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Stoichiometry, Spin Fluctuations, and Superconductivity in LaNiPO

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Abstract

Superconductivity in LaNiPO is disrupted by small ($\sim 5\%$) amounts of non-stoichiometry on the lanthanum site, even though the electronic contribution to the heat capacity increases with increasing non-stoichiometry. All samples also exhibit specific heat anomalies consistent with the presence of ferromagnetic spin fluctuations ($T_{sf} \approx 14K$). Comparison of layered nickel phosphide and nickel borocarbide superconductors reveals different structure-property correlations in the two families.

Introduction

Superconductors based on two dimensional Fe_2As_2 planes containing layers of edge-sharing Fe-As tetrahedra have received considerable attention, with T_c 's reaching as high as $55 K$ ¹⁻¹¹. Structurally related compounds based on nickel have also been reported¹²⁻¹⁵, but have been the subject of fewer studies due to their lower transition temperatures and band structure calculations suggesting that the Ni variants are 'normal' electron-phonon superconductors^{16, 17}. Of the known Ni-P compounds, $BaNi_2P_2$ is superconducting at $3 K$ ¹³ and $La_3Ni_4P_4O_2$ at $2.2 K$ ¹². LaNiPO has been reported to superconduct at $3 K$ ¹⁵ or $4.2 K$ ¹⁴, with no apparent explanation for the difference in T_c . Here we show that LaNiPO containing $\sim 4\%$ oxygen vacancies is superconducting at $4.2 K$, but that a La deficiency of 5% is sufficient to kill the superconductivity, despite a 25% increase in the Sommerfeld coefficient. Furthermore, there is an extra contribution to the specific heat that

characteristic of ferromagnetic spin fluctuations, suggesting that spin interactions may play a role in the observed superconductivity in LaNiPO.

Experimental

Three polycrystalline samples of LaNiPO, designated “A”, “B”, and “C”, were prepared in the same fashion. Stoichiometric quantities of dried La_2O_3 , fresh La shavings, Ni_5P_4 (prepared by reaction of Ni and P by slow heating from 400 to 800 °C), and purified and dried P were pressed into pellets, placed in dry alumina crucibles, sealed in evacuated silica ampoules, and heated from 750 °C to 1050 °C over 1 hr. Each sample was then reground, repressed, placed back in an alumina crucible in an evacuated quartz tube with 2% excess P, and heated at 1200 °C overnight. After that, each sample was reground, repressed, placed in an alumina crucible in a quartz tube backfilled with 1/3 atm Ar (99.999%), and heated at 1200 °C overnight. This final step was repeated once for “A” and “B”, and three times for “C”. Neutron diffraction (NPD) data were collected at the NIST Center for Neutron Research on the BT-1 powder neutron diffractometer with neutrons of wavelength 1.5403 Å produced by a Cu(311) monochromator. Collimators with horizontal divergences of 15' and 20' of arc were used before and after the monochromator, and a collimator with a horizontal divergence of 7' was used after the sample. Data were collected in the 2θ range of 3°–168° with a step size of 0.05°. Rietveld refinements of the structures were performed with GSAS¹⁸ using the EXPGUI¹⁹ interface. The neutron scattering amplitudes used in the refinements were La = 0.824, Ni = 1.030, P = 0.513 and O = 0.581×10^{-12} cm respectively. Physical property characterizations were performed on a Quantum Design Physical Properties Measurement System equipped with a ^3He refrigerator.

Results and Discussion

Despite being prepared in nominally the same way, each of the three samples of LaNiPO exhibit different superconducting properties. Fig. 1 shows zero field cooled DC susceptibility data for each sample. Samples “A” and “B” both display bulk superconductivity, with transition temperatures of 4.2 K and 3.2 K respectively. The bulk nature of the superconductivity in samples “A” and “B” is confirmed by the presence of anomalies in the specific heat at T_c (inset). In contrast, sample “C” displays only a trace of superconductivity.

Rietveld refinement of NPD data was used to understand the differences between the three samples. The structure of LaNiPO consists of Ni_2P_2 layers of edge-sharing Ni-P tetrahedra, separated by La-O₂-La units (Fig. 2(a) inset). In the unit cell, only the positions along the c axis of the lanthanum and phosphorus are not fixed by symmetry. Structural parameters were freely refined in the fits, including isotropic thermal parameters for all atoms, one positional parameter for La and P, and the occupancies of the La and O sites. The occupancies of the Ni and P sites were found not to deviate significantly from full occupancy and were therefore fixed at one for the final refinements. None of the samples are stoichiometric: all were found to be slightly (4-5%) oxygen deficient. A typical fit is shown in Fig. 2(a), and final refinement atomic parameters and agreement values are shown in Table I. The lanthanum and phosphorus positional parameters and the oxygen site occupancies are the same for all samples within the standard deviations. However, the refined occupancy of the lanthanum site in non-superconducting sample “C” (0.951(13)) is less than that in the best superconductor, “A” (0.995(9)). This is statistically significant at the 4σ level. As a further confirmation that sample “C” is lanthanum deficient, a second series of refinements was performed in a fashion that minimizes correlations between occupancy and thermal parameters: occupancies were fixed at a systematic series of values near the optimal, and all other parameters were allowed to refine freely. A plot of the fit

