Inorg. Chem. **2007**, *46*, 7719–7721

Inorganic Chemistry
Communication

Nickel-Based Oxyphosphide Superconductor with a Layered Crystal Structure, LaNiOP

Takumi Watanabe,[†] Hiroshi Yanagi,[†] Toshio Kamiya,[†,‡] Yoichi Kamihara,[‡] Hidenori Hiramatsu,[‡] Masahiro Hirano,[‡,§] and Hideo Hosono*,[†,‡,§]

Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama, Japan, ERATO-SORST, JST, in the Frontier Collaborative Research Center, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Japan, and Frontier Collaborative Research Center, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Japan

Received June 19, 2007

A layered oxyphosphide, LaNiOP, was synthesized by solid-state reactions. This crystal was confirmed to have a layered structure composed of an alternating stack of $(La^{3+}O^{2-})^{+}$ and $(Ni^{2+}P^{3-})^{-}$. We found that the resulting LaNiOP shows a superconducting transition at ∼3 K. This material exhibited metallic conduction and Pauli paramagnetism in the temperature range of 4–300 K. The resistivity sharply dropped to zero and the magnetic susceptibility became negative at <4 K, indicating that a superconducting transition occurs. The volume fraction of the superconducting phase estimated from the diamagnetic susceptibility reached ∼40 vol % at 1.8 K, substantiating that LaNiOP is a bulk superconductor.

Since the discovery of high-transition-temperature (high-T_c) Cu-based superconducting oxides, numerous efforts have been devoted to exploring higher T_c superconductors in a variety of other materials. One of the attractive systems is Cu-based and other transition-metal-based oxides because the high T_c reflects the strong electron correlation among 3d electrons. These efforts on cuprate oxides have led to discoveries of many superconductors with different crystal structures, which have raised T_c to 133 K.[1] In contrast, research on non-Cu-based compounds (oxide, pnictide, etc.) is less active because materials with a T_c higher than those of the Cu-based ones have yet to be discovered. However, the discovery of Sr_2RuO_4,[2] $Na_xCoO_2 \cdot yH_2O$,[3] electron-doped HfNCl,[4] and Li_xNbO_2[5] has largely impacted the physics and chemistry of superconductors; it has provided complementary information to better understand the mechanism of superconductivity and clues for exploring new material systems for higher T_c superconductors.

We have studied a series of quaternary oxyphosphides, LaMOP (M = divalent transition-metal cations such as Mn^{2+}, Fe^{2+}, and Co^{2+}), with the expectation of a new correlated electron system. These studies have led to the discovery of a new Fe-based superconductor, LaFeOP.[6] In this crystal structure, the LaO and MP layers are alternately stacked along the *c* axis, as shown in Figure 1. Systematic research on isostructural oxychalcogenides, LaCuOCh (Ch = S, Se, and Te), has indicated that the CuCh layer, which is sandwiched by larger-energy-gap LaO layers, works as a hole transport path.[7] As an analogue, the MP layer in LaMOP is also expected to be a carrier conduction layer sandwiched by the LaO insulating layers. This two-dimensional crystal structure, which contains transition-metal cations, has led to the expectation that interesting electronic and/or magnetic properties will be discovered based on the electron correlation. In this work, a new member in the LaMOP system, LaNiOP, which is another superconductor, is synthesized.

Samples were prepared by solid-state reactions of the starting materials, La (Shin-etsu Chemical, purity 99.5%), P (Rare Metallic, 99.9999%), and NiO (Kojundo Chemical Laboratory, 99.97%). First, a stoichiometric mixture of La metal powder and P was heated in an evacuated silica tube at 400 °C for 12 h, and subsequent heating at 700 °C for 6 h resulted in single-phase LaP. Then a stoichiometric mixture of LaP and NiO was pressed into a pellet, which was heated at 1000 °C for 1 day in an evacuated silica tube. The resulting sample was characterized by high-power X-ray diffraction

---

* To whom correspondence should be addressed. E-mail: hosono@msl.titech.ac.jp.

[†] Materials and Structures Laboratory, Tokyo Institute of Technology.

[‡] ERATO-SORST, JST.

[§] Frontier Collaborative Research Center, Tokyo Institute of Technology.

(1) Schilling, A.; Cantoni, M.; Guo, J. D.; Ott, H. R. *Nature (London)* **1993**, *363*, 56−58.

(2) Maeno, Y.; Hashimoto, H.; Yoshida, K.; Nishizaki, S.; Fujita, T.; Bednorz, J. G.; Lichtenberg, F. *Nature (London)* **1994**, *372*, 532−534.

(3) Takada, K.; Sakurai, H.; Takayama-Muromachi, E.; Izumi, F.; Dilanian, R. A.; Sasaki, T. *Nature (London)* **2003**, *422*, 53−55.

(4) Yamanaka, S.; Hotehama, K.; Kawaji, H. *Nature (London)* **1998**, *392*, 580−582.

