Magnetic impurity effects on the superconductivity of noncentrosymmetric $LaNiC_2$: Ce substitution for La

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Effects of paramagnetic impurities on the superconducting transition of noncentrosymmetric $LaNiC_2$ have been studied by Ce substitution for La up to 3 at.%. With the substitution the superconducting transition temperature $T_c \sim 2.8$ K of the pure system decreases dramatically, and disappears with Ce just above 2 at.%. This intense suppression of T_c with the Ce substitution can be explained by the Abrikosov-Gor'kov theory for conventional s-wave superconductors with localized magnetic moments. These results, together with a quite small depression of T_c with nonmagnetic Y impurities, strongly suggest that $LaNiC_2$ is a BCS superconductor with a full superconducting energy gap, not an unconventional one with a nodal gap.

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I. INTRODUCTION

The ternary carbides with the rare-earth atom R and Ni, $R\mathrm{NiC}_2$, show a variety of physical properties with changing R. The systems with some of the heavier rare-earth elements ($R =$ Nd, Sm, Gd, and Tb) exhibit charge density wave (CDW) states at temperatures of the order of 100 K. These CDW states compete with complex magnetic orders appearing at lower temperatures [1,2]. Their crystal structures are simple but noncentrosymmetric. The space group is orthorhombic $Amm2$, and the lattice lacks the inversion symmetry along the c axis, as shown in Fig. 1. Here the Ni and C atoms are located in the (1/2)a plane, and the fractional coordinates of the atoms are reported as R (0, 0, 0), Ni (1/2, 0, $\sim$0.63), and C (1/2, $\sim$0.16, $\sim$0.29) for some systems [3].

The compounds with light rare-earth elements do not show the CDW order. In the system with $R =$ La, $LaNiC_2$, superconductivity appears at about 3 K. For this superconductivity some novelties coming from its noncentrosymmetric structure are expected. The noncentrosymmetry causes the antisymmetric spin-orbit coupling (ASOC) that splits the original electron bands, and this leads to the indistinguishability of spin-singlet and spin-triplet electron pairings. For the superconductivity of $LaNiC_2$, a T^3 dependence of specific heat at low temperatures was reported, suggesting that the superconductivity is unconventional with nodes in the superconducting energy gap [4]. A muon spin relaxation (μSR) experiment showed the breaking of the time-reversal symmetry (TRS) in its superconducting state, which, based on group theory arguments, guides to nonunitary p-wave spin-triplet superconducting pairings with a nodal gap [5]. Recently, an observation of spontaneous bulk magnetization was reported in this superconducting state, which also may indicate the broken TRS [6]. These results indicate that the system constitutes the first example of an intrinsic nonunitary triplet superconductor without a preexisting ferromagnetic exchange splitting. Quite recently, this superconductivity was found to be anomalously affected by pressure, demonstrating that the system is highly correlated with strong electronic interactions [3].

However, the nature of the superconducting pairing in this system is far from being settled since there are competing reports that the superconductivity of this system is likely to be conventional. An NQR study indicated a small but clear enhancement of the nuclear spin relaxation rate ($1/T_1$) just below T_c, implying that the superconductivity of the system can be regarded as a conventional Bardeen-Cooper-Schrieffer (BCS) type at least at temperatures near T_c [7]. After the μSR experiments mentioned above, a comprehensive study on this system was reported, which implies that the London penetration depth and the specific heat can be described by a two-gap BCS model [8]. A recent specific heat measurement on a single crystal of $LaNiC_2$ suggested that its data also can be fitted to the conventional BCS function at low temperatures [9]. However, their single gap model does not explain the experimental results at the higher temperatures around T_c.

To get further information on the superconducting properties of this noncentrosymmetric system, we have studied paramagnetic impurity effects of Ce on its superconductivity. Our aim is to examine the competition between the superconductivity and magnetic interactions, and to clarify the superconducting pairing mechanism of the system.

