Single Crystal Growth and Superconductivity in La$_7$Ni$_3$ without Inversion Symmetry in the Crystal Structure

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Abstract. We succeeded in growing single crystals of La$_7$Ni$_3$ with the non-centrosymmetric hexagonal structure by the Bridgman method, and measured the electrical resistivity and specific heat under magnetic fields. The superconducting transition temperature $T_{sc}$ is 2.4 K. The electronic specific heat coefficient is $44 \text{ mJ/(K}^2\text{f.u.-mol)}$. Correspondingly, the upper critical field $H_{c2}(0)$ in superconductivity is large, $H_{c2} = 27 \text{kOe}$. The electronic specific heat shows the jump at $T_{sc} = 2.4 \text{ K}$, indicating the bulk superconductivity with $\Delta C_e/T_{sc} = 1.2$, which is close to the weak coupling BCS value of 1.43. Although the temperature dependence of specific heat and some parameters of superconductivity are well explained by the conventional BCS model, the temperature dependence of $H_{c2}$ is not consistent with the simple BCS model.

1. Introduction

Superconductivity is a fundamental phenomenon in metallic compounds, which is observed in the $s$- and $p$-electron systems as well as the strongly correlated $d$- and $f$-electron systems. The pairing mechanism is based on phonons in the BCS-type superconductors, while it is due to magnetic spin fluctuations in the strongly correlated electron systems. The typical $d$-electron systems are high-$T_c$ cuprates [1]. Heavy-fermion superconductors such as CeCoIn$_5$ and UPt$_3$ belong to the $f$-electron systems [2]. In these strongly correlated electron systems, the superconducting pairing favors the $d$-wave spin singlet and/or $p$- (or $f$-) wave spin triplet states.

Even if superconductivity belongs to the BCS-type, precise measurements revealed unconventional properties, for example, in CeRu$_2$. The electronic specific heat coefficient $C_e/T$ below $T_{sc}$ does not increase linearly as a function of applied magnetic field $H$ but indicates a nearly $\sqrt{H}$-dependence at 0.5 K ($\sim 0.08T_c$) [3]. From the field-angle-resolved specific heat measurement, it was definitely clarified the gap minimum [4].

Similarly, multigap/multiband superconductivity is another concept of BCS-type superconductivity, which was precisely studied in MgB$_2$, for example. Namely, two different Fermi
surfaces based on the $\sigma$ and $\pi$ bands possess two different gaps \cite{5,6}.

Recently, superconductivity in the non-centrosymmetric compounds attracts our attention \cite{7,8}. A lack of inversion symmetry or non-centrosymmetry in the crystal structure brings about interesting phenomena in superconductivity and magnetism. The antisymmetric spin-orbit interaction lifts not only the degeneracy of conduction electrons but also the spin. The Fermi surface thus splits due to the antisymmetric spin-orbit interaction. The magnetic interaction is based on the so-called Dzyaloshinskii-Moriya interaction. Unique magnetism so-called skyrmion is observed in MnSi \cite{9}. Theoretically, superconductivity is admixture of the spin singlet and spin triplet pairings. The unique upper critical field $H_{c2}(0)$ is observed, for example, in CeIrSi$_3$ with the non-centrosymmetric tetragonal structure; $H_{c2}(0) \approx 450$ kOe for $H \parallel [001]$ and 95 kOe for $H \parallel [110]$ are obtained \cite{8}. Pauli paramagnetic suppression of $H_{c2}$ is not realized only for $H \parallel [001]$ because all the spins of conduction electrons are perpendicular to the magnetic field direction of $H \parallel [001]$.

Considering these points, we studied the superconducting properties of La$_7$Ni$_3$ with the Th$_7$Fe$_3$-type non-centrosymmetric hexagonal structure (space group: $P6_3mc$, #186, $C_{6v}$). We grew single crystals by the Bridgman method and measured the electrical resistivity and specific heat under magnetic fields.

2. Experimental

We succeeded in growing single crystals of La$_7$Ni$_3$ by the Bridgman method. Both compounds are congruent in the binary phase alloy diagram. First, we melted the starting materials of 3N-La and 5N-Ni in an arc furnace. Note that the melting point is 530 $^\circ$C in La$_7$Ni$_3$. The ingot was crashed into small pieces, which were inserted into a yttria crucible. The crucible was encapsulated in a quartz ampoule, which was heated to 650 $^\circ$C and slowly cooled to 480 $^\circ$C, taking 6 days, and finally cooled to room temperature. The quartz ampoule was placed in an electrical furnace with the temperature gradient ($\Delta T \sim 10^\circ$C.) Figure 1 shows the obtained ingot of La$_7$Ni$_3$, cleaved in the $c$-plane in the hexagonal structure.

The electrical resistivity was measured by the four-probe AC method and the specific heat by the thermal relaxation method at temperatures down to 0.4 K and at fields up to 40 kOe.

