Superconductivity without Fe or Ni in the phosphides BaIr$_2$P$_2$ and BaRh$_2$P$_2$

N. Berry, C. Capan, G. Seyfarth, A. D. Bianchi, J. Ziller, and Z. Fisk

$^1$Department of Physics and Astronomy, University of California–Irvine, Irvine, California 92697-4575, USA
$^2$Département de Physique, Université de Montréal, Montréal, Canada H3C 3J7
$^3$Department of Chemistry, University of California–Irvine, Irvine, California 92697-4575, USA

(Received 24 February 2009; published 5 May 2009)

Heat capacity, resistivity, and magnetic susceptibility measurements confirm bulk superconductivity in single crystals of BaIr$_2$P$_2$ ($T_c=2.1$ K) and BaRh$_2$P$_2$ ($T_c=1.0$ K). These compounds form in the ThCr$_2$Si$_2$ (122) structure so they are isostructural to both the Ni and Fe pnictides but not isoelectronic to either of them. This illustrates the importance of structure for the occurrence of superconductivity in the 122 pnictides. Additionally, a comparison between these and other ternary phosphide superconductors suggests that the lack of interlayer P-P bonding favors superconductivity. These stoichiometric and ambient pressure superconductors offer an ideal playground to investigate the role of structure for the mechanism of superconductivity in the absence of magnetism.

DOI: 10.1103/PhysRevB.79.180502 PACS number(s): 74.70.Dd, 74.10.+v, 74.25.Bt, 74.25.Fy

Rare-earth intermetallics in the ThCr$_2$Si$_2$(122) structure have been extensively studied due to their many interesting properties, such as superconductivity (SC), heavy fermion behavior, exotic magnetic order, and quantum criticality. The recent discovery of superconductivity in iron pnictides, first in LaFeAsO at 26 K and soon after in the AF$_2$As$_2$ (A =alkali metal) family, has ignited new interest in non-Cu-based high-$T_c$ SC. The ternary compounds AF$_2$As$_2$ form in the tetragonal 122 structure and contain the same building blocks of FeAs planes as LaFeAsO which forms in the tetragonal ZrCuSiAs(1111) structure. Band-structure calculations show a Fermi surface almost exclusively formed by Fe $d$ bands. $T_c$'s are also very tunable with pressure or chemical substitution, and critical temperatures ($T_c$) have reached as high as 55 K in SmFeAs(O,F) and 38 K in (Ba,K)Fe$_2$As$_2$. In both families of compounds, SC is seen to emerge from the suppression of a commensurate antiferromagnetic order with pressure or doping. Moreover, the long-range magnetic order is preceded by (concomitant to) a structural transition in the 1111 (122) compounds. So far, much research has been focused on the magnetic transition metal elements Fe and Ni with As in place of Si in the ThCr$_2$Si$_2$ structure. The mechanism for SC is still a matter of intensive debate and investigation in these compounds.

The As atom can be replaced by the isoelectronic element P forming ternary phosphides in the same 122 structure, as first investigated by Jeitschko and Reehuis and Jeitschko et al. While SC has not been reported in stoichiometric Fe-based ternary phosphides at ambient pressure, it has been observed in LaRu$_3$P$_2$, BaNi$_2$P$_2$, and SnNi$_2$P$_2$ with $T_c$'s $\leq$4 K. Most ternary phosphides grown with Co exhibit local magnetic moment order unlike their Fe or Ni counterparts. Isostructural transitions (tetragonal to collapsed tetragonal) have also been reported in the ternary phosphides under pressure. Unlike their As counterparts, these compounds do not show a concomitant magnetic transition, except EuCo$_2$P$_2$ with its Eu moment ordering.

This Rapid Communication reports on single-crystal SC in the Co column for the 122 phosphides, namely, in BaIr$_2$P$_2$ and BaRh$_2$P$_2$. This finding emphasizes the importance of the 122 structure for the stability of SC since it occurs in the Fe, Co, and Ni columns of the periodic table. Rh and Ir are nonmagnetic elements in the Co column, between the Fe and Ni columns. This provides the opportunity to investigate SC without infringing upon local magnetic moments known to be detrimental to conventional SC. Further we show from structural analysis that the interlayer P-P bonding might be a relevant parameter for the occurrence of SC in the 122 phosphides.

Single crystals were grown via the standard metal flux technique. The single crystals of BaRh$_2$P$_2$ and CaRh$_2$P$_2$ were grown in Pb flux with a ratio of 1.3:2:2:40. For BaIr$_2$P$_2$, Cu was added to the Pb flux, to increase solubility, with molar ratios of 1.3:2:2:40:5(Ba:Ir:P:Pb:Cu). The mixtures were placed inside an alumina crucible and then sealed in quartz ampoules with inert atmospheres. All three batches were heated at 1150 °C for 168 h and slowly cooled at a rate of 4 °C/h to 450 °C, at which point the excess flux was decanted. The samples were etched in HCl to remove any excess flux. We have also obtained BaIr$_2$P$_2$ in polycrystalline form from solid-state reaction by mixing stoichiometric amounts of each element and heating it at 900 °C for 100 h and then quenched to 300 K.

