compared with that in indium. Similar wide transitions are seen in samples A and B. The broadness is different from sample to sample, which suggests that the wide transitions in LaNiC$_2$ are due to defects or high inhomogeneity.

Figure 3(b) depicts the low-temperature region of $\Delta \lambda(T)$ of samples C and D along with that of indium. No upturn is observed in these samples of LaNiC$_2$, prepared with the purest Ni (99.995%), which could imply that the level of Fe impurities is so small as to affect significantly the superconducting properties. In samples C and D, the low-temperature magnetic penetration
Figure 3. (a) Normalized $\Delta\lambda(T)$ against $T/T_c$ of samples C and D and of conventional indium. (b) Close-up of the low-temperature region showing that LaNiC$_2$ data follow a power law instead of an exponential behavior (as the indium data do). Inset: low-temperature data plotted as a function of $(T/T_c)^2$, where $\Delta\lambda(T) \propto T^2$ is observed below $0.4T_c$ in sample D.

depth goes as $T^n$, with $n \sim 2$–2.4, as opposed to the clearly different exponential behavior observed in the sample of fully gapped superconductor indium (see the figure). The inset to figure 3(b) displays $\Delta\lambda(T)$ versus $(T/T_c)^2$ for samples C and D in the temperature region $T \leq 0.55T_c$. Clearly, $\Delta\lambda(T) \propto T^2$ up to about $0.4T_c$ in sample D. Since the annealed sample D has the sharpest transition and the smallest exponent $n$ in a larger temperature region, we consider the result in this sample to be closest to the true superconducting behavior in LaNiC$_2$.

A $T^2$ dependence of $\lambda(T)$ at the lowest temperatures would only result if the superconducting energy gap has nodes or conventional gapless superconductivity occurs (due to strong scattering effects) [22]. We note that $\Delta\lambda(T) \propto T^2$ is the limiting behavior of gapless superconductivity under impurity scattering; thus the fact that we see a higher exponent $n$ in somewhat lower quality samples would rule out gapless superconductivity. Moreover, gapless

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superconductivity leads to linear temperature behavior in the electronic specific heat $C_e$ and the NMR relaxation time $1/T_1$ [23]. In previous works it was found that $C_e \propto T^3$ in a sample of the same quality as D [11] and that $C_e$ and $1/T_1$ go exponentially with temperature in lower quality samples [13, 14]. Thus, we argue here that the $T^2$ dependence of $\lambda(T)$ suggests the existence of nodes in the gap function and therefore that superconductivity is unconventional in LaNiC$_2$.

We now discuss the node origin of $\Delta \lambda(T) \propto T^2$. Since we used polycrystalline samples both the in-plane and the out-of-plane component of $\lambda(T)$ contributed to our measured signals. Unfortunately, the available information for LaNiC$_2$ is not sufficient to estimate its anisotropy that would allow us to weight the contribution from each penetration-depth component. A $T^2$ response can appear in the out-of-plane component $\Delta \lambda(T)$ if point nodes are present. This would be in agreement with the result $C_e \propto T^3$ found earlier [11] that implies the existence of point nodes in the gap. We note that the TRS-breaking states proposed under symmetry arguments [12, 24] as the candidates for the order parameter of LaNiC$_2$ do not possess point nodes.

A $T^2$ dependence could also be displayed in the in-plane component $\Delta \lambda_{ab}(T)$ because of symmetry-imposed line nodes in the presence of unitary scattering. In this case, the quadratic response would be the result of a crossover from the linear behavior of $\Delta \lambda_{ab}(T)$ expected for a clean and pure material [25]. In LaNiC$_2$ impurities/defects may act as strong scatterers, since they change the low-$T$ behavior of $\lambda(T)$. The crossover temperature $T^* \sim \Delta(0) \sqrt{(T_c - T_c0)/T_c0}$ (with $T_c0$ the impurity-free $T_c$) [25] may apply up to a correction factor of the order of one in noncentrosymmetric superconductors [3, 26, 27]. In LaNiC$_2$ $T_c0$ is unknown and a fit to the crossover expression $\Delta \lambda(T) = a T^2/(T^* + T)$ yielded $T^* > T_c$, consistent with the fact that $\Delta \lambda(T) \propto T^2$ up to high temperatures. This result indicates that the impurity-free critical temperature should be appreciably higher than $3–3.6$ K, and there is no evidence of it. Thus, it is unclear whether line nodes affected by impurities/defects may cause the $T^2$ dependence. It is worth mentioning that in the noncentrosymmetric superconductor CePt$_3$Si the linear behavior of $\lambda(T)$ at low temperatures was found to be robust against impurities/defects [3].