(5) Geselbracht, M. J.; Richardson, T. J.; Stacy, A. M. *Nature (London)* **1990**, *345*, 324−326.

(6) Kamihara, Y.; Hiramatsu, H.; Hirano, M.; Kawamura, R.; Yanagi, H.; Kamiya, T.; Hosono, H. *J. Am. Chem. Soc.* **2006**, *128*, 10012−10013.

(7) Hiramatsu, H.; Kamioka, H.; Ueda, K.; Ohta, H.; Kamiya, T.; Hirano, M.; Hosono, H. *Phys. Status Solidi A* **2006**, *203*, 2800−2811.

10.1021/ic701200e CCC: $37.00

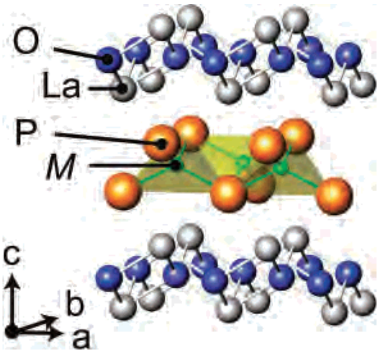

Figure 1. Crystal structure of LaMOP (M = divalent transition-metal cation). The yellow polyhedron indicates the MP_4 tetrahedron. LaO and MP layers are alternately stacked along the *c* axis.

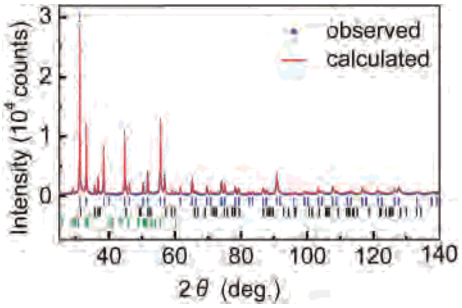

Figure 2. XRD pattern of LaNiOP measured (blue dots) and refined by the Rietveld method (red lines). Vertical bars at the bottom show the calculated positions of the Bragg diffractions of LaNiOP (upper), $LaNi_2P_2$ (middle), and La_3PO_7 (bottom, which only shows strong peaks).

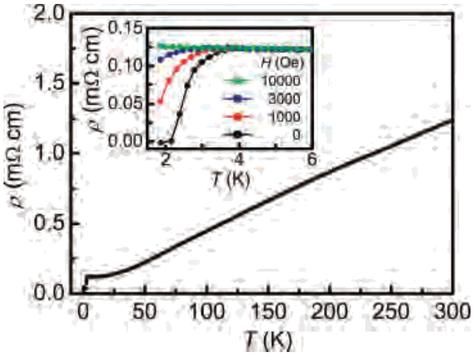

Figure 3. Temperature (*T*) dependence of the electrical resistivity (ρ) at 0 Oe. The inset shows the $\rho-T$ curves as a function of the magnetic field magnified in the temperature range of 1.9−10 K.

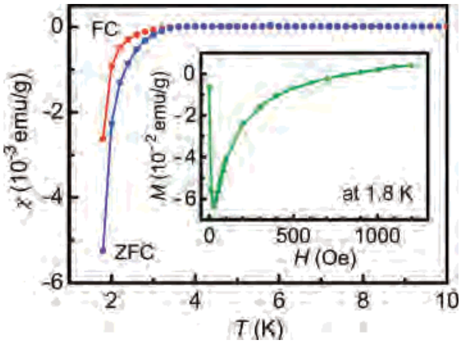

Figure 4. Temperature (*T*) dependence of the magnetic susceptibility (χ) in the temperature range of 1.8−10 K under conditions of ZFC and FC at 10 Oe. The inset shows the field (*H*) dependence of magnetization (*M*) at 1.8 K.

(XRD; D8 ADVANCE-TXS, Bruker AXS) with Cu Kα radiation. It was found that the highest phase purity sample obtained to date contains $LaNi_2P_2$ and La_3PO_7 as impurity phases. Thus, three-phase Rietveld analyses were carried out to extract the volume fractions of the impurities using the code TOPAS3.[8] The crystal structure of LaNiOP was refined with the space group of *P*4/*nmm*, and the initial structure parameters were taken from that of isostructural compound LaCoOP.[9]

The electrical resistivity of the sintered pellets (apparent density ~50%) was measured in the temperature range of 1.9−300 K by a four-probe technique (using PPMS, Quantum Design). Ohmic contacts were formed with a silver paste. The magnetic properties were measured with a superconducting quantum interference device magnetometer (SQUID, using MPMS, Quantum Design). The temperature dependence of the magnetic susceptibility was measured from 1.8 to 300 K under conditions of zero-field cooling (ZFC) and field cooling (FC) at $H_{FC} = 10$ Oe.