quality factor versus La occupancy from such refinements is shown in Fig. 2(b) for each of the three samples. While the La content of “A” and “B” are very similar, the best fit (minimum) for “C” occurs at a lower La occupancy. In addition, there is a small amount of La_2O_3 impurity phase (3%) in sample “C” that is not present in “A” or “B”; this is also consistent with a lower La content of the main phase. Thus the structure refinements and property characterizations indicate that lanthanum deficiency destroys superconductivity in LaNiPO .

The normal state electronic contributions to the specific heat are consistent with the differences in stoichiometry. The region above T_c is not linear on a C/T vs. T^2 plot for any of the samples, even when the superconductivity has been suppressed by application of a 9 T magnetic field (Fig. 3(a) inset). Instead, there is an upturn at low temperatures, suggestive of spin fluctuations. The low temperature specific heat for a spin fluctuation system is

$C = \gamma T + \beta_3 T^3 + AT^3 \ln(T/T_{sf})^{20}$, which includes contributions from the electrons, the lattice, and spin fluctuations respectively. Using the rules of logarithms, this can be rewritten in a form suitable for data fitting, $C/T = \gamma + \beta T^2 + AT^2 \ln(T)$, where $\beta = \beta_3 - A \ln(T_{sf})$. This expression fits the observed data very well (Fig. 3(a)). To fit the upturns below 1 K seen for two of the high field measurements, a B/T^3 contribution to C/T , representing the high temperature part of a nuclear Schottky anomaly, was also included. A similar anomaly was observed in LaFePO^{21} and LaNiAsO^{22} , and is ascribed to the freezing out of $^{139}\text{La}(S=7/2)$ nuclear spins. The fitted values are tabulated in Table II. Under zero field, the Sommerfeld coefficient (γ) is significantly different for the three samples. The superconductor with the highest transition temperature, “A”, has $\gamma = 5.1(2) \frac{\text{mJ}}{\text{molNiK}^2}$. γ increases as T_c decreases (“B”, $\gamma = 5.4(2) \frac{\text{mJ}}{\text{molNiK}^2}$) and finally is largest when superconductivity disappears (“C”, $\gamma = 6.5(2) \frac{\text{mJ}}{\text{molNiK}^2}$). This increase in the electronic contribution to the specific heat is consistent with greater chemical doping in “B” and “C”,

which apparently arises as a result of the lanthanum deficiency found in the NPD refinements (Fig. 3(b) inset). In contrast, the spin fluctuation contributions are similar for the three samples. From the definition $\beta = \beta_3 - A \ln(T_{sf})$, a plot of β versus A should be linear, with slope $-\ln(T_{sf})$ and intercept β_3 , corresponding to the spin fluctuation and lattice contributions respectively. A straight line is observed for all of the fitted values of β and A (Fig. 3(b)). Furthermore, there is no substantial difference of the spin fluctuation contribution between the three samples: within error, all lie on the same line. The extracted lattice contribution is $\beta_3 = 0.278(9) \frac{mJ}{molNiK^4}$, corresponding to a Debye temperature of $\theta_D = 300K$. This Debye temperature is similar to what has been observed for LaFePO²¹ and LaNiAsO²². The calculated spin fluctuation temperature is $T_{sf} = 14K$. This is remarkably similar to the value obtained for LaFePO ($T_{sf} = 14.3K$ ²¹), and suggests that similar phenomena may be occurring in both compounds. This low value of T_{sf} is consistent with the observed decrease in the Sommerfeld coefficient under an applied field (Table II, all three samples), where the field tends to suppress the mass enhancement due to the spin fluctuations²⁰. Quantitative analysis of the dependence of γ on applied field was not performed due to the large uncertainties in the values.

Conclusion

All samples show the presence of 4-5% oxygen vacancies, but whether this non-stoichiometry is necessary for superconductivity was not addressed in the current study. It is found that 5% La vacancies are sufficient to suppress superconductivity, despite a 25% increase in the Sommerfeld coefficient. We speculate that prolonged heating in silica tubes with trace amounts of oxygen is what results in the lanthanum deficiency. The presence of spin fluctuations, and the fact that T_c is highest in the samples with the smallest γ , suggests that the origin of the superconductivity in LaNiPO is unconventional. A comparison to related Nickel

compounds supports this hypothesis. Fig. 4 shows the observed superconducting transition temperatures of Ni_2P_2 - and Ni_2As_2 - based materials^{12-14, 23-26}. As the across-plane X-Ni-X bond angle decreases (i.e. as the tetrahedron becomes less ideal), T_c increases. This is even as the Nickel atoms in the square planes get further apart. This is in contrast to the nickel borocarbide superconductors²⁷⁻³¹, which contain Ni_2B_2 -layers analogous to the Ni_2P_2 and Ni_2As_2 layers, where T_c goes up at the Nickel-Nickel distances decrease and the tetrahedra become more ideal (Fig. 4). This suggests that further study of the Ni_2P_2 -based materials should be carried out to determine if spin fluctuations play a role in the observed superconductivity.