3. Experimental Results and Analyses

We measured the electrical resistivity and specific heat for La$_7$Ni$_3$, as shown in Figs. 2 and 3, respectively. The temperature dependence of resistivity shows the convex curvature at high temperature, which is not common in La-based compounds. This is probably due to the 3$d$ electrons of Ni. The resistivity follows the $T^2$-dependence below 11 K. The coefficient $A$ and the residual resistivity $\rho_0$ are 0.016 $\mu\Omega\cdot$cm/K$^2$ and 71.6 $\mu\Omega\cdot$cm, respectively. At low temperature, the superconductivity is observed at $T_{sc} = 2.4$ K, defined by the midpoint of the resistivity drop.

The superconductivity is also observed in the specific heat measurements, indicating the bulk superconductivity, as shown in Fig. 3 the transition temperature is $T_{sc} = 2.4$ K, and

![La7Ni3](image-url)
Figure 2. Temperature dependences of electrical resistivity $\rho$ in La$_7$Ni$_3$.

Figure 3. (a) Temperature dependence of the specific heat in La$_7$Ni$_3$. The broken line is the result of fitting above $T_{sc}$ by $C/T = \gamma + \beta T^2$. (b) Temperature dependence of the electronic specific heat in the form of $C_e/T$ v.s. $T$. 

$\ce{La_7Ni_3}$

$J//[10\bar{1}0]$
the electrical specific heat coefficient is \( \gamma = 44 \text{ mJ/(K}^2\cdot\text{f.u.-mol)} \). The \( \gamma \)-value approximately follows the universal value obtained by the Kadowaki–Woods ratio. The specific heat jump is \( \Delta C_e/\gamma T_c = 1.2 \), which is slightly lower than the weak coupling BCS-value, 1.43. The low temperature data below 0.7 K follow the BCS asymptotic formula, \( \Delta C_e/T = \gamma_0 + 3.15(\Delta/1.76k_BT)^{1/2}\gamma \exp[-\Delta/k_BT] \). The obtained gap energy is \( \Delta = 4.0 \text{ K} \) and \( 2\Delta/k_BT_{sc} = 3.34 \), which is also consistent with the BCS value. The thermodynamical critical field \( H_c \) is calculated from the relation \( \mu_0H_c^2/2 = \int_0^{T_c}[S_s(T) - S_u(T)]dT \), where the entropy of superconducting (\( S_s \)) and normal state (\( S_u \)) is obtained from \( S = \int C_e/TdT \). The thermodynamical critical field \( H_c \) at 0 K is \( H_c(0) = 0.026 \text{ T} \).

We also measured the field dependence of the electrical resistivity in the temperature range from 2.3 to 0.4 K, as shown in Fig. 4(a). The temperature dependence of \( H_{c2} \) is quite isotropic between \( H || [0001] \) and [1120]. The upper critical field is \( H_{c2}(0) \approx 2.7 \text{ T} \) for both \( H || [0001] \) and [1120], as shown in Fig. 4(b). The value of \( H_{c2}(0) \) is below the Pauli limit. \( T_P = 1.86T_c \), but is relatively large, compared to many La-based superconductors. The coherence length obtained from \( H_{c2} = \phi_0/2\pi\xi^2 \) is \( \xi = 110 \text{ Å} \). It should be noted that the temperature dependence of \( H_{c2} \) does not follow the so-called WHH model based on the dirty limit case. The initial slope of \( H_{c2} \) at \( H \to 0 \) is \( -dH_{c2}/dT = 1.4 \text{ T/K} \). This large initial slope of \( H_{c2} \) corresponds to the moderately enhanced \( \gamma \)-value, which is most likely due to the 3d electrons from Ni and the characteristic crystal structure without inversion symmetry. The mean free path, \( \ell \), which can be calculated from \( \rho_0, T_c \), and \( \gamma \)-value, is \( \ell \approx 110 \text{ Å} \), assuming the spherical Fermi surface [12]. Since the obtained mean free path is smaller or comparable to the coherence length, La\(_7\)Ni\(_3\) is conventional BCS-type superconductor in the dirty limit.

4. Summary
We measured the electrical resistivity and specific heat under magnetic fields using single crystals of Th\(_7\)Ni\(_3\) and La\(_7\)Ni\(_3\) with the non-centrocymmetric hexagonal structure. The characteristic features are summarized as follows:

1) Bulk-superconductivity is realized below \( T_{sc} = 2.4 \text{ K} \) in La\(_7\)Ni\(_3\).

2) The electronic specific heat \( C_e \) below \( T_{sc} \) approximately follows the conventional BCS single-gap weak-coupling in both compounds.

Figure 4. Temperature dependences of (a) field dependences of electrical resistivity and (b) temperature dependence of upper critical fields \( H_{c2} \) for \( H || [0001] \) and [1120] in La\(_7\)Ni\(_3\).
3) The relatively large $H_{c2}(0)$ and the large initial slope are probably due to the Ni 3$d$-based and the characteristic crystal structure without inversion symmetry.

Acknowledgments
This work was supported by JSPS KAKENHI Grant Numbers 25247055, 15K05156, 15H05884, 15H05882, and 16H04006 and start-up research costs from the Project to Promote Gender Equality and Support Female Researchers from Tohoku University.

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