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Anomalous pressure dependence of the superconductivity in noncentrosymmetric $LaNiC_2$: Evidence of strong electronic correlations

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The superconductivity of the noncentrosymmetric system $LaNiC_2$ has been studied under high pressures up to 30 GPa with electrical resistivity measurements. For this superconducting state, the breaking of time-reversal symmetry was shown recently in a muon spin relaxation (μSR) experiment, which leads to nonunitary spin-triplet superconductive pairings. The present experiments on this superconductor reveal that the transition temperature T_c greatly increases at the rate of 0.25 ($\pm$0.01) K/GPa up to 3 GPa. However, above this pressure, T_c gradually decreases; and at the pressures over 8 GPa, the superconductivity disappears completely. With this disappearance of the superconductivity, a different state with a high-energy scale dramatically emerges. These results indicate that the system is not a simple normal metal, but is rather highly correlated with strong electronic interactions which would contribute to its superconductivity.

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The superconductivity of noncentrosymmetric systems has attracted great interest since the discovery of a heavy fermion superconductor without the inversion symmetry, $CePt_3Si$ [1]. This noncentrosymmetry causes the antisymmetric spin-orbit coupling (ASOC) that splits the original electron bands, and leads to the indistinguishability of spin-singlet and spin-triplet electron pairings. Up to now, only a few systems have been reported for these unusual superconductors. They are separated into two groups. One of them is a group of heavy fermion systems with strong electron correlations, including $CePt_3Si$ mentioned above, UIr [2], $CeRhSi_3$ [3], $CeCoGe_3$ [4], and so forth. The superconductivity of these systems appears in an antiferromagnetic ordered phase, or mostly around a magnetic quantum critical point. This suggests that the behavior observed in these systems relates to the magnetic correlations and ASOC. The other is a group with weak electron correlations and no magnetic ordering, such as $Li_2(Pd, Pt)_3B$ [5,6] and $Mg_{10}Ir_{19}B_{16}$ [7].

The system $LaNiC_2$ is paramagnetic and is thought to be categorized in the second group. The crystal structure is simple but noncentrosymmetric, as shown in Fig. 1. The space group is orthorhombic $Amm2$ and the lattice lacks inversion symmetry along the c axis. The system exhibits superconductivity below the transition temperature T_c of about 3 K. On this superconductivity, a T^3 dependence of specific heat at low temperatures was reported before, suggesting that the superconductivity is unconventional with nodes in the energy gap [8]. A recent muon spin relaxation (μSR) experiment, furthermore, showed the breaking of the time-reversal symmetry (TRS) in the superconducting state, which leads to nonunitary p-wave spin-triplet pairings [9]. This result indicates that the system constitutes an example of an intrinsically nonunitary triplet superconductor without a preexisting ferromagnetic exchange splitting. The calculation of the electronic structure of the system that Hase presented showed that the Fermi surfaces are rather simple and are split by comparatively small ASOC [10]. On the other hand, a nuclear quadrupole resonance (NQR) study indicated an enhancement of the nuclear spin-relaxation rate ($1/T_1$) just below T_c, suggesting that the superconductivity of this system can be regarded as a conventional BCS type, at least at temperatures near T_c [11].

In the present work, the superconductivity of $LaNiC_2$ was studied with a polycrystalline sample carefully prepared and characterized. Very recently, a magnetic-penetration-depth (MPD) measurement of this system revealed that only a high-quality sample exhibits the spin-pairing symmetry correctly [12]. The present work, using a good qualified sample, has shown that pressure effects on the superconductivity of this system are quite anomalous. On the basis of these experimental results, the superconducting properties of $LaNiC_2$ will be discussed.