Even though the present results indicate that the energy gap of LaNiC$_2$ has nodes, we believe that the type of node will be elucidated only when pure single crystals become available.

In figure 4, we compare the superfluid density $\rho(T) \propto \lambda^2(0)/\lambda^2(T)$ of sample D with the numerical data of a conventional s-wave local model. We estimated $\lambda(0) \sim 1230$ Å from $\gamma_n \approx 7$ mJ mol$^{-1}$ K$^{-2}$ and $H_{c2}(0) \sim 1250$ Oe [11, 13]. Since $\lambda(0)$ has not been experimentally obtained, in figure 4 we plotted $\rho(T)$ for several values of $\lambda(0)$. In all cases the disagreement between theory and experiment is evident, which supports the argument that LaNiC$_2$ does not behave as a conventional s-wave superconductor. The inset to this figure shows that at low temperatures the superfluid density goes as $T^2$ independently of the value of $\lambda(0)$, in accordance with the penetration-depth data.

The strong suppression of the superfluid density at high temperatures is similar to that found in other noncentrosymmetric superconductors with and without nodes [28, 29]. Moreover, in the well-established d-wave superconductors $\kappa-(ET)_2$Cu[N(CN)$_2$]Br and $\kappa-(ET)_2$Cu(NCS)$_2$, the superfluid density shows upward curvature [30]. In recent years, however, it has been widely considered that an upward curvature in the superfluid density is a signature of two-gap superconductivity. We argue that, regardless of the curvature of the superfluid density, in the true low-temperature limit two-isotropic-gap superconductors display a temperature-independent behavior, whereas superconductors with nodes in the energy gap show a power-law response.
Figure 4. Superfluid density $\rho(T) \propto \lambda^2(0)/\lambda^2(T)$ of sample D and the numerical data of a conventional s-wave local model (dashed line). Due to the uncertainty in $\lambda(0)$, $\rho(T)$ was plotted for several values of $\lambda(0)$. Inset: low-temperature $\rho(T)$ as a function of $(T/T_c)^2$ for $\lambda(0) = 1230$ Å and $\lambda(0) = 2000$ Å. In both cases, the data follow a $T^2$ law. The solid lines are a guide to the eye.

That is, as $T \to 0$ a temperature-independent behavior of $\lambda(T)$ or $\rho(T)$ implies a nodeless energy gap, while a power-law response is very strong evidence of nodes.

Our results indicate that (1) previous measurements in low-quality samples that suggest conventional s-wave behavior may have been affected by magnetic impurities and (2) in higher quality samples (like our sample D) the superconducting properties of LaNiC$_2$ are characterized by an energy gap with nodes. Thus, LaNiC$_2$ is only the second noncentrosymmetric superconductor without magnetic phases or strong electron correlations found to have nodes in the energy gap. Until now, Li$_2$Pt$_3$B, which also has a relatively strong ASOC, was the only example of such a superconductor. Based on the results in CePt$_3$Si, CeIrSi$_3$ and CeRhSi$_3$, most recent models for noncentrosymmetric superconductors indicate that the existence of (accidental) nodes requires the presence of both an antiferromagnetic interaction and a sizable ASOC [9, 10]. Our results in LaNiC$_2$ suggest that an antiferromagnetic coupling may not be required for the existence of nodes in superconductors without inversion symmetry.

4. Conclusions

In summary, we have reported measurements of the magnetic penetration depth in polycrystalline samples of noncentrosymmetric LaNiC$_2$. The very-low-temperature penetration depth of our highest-quality sample followed a $T^2$ law that strongly suggests nodes in the energy gap. We believe that previous results indicating conventional s-wave behavior were most probably affected by magnetic impurities.
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