II. EXPERIMENTAL

Polycrystalline samples of $(La_{1-x}Ce_x)NiC_2$ with 0, 0.5, 1, 1.5, 2, 2.5, 3 at.% Ce were synthesized with La (purity: 99.9%), Ce (99.9%), Ni (99.998%), and C (99.9995%) in an argon-arc furnace. Taking into account of the high vapor pressure of

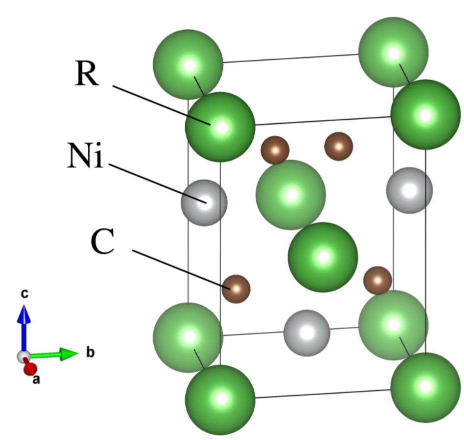

FIG. 1. Crystal structure of $R\mathrm{NiC}_2$ (Orthorhombic $CeNiC_2$-type, $Amm2$). R indicates La and/or Ce atoms.

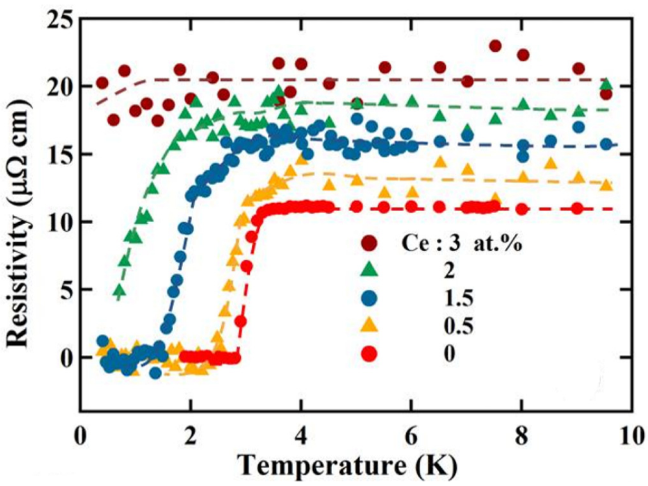

FIG. 2. Resistivity at low temperatures for the samples containing Ce up to 3 at.%. The broken lines are guides to the eyes.

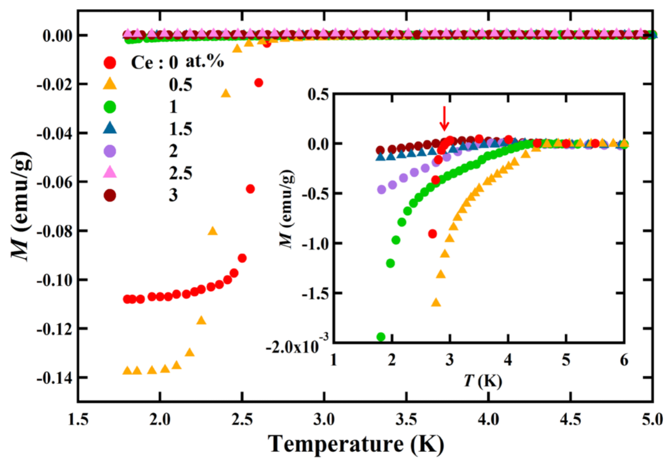

FIG. 3. Temperature dependence of the zero-field cooled (ZFC) magnetization for the samples with Ce below 3 at.% measured in $H = 10$ Oe. The inset shows the magnetization near T_c. The vertical arrow in the inset shows T_c of pure $LaNiC_2$. The magnetization for some samples starts to drop at a temperature that is higher than the T_c of $LaNiC_2$.

C, the amount of C was increased by about 4 at.% from its stoichiometry. In order to ensure the homogeneity of the sample, each ingot was reversed and remelted several times. These samples were checked by powder x-ray diffraction (XRD) at room temperature using Cu $K\alpha$ line. All samples showed the orthorhombic $CeNiC_2$-type structure without any significant impurity phases. Some samples were further examined with a scanning electron microscope (SEM) and an energy dispersive x-ray spectroscope (EDX). Their results showed that the samples are homogeneous enough over the whole concentration range.

The electrical resistivity and specific heat of the samples were measured in a ^{3}He cryostat, PPMS (Physical Properties Measurement System, Quantum Design), from 0.4 to 300 K with a four-probe method and a relaxation method, respectively. Magnetization measurements were made from 1.8 to 300 K using a SQUID magnetometer, MPMS (Magnetic Property Measurement System, Quantum Design). Superconducting transitions were determined by resistivity, magnetization in the zero-field cooling (ZFC) and the field cooling (FC) in 10 Oe, and specific heat. The systematic changes with Ce substitution of the lattice constants and the residual resistivities observed give us further confidence that the actual and nominal compositions are sufficiently close in the present study.