A polycrystalline sample was prepared by arc melting with rather high-purity La (99.9%), Ni (99.997%), and C (99.9995%). X-ray and neutron diffraction of this compound showed that the sample is a single phase with no impurity phases. The x-ray-diffraction pattern was analyzed by a Rietveld program quite successfully with the space group $Amm2$. The fitting factors $R_{WP} = 7.30$ and $S = 1.20$. The lattice constants $a = 3.952\,(1)$, $b = 4.557\,(1)$, and $c = 6.193\,(2)$ Å. The fractional coordinates of the atoms are as follows: La

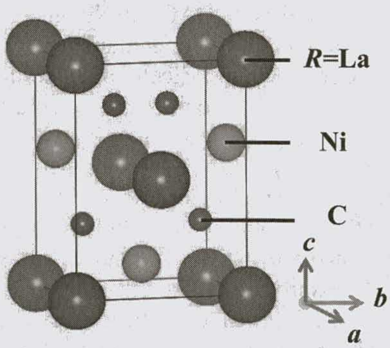

FIG. 1. (Color online) Crystal structure of $LaNiC_2$. There is no centrosymmetry along the c axis.

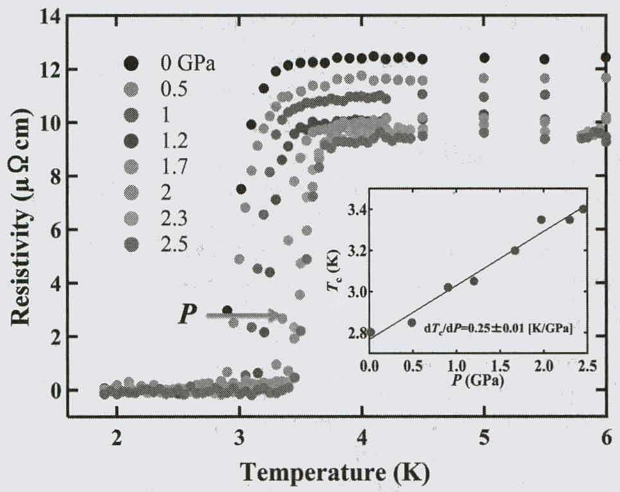

FIG. 2. (Color online) Electrical resistivity under high pressures up to about 3 GPa obtained with the piston-cylinder cell. Inset: The pressure dependence of the superconducting transition temperature T_c.

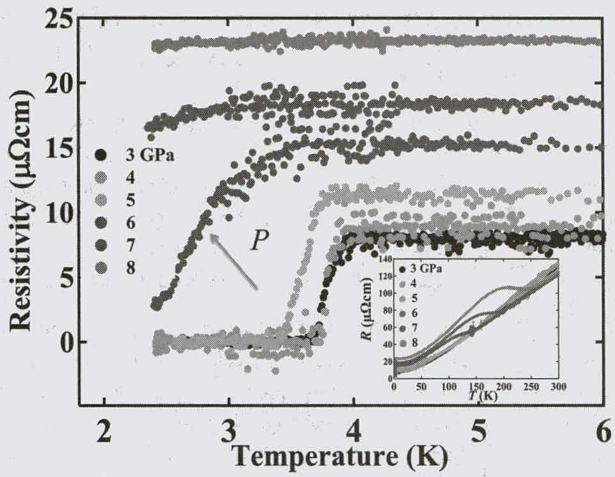

FIG. 3. (Color online) Electrical resistivity under high pressures up to 8 GPa obtained with the cubic-anvil cell. Inset: The resistivity under high pressures at high temperatures.

(0, 0, 0), Ni (1/2, 0, 0.626), and C (1/2, 0.160, 0.289). All of these values are in good agreement with those in the literature. The neutron-diffraction data, which is favorable to study light atoms, showed that the carbon C content is very close to the stoichiometric value of 2.0. Specific-heat and magnetization measurements showed that the present sample exhibits bulk superconductivity with T_c of 2.8 K. Electrical resistivity under high pressures were measured by a standard four-probe technique between about 2.0 K and room temperature (RT). The measurements up to 3 GPa were done using a piston-cylinder cell made of Cu-Be/Ni-Cr-Al alloys. The inner diameter of the sample cell made of Teflon was 4.5 mm at ambient pressure (AP). The pressure-transmitting medium was glycerol, and the hydrostatic property of this cell is good enough to measure physical properties of materials. The pressure was determined by the superconducting transition temperature of Pb. The data up to 8 GPa were obtained with the cubic-anvil-type high-pressure apparatus at the Institute of Solid State Physics of the University of Tokyo. The inner diameter of the sample cell made of Teflon was 1.5 mm at AP, and the pressure-transmitting medium was glycerol. Owing to a multianvil geometry, this apparatus can generate hydrostatic pressure up to those high pressures. The pressure was determined also by the superconducting transition of Pb. The experiments over this pressure and up to 30 GPa were made using a diamond-anvil cell (DAC) at Nihon University. The sample was set in a space of the inner diameter of 0.5 mm at AP, which was made in a stainless-steel gasket. In this space, the sample was surrounded by the pressure-transmitting medium of NaCl powders enclosed by an electric insulator of Al_2O_3. The pressure was determined by the standard ruby fluorescence method. To get higher pressures, the hydrostaticity of this cell is a little worse than the others above. In these experiments, the reproducibility of the resistivity measurements was checked after releasing pressure and with increasing pressure again.