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Table 1. Refined structural parameters for three samples of LaNiPO at 298 K from powder neutron data. Space group $P4/nmm$ (# 129). Atomic positions: **La**: 2c (1/4,1/4,z), **Ni**: 2b (3/4,1/4,1/2), **P**: 2c (1/4,1/4,z), **O**: 2a (3/4,1/4,0). Lattice parameters are in units of $\text{\AA}$, and thermal parameters are in units of $10^{-2} \text{\AA}^2$. All samples contain small a impurity phase of LaNi_5P_3 . “A” sample also contains <1% $\text{La}_3\text{Ni}_4\text{P}_4\text{O}_2$.

LaNiPO		“A”	“B”	“C”
La	a	4.04669(6)	4.04768(7)	4.04766(9)
	c	8.1089(2)	8.1104(2)	8.1102(3)
	z	0.1530(2)	0.1529(3)	0.1529(3)
	U _{iso}	0.78(5)	0.63(6)	0.44(7)
	occ	0.995(9)	0.985(11)	0.951(13)
Ni	U _{iso}	1.33(4)	1.35(5)	1.48(6)
P	z	0.6244(4)	0.6246(5)	0.6247(6)
	U _{iso}	1.42(6)	1.45(8)	1.67(10)
O	U _{iso}	0.51(6)	0.22(7)	0.19(9)
	occ	0.966(9)	0.951(11)	0.954(13)
χ^2		1.136	0.9846	1.134
R _{wp}		5.58%	5.65%	5.83%
R _p		4.55%	4.53%	4.73%
R(F ²)		8.27%	12.49%	15.91%

Table 2. Parameters extracted from fits of the low temperature specific heat of the LaNiPO samples under applied magnetic fields. The fit is to the equation $C/T = \gamma + \beta T^2 + AT^2 \ln(T)$. A B/T^3 contribution to C/T , representing the high temperature part of a nuclear Schottky anomaly, was also included for the 9 T fits. The data ranges used were 0.4 to 10 K for 3+ T fields, and 5.5 to 10 K for fields < 3 T (to avoid the superconducting transition contribution).

	Field	γ (mJ/mol*K ²)	β (mJ/mol*K ⁴)	A (mJ/mol*K ⁴)	B (mJ*K/mol)
“A”	0 T	5.1(2)	-0.0101(15)	0.1140(53)	-
	9 T	4.3(1)	0.106(10)	0.0680(40)	-
“B”	0 T	5.4(2)	0.0046(16)	0.1023(65)	-
	9 T	4.5(1)	0.1303(26)	0.0540(5)	0.05(2)
“C”	0 T	6.5(2)	-0.0220(23)	0.1119(9)	-
	1 T	6.0(3)	0.0700(28)	0.080(11)	-
	3 T	5.96(3)	0.064(6)	0.0840(28)	-
	5 T	5.79(3)	0.0773(53)	0.0782(23)	-
	9 T	5.3(1)	0.0828(17)	0.0763(74)	0.091(8)

Figure 1. DC magnetization and specific heat data show that superconductivity in LaNiPO is very sensitive to small changes in composition. The best samples superconduct at 4.2 K. All samples contain 4-5% oxygen vacancies. Superconductivity is suppressed by a 5% lanthanum deficiency.

Figure 2. (a) Final NPD refinement of the sample showing the highest T_c , "A". (b) Plots of the refinement statistic χ^2 (normalized for when $x = 1$) versus lanthanum occupancy, demonstrating that "C", which shows little superconductivity, is the most La-deficient.

Figure 3. (a) The specific heat data on all three samples under various applied fields are well described by including spin fluctuations as well as electronic and lattice terms (see text). Inset shows plots of C/T vs T^2 at 9 T. (b) A plot of β vs A is linear, allowing extraction of both the lattice contribution and the characteristic spin fluctuation temperature (see text). All three samples show the same characteristic temperature. However, an increase in the zero field Sommerfeld coefficient correlates with both a decrease in T_c and greater La deficiency (inset).

Figure 4. LaNiPO and the other Ni_2P_2 -based superconductors form a single family where greater T_c 's correlate with less ideal (more stretched, greater Ni-Ni distance) Ni-P tetrahedra. The nickel-arsenide compounds show a similar dependence. This is in contrast to the nickel borocarbide superconductors (structurally based on Ni_2B_2 planes), where T_c increases when the Ni-B tetrahedra become more regular (less stretched, closer Ni-Ni distance).

Figure 1

Figure 2

Figure 3

Figure 4

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