III. RESULTS AND DISCUSSION

A. Resistivity

Figure 2 shows the low-temperature resistivity for the samples with Ce concentration up to 3 at.%. The superconducting transitions observed in these samples are destroyed rapidly with the Ce impurities. Their resistivity data show some fluctuations, and the superconducting transitions are rather broadened. Compare them with the resistivity of pure $LaNiC_2$, whose statistics of the data is fairly good. Therefore those fluctuations or scatterings of the data might be due to the magnetic impurities doped in the samples. It is furthermore noted that the resistivity for 0.5 to 2 at.% Ce shows transitions with a two-step decrease. The initial decrease starts at a temperature above 2.8 K, the T_c of $LaNiC_2$. As shown later, the broadening of the transition with a two-step decrease is observed also in the magnetization measurements. See the data shown in Fig. 3. This behavior implies local enhancements of the superconductivity, suggesting some superconducting fluctuations.

The bulk T_c determined by the zero-resistivity significantly decreases with Ce content, and disappears completely for 3 at.% Ce. At 2 at.% Ce, the zero-resistivity is not observed down to 0.4 K, the lowest temperature examined in the present study; however, the extrapolation of the data indicates that the zero-resistivity would occur at about 0.1 K. The resistivity of 2.5 at.% Ce does not show the zero-resistivity. We therefore conclude that the critical concentration for the superconducting transition is between 2 and 2.5 at.% Ce. Here that is estimated to be about 2.2 at.%.

We further note that although the data of the Ce substituted samples scatter a little, a *small but certain* increase in the resistivity is observed below 10 K down to the superconducting temperature. See the differences between the slopes of the resistivity-temperature data of the doped samples and those of the pure and Ce-3 at.% doped specimen: the negative slopes of the resistivity-temperature curves of the doped samples are obvious. These increases in the resistivity at the low temperatures could be attributed to the Kondo effect caused by the localized magnetic moments of Ce formed in the system. The Kondo behavior of this system will be discussed latter in the subsection D for the superconducting transition temperature again.

B. Magnetization

In Fig. 3, the zero-field cooled (ZFC) magnetization curves for the samples containing Ce below 3 at.% measured in $H = 10$ Oe at temperatures between 1.8 and 5 K are shown. The effective magnetic moments $\mu_{\rm eff}$ per Ce calculated from the Curie constants obtained in the high-temperature data above about 100 K (not shown as a figure) agree well with the theoretical value of 2.52 μ_B of the Ce^{3+} free ions over all Ce concentration within the experimental accuracy.

The diamagnetism is observed for the samples with Ce below 2 at.%. The value of the diamagnetic susceptibility for pure $LaNiC_2$ is calculated to be about $-1/(4\pi)$ (emu/cc); this shows that the sample is an ideal bulk-superconductor. A larger value for the sample with 0.5 at.% Ce might be due to the geometrical demagnetization factor coming from the shape of the specimen: the sample was not long enough in the field direction. The Meissner flux repulsion observed by the field cooled (FC) magnetization (not shown in the figure for the clarity) is about 3 % of the diamagnetic flux repulsion, indicating a relatively strong pinning.

For 0.5, 1, 1.5, and 2 at.% Ce, it is clearly observed that the magnetization starts to drop at a temperature that is higher than the T_c of $LaNiC_2$. As indicated in the resistivity measurements above, this is likely due to superconducting fluctuations induced locally and/or microscopically in the sample. This is a sign of incipient superconductivity that appears above the T_c of the pure system, and might be attributed to some fluctuations induced by the localized magnetic moments of Ce.

On the other hand, the bulk superconducting transition temperature T_c, which was determined by the starting temperature of the large decrease of the magnetization below the small initial decrease mentioned above, decreases rapidly with Ce doping with an initial slope of about −0.9 K/at.% Ce and disappears at around 2 at.%. This result coincides with the result of the resistivity measurements.

C. Specific heat

Figure 4 shows the temperature dependence of specific heat C below 5 K down to 0.4 K for the samples with Ce up to 3 at.%. With increasing Ce concentration, the distinct peak characterizing the bulk superconducting transition significantly fades away. This might be related with the scattering of the data observed in resistivity and with incipient fluctuations in magnetic susceptibility. The transition temperature T_c was determined by the inflection point of the steep anomaly of the specific heat data, which agrees well with the temperature obtained from the zero-resistivity and the magnetization anomaly. The anomaly in the specific heat is not clear in the data for 2 at.%Ce; that is, the superconductivity disappears at around this concentration, which is also consistent with the results of the resistivity and susceptibility measurements.