The temperature dependence of the electrical resistivity of $LaNiC_2$ under high pressures up to about 3 GPa is shown in Fig. 2. At ambient pressure, the residual resistivity at around 4 K is about 8.5 $\mu\Omega$cm, and the resistivity ratio between RT and 4 K is over 20. The zero resistivity occurs at 2.80 (±0.03) K. This superconducting transition temperature T_c together with that obtained from specific heat and magnetization agrees well with the previous work done by Lee *et al.* [8].

Under high pressures, the transition temperature T_c of the sample is greatly enhanced at the rate of 0.25 K/GPa up to 3 GPa. According to the conventional BCS theory, the transition temperature is expressed as $T_c \approx \Theta_D \cdot \exp\{-1/\eta\}$, where $\eta = D(E_F) \cdot U$. Here, Θ_D is the Debye temperature, and $D(E_F)$ and U are the electron density at the Fermi energy E_F and the electron-phonon interaction potential, respectively. In this expression, $D(E_F)$ plays a prominent role. This situation is the same as in the McMillan equation, taking into account the electronic Coulomb repulsions based on the BCS theory, where T_c is expressed as $(\Theta_D/1.45) \cdot \exp\{-1/g\}$. Here, $g = \{\lambda - \mu(1 + 0.62\lambda)\}/1.04(1 + \lambda)$ and $\lambda = D(E_F)U/\langle M\omega^2\rangle$: M is the atomic mass, ω is the averaged phonon frequency, and μ is the Coulomb repulsion whose order is 0.1 and relatively small. For normal conventional metals, pressure contracts their lattices and, generally, the electron density $D(E_F)$ at the Fermi energy E_F decreases. From the expressions, therefore, T_c would decrease with increasing pressure. In fact, substituting La by isoelectronic Y in $LaNiC_2$, the lattices contract and the transition temperature T_c is substantially decreased with reducing $D(E_F)$ [13]. In the present case, the electronic structure of the system is rather simple [10], and thus the decreasing of $D(E_F)$ under pressures is expected. Therefore, the experimental result which shows that T_c is substantially increased is quite surprising. Contrary to the Y substitution case, pressure would increase $D(E_F)$ very strongly; that is, the electronic structure of the system is dramatically altered with pressure. This corresponds with the fact that the residual resistivity at low temperatures is greatly decreased from about 12 $\mu\Omega$cm at ambient pressure to 9 $\mu\Omega$cm at 2.5 GPa. It is suggested, therefore, that some exotic mechanisms may contribute to this superconductivity.

Above the pressure of 3 GPa, which is surprisingly higher, the superconductivity once enhanced is heavily suppressed. Figure 3, with the resistivity under pressures up to 8 GPa,

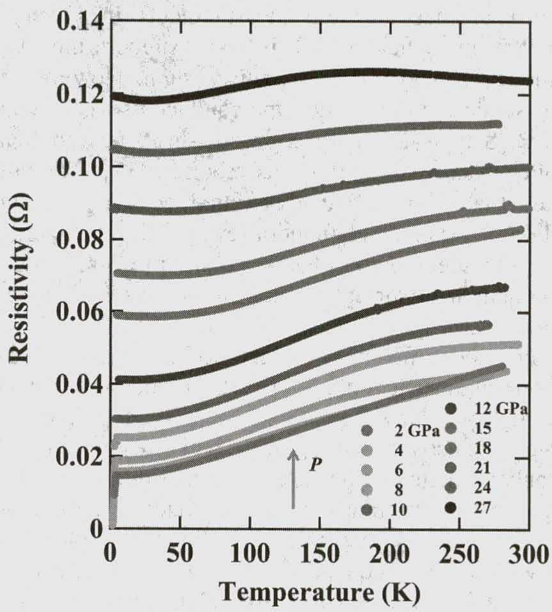

FIG. 4. (Color online) Electrical resistivity under high pressures up to about 30 GPa obtained with the diamond-anvil cell.