The obtained LaNiOP is chemically stable in air and dark gray. Figure 2 shows the XRD patterns measured (blue dots) and simulated by the Rietveld analysis using the refined result (red line). The three-phase Rietveld analyses reveal that the obtained sample is mainly LaNiOP with ~8 vol % of $LaNi_2P_2$ and <1 vol % of La_3PO_7. The refined crystal structure of LaNiOP is summarized in supplemental information, which shows that NiP_4 has a distorted tetrahedral coordination having two different P−Ni−P angles of 101.7° and 126.4°.

Figure 3 shows the temperature dependence of the electrical resistivity (ρ) at $H_{ext} = 0$ Oe. ρ at 300 K is very low, 1.2 mΩ·cm, and exhibits a metallic behavior at temperatures down to 4 K. The inset shows a magnified view in the temperature range of 1.9−6 K. The resistivity begins to drop around 4 K and becomes zero around 2 K. The onset temperature shifts to a lower temperature as H_{ext} increases, and the drop in ρ vanishes at $H_{ext} = 10\,000$ Oe. These results suggest that the obtained product exhibits a superconducting transition at ~3 K.

Figure 4 shows the temperature dependence of the magnetic susceptibility (χ) measured under ZFC and FC at 10 Oe. χ is very small and is nearly independent of the temperature between 4 and 300 K, implying Pauli paramagnetism. However, χ begins to drop and becomes negative at ~3 K. It reaches a large negative value of -5.3×10^{-3} emu/g at 1.8 K. These results, together with the zero resistance, clearly indicate that LaNiOP exhibits superconductivity at temperatures below 4 K. The volume fraction of the superconducting phase estimated from the χ value at 1.8 K is ~40 vol %. The $M-H_{ext}$ curve (field dependence of magnetization) in the inset shows that the increase in the negative magnetization is proportional to H_{ext} at $H_{ext} = \leq 20$ Oe and then decreases, indicating that χ is a constant value of ~40 vol % of the perfect diamagnetic phase when H_{ext} is ≤ 20 Oe and decreases to zero up to $H_{ext} = 800$ Oe. These

---

(8) Bruker AXS. *TOPAS*, version 3; Bruker AXS: Karlsruhe, Germany, 2005.

(9) Zimmer, B. I.; Jeitschko, W.; Albering, J. H.; Glaum, R.; Reehuis, M. *J. Alloys Compd.* **1995**, *229*, 238−242.

observations indicate that LaNiOP is a type II superconductor with lower and upper critical magnetic fields of $H_{c1} = \sim20$ Oe and $H_{c2} = \sim800$ Oe, respectively.

Herein, the effects of the impurity phases should be assessed. Among the impurity phases found in the XRD pattern, only $LaNi_2P_2$ shows an electronic conduction. Jeitschko and Reehuis have reported that $LaNi_2P_2$ does not exhibit a superconducting transition down at least to 1.8 K.[10] We also measured the $M-H$ curves of single-phase $LaNi_2P_2$ samples at 2 K and confirmed that they do not show diamagnetism. In addition, the volume fractions of the $LaNi_2P_2$ (∼8 vol %) and La_3PO_7 (<1 vol %) phases are safely smaller than that of the superconducting phase (∼40 vol %). Accordingly, we conclude that LaNiOP becomes a superconducting phase at <4 K. Ni-based superconductors, $LnNi_2B_2C$ (Ln = Y, Tm, Er, Ho, and Lu) and $La_3Ni_2B_2N$,[11,12] have been reported by Cava et al. as high-T_c intermetallic superconductors; T_c of $LuNi_2B_2C$ and $La_3Ni_2B_2N$ are 16.6 and 13.2 K, respectively. The crystal structures of these superconductors have layered structures similar to that of LaNiOP: Ni is tetrahedrally coordinated by not P but B, and the LaO layers with the PbO-type structure in LaNiOP are replaced by rocksalt-type layers.

In summary, a layered compound of LaNiOP was first synthesized by solid-state reactions. It exhibits a type II superconducting transition of ∼3 K with a lower critical magnetic field of ∼20 Oe and an upper field of ∼800 Oe. Systematic study on the derivatives of LaMOP by replacing La, M, and P with other lanthanides, transition metals, and N group elements, respectively, would help to understand the superconductivity mechanism and lead to the discovery of a new superconductor.

Supporting Information Available: X-ray crystallographic data for LaNiOP in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701200E

---

(10) Jeitschko, W.; Reehuis, M. *J. Phys. Chem. Solids* **1987**, *48*, 667−673.

(11) Cava, R. J.; Takagi, H.; Zandbergen, H. W.; Krajewski, J. J.; Peck, W. F., Jr.; Siegrist, T.; Batlogg, B.; van Dover, R. B.; Felder, R. J.; Mizuhashi, K.; Lee, J. O.; Eisaki, H.; Uchida, S. *Nature (London)* **1994**, *367*, 252−253.

(12) Zandbergen, H. W.; Jansen, J.; Cava, R. J.; Krajewski, J. J.; Peck, W. F., Jr. *Nature (London)* **1994**, 372, 759−761.