We note here the temperature dependence of the specific heat of the pure sample. The data below 1 K tend to zero, and does not seem to follow the power of T. The whole data can be explained well by the BCS function with the energy gap. Furthermore, they can be fitted by two gaps with the energy of about 0.32 meV for the lower temperatures and of about 0.47 meV for the higher temperatures, rather than by a single energy gap. These results are consistent with those of the previous work reported by Chen *et al.* [8], suggesting that the superconductivity of the system is a two-gap BCS type. This consequence implies that the system is fully gapped.

From the low temperature data, the coefficient of the electronic specific heat γ can be obtained by

$$C/T = \gamma + \beta T^2. \tag{1}$$

With the value of γ we can calculate the density of states at the Fermi level $N(0)$ from

$$N(0) = \frac{3\gamma}{2\pi^2 k_B^2}. \tag{2}$$

In the BCS theory, the superconducting transition temperature T_c depends on the density of state at the Fermi level $N(0)$ with the interaction parameter V as

$$T_c = 1.13\Theta \exp\left(-\frac{1}{N(0)V}\right), \tag{3}$$

where Θ is the Debye temperature. The factor $N(0)$ itself would change the T_c's of other non-BCS superconductors also, including unconventional ones, essentially in a similar manner.

The values of γ obtained from Eq. (1) do not change much in this concentration range; therefore as indicated in Fig. 5 the density of states $N(0)$ calculated from Eq. (2) is almost constant. (The same analysis was done for the related compound

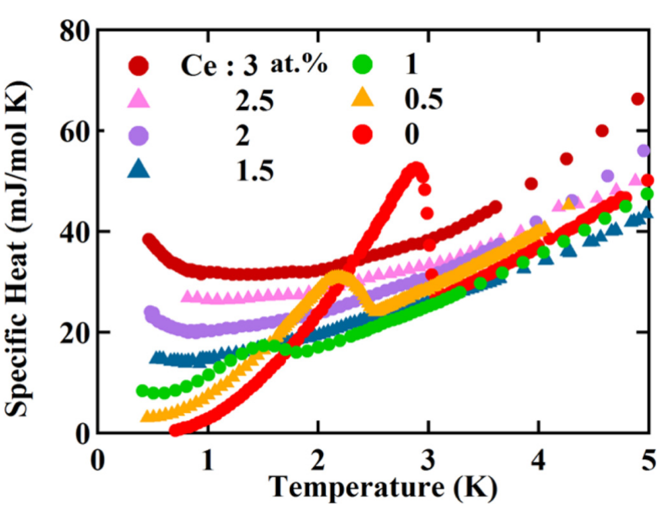

FIG. 4. Temperature dependence of specific heat for the samples with 0 to 3 at.% Ce.

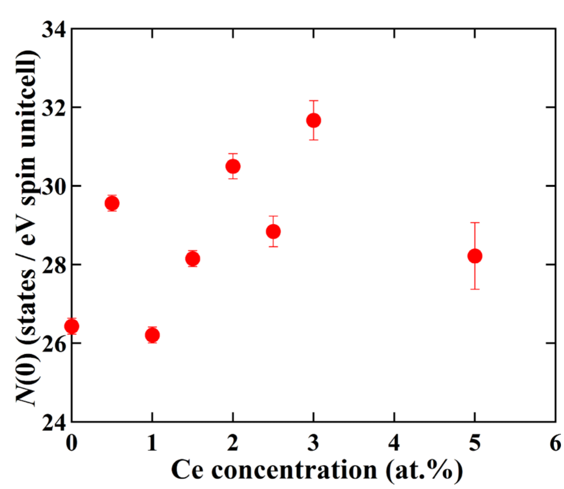

FIG. 5. Ce concentration dependence of the density of states at the Fermi level $N(0)$ calculated from the coefficient of the electronic specific heat.