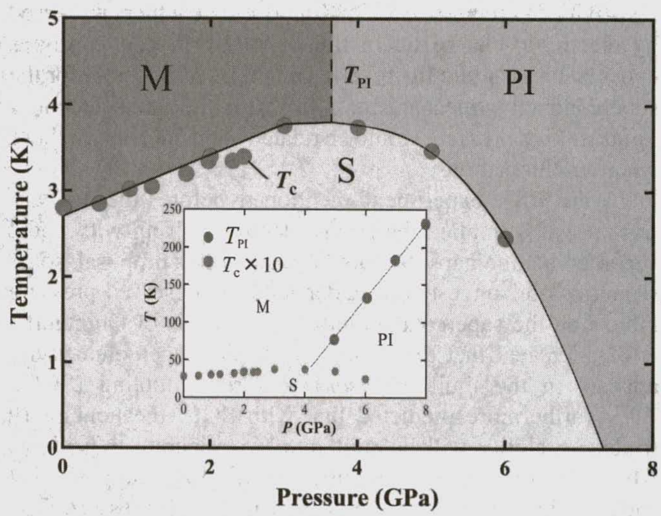

FIG. 5. (Color online) P-T phase diagram of $LaNiC_2$. The mark of M denotes metal, S shows superconductivity, and PI indicates a pressure induced state with a high energy scale. The PI is characterized by large and broad anomalies appearing in the resistivity. Inset: The data up to 250 K. There the superconducting transition temperature is multiplied by the factor of 10.

shows that the superconductivity disappears dramatically while the residual resistivity is strongly increased. The superconductivity that disappears here does not come out again even at 27 GPa, as displayed in Fig. 4. The resistivity increases up to surprisingly high values under these pressures. In this figure, a trace of the superconducting transition is seen in the data at 8 GPa. However, this is due to the hydrostatic property of the diamond-anvil cell used to attain very high pressures. That is, the hydrostaticity of this pressure cell is rather worse in the range of those lower pressures, compared with that of the other cells.

The inset of Fig. 3 shows the resistivity at higher temperatures. Amazingly, above 5 GPa, the resistivity shows a clear anomaly at around 100 K and over. The temperature observed as this anomalous hump increases with pressure up to room temperature at a rate as high as 51.5 ($\pm$0.1) K/GPa. These results show that a different state is evidently induced under high pressures. With the appearance of this state, the superconductivity is intensely suppressed. Figure 5 shows a phase diagram obtained up to 8 GPa. In this diagram, PI denotes the pressure-induced state. The pressure dependence of the transition temperature T_{PI} is plotted in the inset of this figure.

The present results, showing a dome-type strong pressure dependence of the superconducting transition and an appearance of a different state, reveal that the system $LaNiC_2$ is not a simple metal, but is strongly correlated with electronic interactions, *not* with magnetic ones. The phase diagram looks opposite to the usually observed superconducting dome. There the nonsuperconducting magnetic phase at ambient pressure is suppressed and the superconductivity is induced under high pressures accompanied by the quantum critical point (QCP). Here a superconducting state already exists at ambient pressure, and another state with a different high-energy scale is revealed with increasing pressure. The phase diagram is therefore *mirror symmetric* to those of commonly observed ones.

For this different state, it remains that some $R$$NiC_2$ (R are rare-earth elements) systems show charge density wave (CDW) states at high temperatures [14]. It might therefore be natural that the anomalous hump observed at the temperatures over 100 K originates from the phase transition to the CDW state. This induced state is strongly enhanced under high pressures; however, that is quite robust up to the highest pressure of the present work. In many cases, the state of CDW is rather unstable under high pressures. There the pressure effectively makes the electronic structures of the system unfavorable for the formation of CDW with breaking down of nesting conditions at the Fermi surfaces. If this induced state is a CDW, its robustness observed in this experiment is rather anomalous.