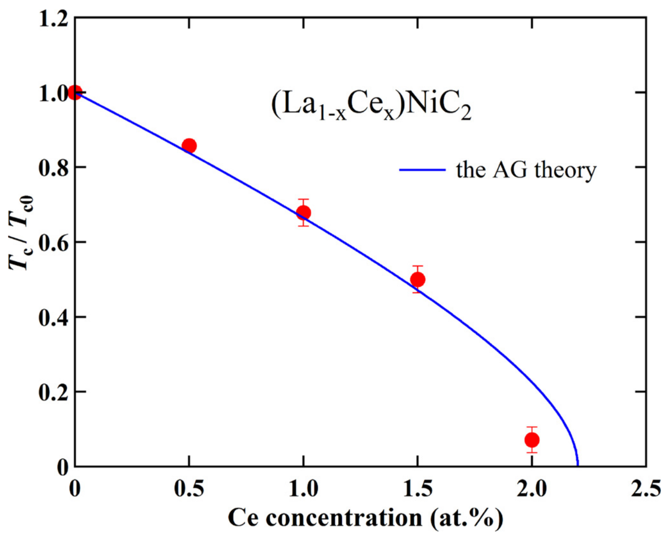

FIG. 6. Normalized superconducting transition temperature T_c/T_{c0} vs Ce concentration for $LaNiC_2$. The solid line represents the AG theory with the critical concentration n_{cr}. Here the initial decrease of T_c/T_{c0} observed in the experiments was fitted to that of the AG curve. A reasonable fit to this curve is obtained for the critical concentration $n_{cr} = 2.2$.

(La,Y)NiC_2. The values shown in the figure are essentially equivalent to those given there [10].) The rapid decrease in T_c therefore cannot be explained by the change in the density of states at the Fermi level $N(0)$. Instead, the strong suppression of superconductivity in this system is most likely caused by the increase of the localized magnetic moments of Ce.

D. Superconducting transition temperature

It was reported that the superconducting transition temperature T_c of $LaNiC_2$ is strongly enhanced with pressures up to 3 GPa, which implies that the system is highly correlated with strong electronic interactions [3]. This result shows a sharp contrast to the effect of the chemical pressure on the conventional superconductivity. Under chemical pressure, the superconducting transition temperature T_c is usually decreased with decreasing in the density of states at the Fermi level $N(0)$. In fact, the substitution of La by Y contracts its lattice, and T_c decreases a little in proportion with the reduction of the density of states [10]. In the case of the Ce substitution, the lattice is also contracted, and T_c is decreased quite significantly. However, as discussed above, the density of states $N(0)$ at the Fermi level of this system does not change greatly over the superconducting phase. We therefore conclude that the pair breaking caused by the Ce localized magnetic moments is much more effective on the suppression of T_c, rather than the chemical pressure by the Ce substitution.

In Fig. 6, the reduced superconducting transition temperature T_c/T_{c0} is plotted as a function of the Ce concentration. Here, T_{c0} is the transition temperature of pure $LaNiC_2$. As mentioned before, the superconducting transition temperatures determined by resistivity, magnetization, and specific heat were consistent with each other; however, the magnetization and specific heat data of the samples with the higher concentration of Ce are a little difficult to be analyzed because of the small and broadened anomalies of them. On the other hand, the transition temperature T_c can be obtained from the zero-resistivity rather accurately; therefore, the temperatures T_c determined by the zero-resistivity were plotted in the figure. The errors of them were estimated to be about 0.1 K for the samples with the higher Ce content.

The solid line in this figure shows the AG (Abrikosov-Gor'kov) theory given in terms of the diagamma function of ψ as

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + 0.14\frac{nT_{c0}}{n_{cr}T_c}\right), \qquad (4)$$

where n_{cr} is the critical concentration at which the superconductivity disappears. In the figure, the initial decrease of T_c/T_{c0} observed in the experiments was fitted to the AG curve; and a reasonable fit to this form was derived for $n_{cr} = 2.2$. Note that this critical concentration is consistent with the estimation from our resistivity data indicated in the previous section, where the superconductivity is observed for the sample with 2 at.% Ce, but not for 2.5 at.% Ce. The same kinds of fits to the AG theory were reported for several superconducting systems with paramagnetic impurities. The well-known example is $LaAl_2$ substituted by Gd for La. There $LaAl_2$ is a typical s-wave BCS superconductor with a full energy gap. Its transition temperature T_c is 3.2 K and disappears completely with 0.9 at.% Gd [11,12].