The temperature dependence of the resistivity has been analyzed with $\rho = \rho_{res} + \sum_i a_i T^{\alpha_i}$. For the data up to 8 GPa measured under good hydrostatic conditions, the resistivity is almost constant between 3 and 10 K (the residual resistivity ρ_{res}), and then increases as aT^{α}. Here the exponent α is fit to 2.5 between 10 K and about 50 K, then changes to about 1.5 for the higher temperatures. These exponents might be regarded approximately as conventional 2 over those temperatures. Above about 180 K, the resistivity can be fit to T linear. The coefficients a for the fit to the exponent 2 do not largely change over all of the pressure range. Thus a critical behavior upon the transition to the different state is rather weak. The residual resistivity also becomes a minimum (*not* a maximum) at the pressures where T_c shows a maximum. Therefore, this transition may not be second order but first-order like, or some other exotic physics may be hidden in the system. The CDW transition would be a first order; however, as mentioned before, the induced state is quite robust under high pressures, which shows a sharp contrast to the usual CDW states that is rather unstable with pressure. This state may thus be an exotic one with another high-energy scale. A Kondo state might be a possible candidate for that. The broad anomaly in the resistivity is suggestive of a Kondo effect which is caused by electronic charge fluctuations (not by magnetic origins here). Such quantum fluctuations might be responsible for the superconducting mechanism. In this case, the enhancement of T_c under high pressure would be related to the increase in those quantum fluctuations.

In the μSR experiment mentioned before, the analysis of the results implied the *triplet* electron pairing with nodal superconducting gaps [9]. On the basis of this proposal, some scenarios are suggested to understand the observed pressure effects on the superconductivity. The analysis of Quintanilla *et al.* indicated that the nonunitary triplet superconductivity appears in the limit of *weak* spin-orbit coupling (SOC). They furthermore predicted that with SOC, the nonunitary triplet instability will be split into two separate transitions, whose splitting must be quite small [15]. Suppose that such a spin-orbit interaction is increased with pressure. The higher one would no longer break the time-reversal symmetry (TRS), but the lower one would break it [15]. In the state of the higher transition, the superconductivity may have an s-wave character, and the transition temperature T_c would increase with pressure, as was mentioned before. The lower superconducting transition, unfortunately, is not observable in resistivity measurements such as this experiment. Another possibility to explain the increase of T_c may be related to the fact that the residual resistivity decreases with pressure. For the triplet state, T_c is expected to increase when the scattering by nonmagnetic impurities diminishes since the triplet pairings are rather sensitive to the nonmagnetic impurities. The decrease in the residual resistivity under high pressure might be correlated with the decrease in the impurity scatterings which are nonmagnetic.

Up to now, some experiments have indicated a possibility that the superconductivity of this system is an unconventional p-wave state with nodal energy gaps. As in the μSR experiment, quite recently a spontaneous magnetization was observed in magnetization measurements in a very low residual magnetic field [16]. This further supports the breaking of time-reversal symmetry in this system. However, some others suggested that this superconductivity is a conventional BCS type. Recently, a specific-heat measurement on a single crystal of $LaNiC_2$ was reported [17]. The authors asserted that their data can be fitted well to the conventional BCS exponential function even at low temperatures, contrary to the previous heat-capacity measurements. The superconducting pairing mechanism of this system is still controversial.

To conclude, the superconductivity at around 3 K in the noncentrosymmetric $LaNiC_2$ has been measured precisely under high pressures up to 30 GPa. The experiments show a large enhancement of T_c with pressures up to 3 GPa. This enhancement, however, is strongly suppressed with an emergence of a different state characterized by a high-energy scale. Consequently, the superconducting transition exhibits a dome with the induced state in the T-P phase diagram. This state is highly correlated with strong electronic interactions; therefore, the superconductivity of the system could be related to quantum fluctuations of this state. To further understand the superconductivity and its anomalous pressure effects of the noncentrosymmetric $LaNiC_2$, both experimental and theoretical studies of electronic states and the spin-orbit couplings under pressures are required. Experiments to clarify the physical properties of the strongly correlated electronic state induced under high pressures are now proceeding by the present authors.

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