In the case of Ce impurities for the $LaAl_2$ system, the data for T_c/T_{c0} versus the Ce concentration falls apart from the AG theory near the critical concentration and shows a re-entrant superconducting behavior in a narrow range near n_{cr} [13,14]. This phenomenon is caused by the Kondo effect with magnetic impurities of Ce. In the present case also, the result of 2 at.% Ce deviates a little down from the AG theoretical curve, but does not indicate the re-entrant superconductivity; therefore, the influence of the Kondo effect might exist but is quite small. This coincides with the small but clear increase in the resistivity below about 10 K down to the superconducting transition temperature, which should be a sign of the Kondo effect as mentioned before.

The experimental fact that the superconducting transition is significantly suppressed with the localized magnetic moment, together with the result that the reduction of T_c is well described by the AG theory strongly suggests that the superconductivity of the system is characterized by the s-wave BCS type with a full energy gap. This shows a sharp contrast with the fact that nonmagnetic impurities for s-wave superconductors decrease T_c very little. Refer the results of (La,Y)NiC_2 again, where La is replaced by nonmagnetic Y [10]. Its transition temperature T_c is decreased at the rate of only 0.07 K/at.% Y, and the superconductivity remains at 1 K even with 35 at.% Y, the solubility limit of Y in that system. That result coincides with the discussion by Anderson that the nonmagnetic impurity essentially does not change the T_c of the s-wave BCS superconductors [15].

On the other hand, the unconventional superconductivity with a momentum k-dependent nodal gap is strongly destroyed by nonmagnetic impurities, as was actually observed in $CeCu_2Si_2$ and others [16]. The results on (La,Y)NiC_2 mentioned above, in which the effect of the nonmagnetic Y impurity is quite small, furthermore again support that the present system is not an unconventional nodal-gapped superconductor but is a conventional BCS one. For the magnetic impurities in unconventional p- or d-wave superconductors, their effects on T_c would be rather small when the spin correlations of the conduction electrons are coherent with the spins of magnetic imputities. Refer to the experimental results that the magnetic impurity effects on the superconductivity of high-T_c Cu oxides are rather weak. Such a small effects of magnetic impurities for unconventional systems will exhibit a clear contrast with the dramatic suppression of T_c by the localized paramagnetic impurities in the present system.

The results obtained here therefore, with those of other experimental facts mentioned above, indicate that the $LaNiC_2$ system is a conventional and fully gapped superconductor without k-dependent nodes, and does not seem to fit the picture of the unconventional nodal p-wave superconductor [5].

The effects of grains of the polycrystalline samples should be considered. The differences in T_c and other bulk physical properties observed in the resistivity, magnetization, and specific heat are quite small between our polycrystalline sample and the single crystal of the pure impurity-free $LaNiC_2$. From these results, it is expected that effects of grains to the bulk superconductivity would be small enough, as observed in other systems including the reference materials mentioned above. However, superconducting fluctuations and so forth of the doped polycrystalline samples may be affected considerably by the grains locally and/or microscopically.

IV. CONCLUSIONS

The superconductivity of the noncentrosymmetric system $LaNiC_2$ is dramatically destroyed with the substitution of Ce magnetic impurities for La. Since the density of the state at the Fermi level $N(0)$ calculated from the specific heat does not change significantly in the superconducting state, the decreases in T_c is not due to the decrease in $N(0)$ but is to the pair breaking effect caused by the localized magnetic moments. The dramatic decrease in T_c with the Ce concentration can be explained by the AG (Abrikosov-Gor'kov) theory which is applied to the systems of the conventional s-wave superconductors with the localized magnetic moments. These results, which contrast with the very small effects of the nonmagnetic impurities on $LaNiC_2$, imply that the system is a BCS s-wave superconductor with full gaps. This would be supported by the results that the specific heat of the system can be explained by the term of the two full gaps both in the present experiments and in the studies done by Chen *et al*. [8]. It is furthermore noted here that our collaborators, Mizukami *et al.* recently obtained further evidence of the s-wave full-gapped superconductivity for this system from studies of the effects on T_c with nonmagnetic impurities created by electron beam irradiation, and from measurements of the temperature dependence of magnetic penetration depth and thermal conductivity in the superconducting state [17]. Quite recent experiments on $LaNiGa_2$ together with those on the present system implied that these systems are nodeless superconductors with two BCS gaps. In that paper, the authors further proposed a novel nonunitary triplet state where the gap symmetry has even parity [18]. Therefore the situation of the system may be more complicated. To make the superconducting mechanism of $LaNiC_2$ clear much more, further detailed experimental and theoretical studies would be necessary. We, however, believe that our work will play an important role to understand the superconducting mechanism of the system together with those future studies.

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