The reaction results are first identified by powder x-ray diffraction. Figure 1 shows the intensity vs scattering angle $\Theta$ for BaRh$_2$P$_2$ single crystals and for polycrystalline BaIr$_2$P$_2$ powder. The polycrystalline powder has a composition of 85% BaIr$_2$P$_2$, 10% Ba$_3$(PO$_4$)$_2$, and only a few percent of Ir$_2$P and IrP$_2$ binaries. Additional peaks in the BaRh$_2$P$_2$ spectra are from the Pb flux. Single crystals of both BaRh$_2$P$_2$ and BaIr$_2$P$_2$ are also characterized by a rotating crystal x-ray diffractometer. The Rietveld refinement results are shown in Table I and agree with previous reports.

Magnetic properties are measured using a commercial superconducting quantum interference device (SQUID) vibrating sample magnetometer. Heat capacity (C) has been measured using a quasadiabatic heat pulse technique in a physical properties measurement system (PPMS). The resistivity is measured on a LR700 ac resistance bridge using Pt wires.
FIG. 1. (Color online) Intensity vs scattering angle Θ obtained in powder x-ray diffraction for BaRh$_2$P$_2$ (single crystals) and BaIr$_2$P$_2$ (polycrystals). The vertical lines correspond to the reference pattern of BaRh$_2$P$_2$, Pb, and Ba$_3$(PO$_4$)$_2$.25 The inset represents the tetragonal unit cell of BaRh$_2$P$_2$.

attached with silver paint. The single crystals of BaIr$_2$P$_2$ were too small for reliable heat capacity and magnetization measurements, so these were carried out on polycrystalline pellets.

The temperature ($T$) dependence of resistivity ($\rho$) in single crystals of BaIr$_2$P$_2$ and BaRh$_2$P$_2$ is shown in Fig. 2(a) from 300 down to 0.5 K. The high quality of crystals is evidenced by the large residual resistivity ratios (RRR = $\rho(300$ K)/$\rho(3$ K)) = 16.5 in BaIr$_2$P$_2$ and 7.5 in BaRh$_2$P$_2$ as well as by the low values of the residual resistivities (8.7 and 1.2 $\mu\Omega$ cm in Ir and Rh samples). In both systems, $\rho(T)$ exhibits a $T$-linear dependence above 100 K without any sign of saturation up to 300 K. There is no evidence for structural or magnetic transitions in $\rho$ up to 300 K. At low temperatures, a sharp drop to $\rho=0$ indicates the onset of SC at $T_c$ = 2.1 K in BaIr$_2$P$_2$ and 1 K in BaRh$_2$P$_2$.

The temperature and magnetic field dependence of magnetization ($M$) are shown in Figs. 2(b) and 2(c) for polycrystalline BaIr$_2$P$_2$. The diamagnetic jump in $M(T)$ corresponds to the same $T_c$ as determined from $\rho(T)$. The magnetization loop $M(H)$ at 1.8 K shows hysteresis and rather broad extrema. The average of their field positions (necessary due to trapped flux in the magnet) yields 45 Oe as an upper bound for the lower critical field $H_{c1}$ (we adopt the type-II SC scheme since the critical field determined by $\rho(T,H)$ and $C(T,H)$ is significantly higher; see below). The slope of $M(H)$ below $H_{c1}$ is used to estimate that 100% of the volume is superconducting.

The bulk nature of SC is also confirmed with a sharp anomaly in $C(T)$, observed in both compounds [Figs. 3(a) and 3(b)]. The good agreement between the thermodynamic and resistive $T_c$ and the sharpness of the transition even for the polycrystalline sample imply that $T_c$ does not show any distribution. At zero field, the ratio $\frac{\Delta C}{\gamma T_c}$ equals 1.41 and 1.17 for BaIr$_2$P$_2$ and BaRh$_2$P$_2$, consistent with Bardeen-Cooper-Schrieffer (BCS) theory. The values of the electronic specific heat coefficient $\gamma$ are obtained from a linear fit to $\frac{\Delta C}{\gamma T^2}$ in the range 0.4–2.4 K (BaIr$_2$P$_2$) and 0.5–1.0 K (BaRh$_2$P$_2$) (see Table I). The $\gamma$ and $T_c$ shown here are consistent with those reported on polycrystals.25

The suppression of $T_c$ with magnetic field is seen in $\frac{\Delta C}{\gamma T_c}$ [Figs. 3(a) and 3(b)] and $\rho(T)$ [Figs. 3(c) and 3(d)]. In both compounds, the superconducting transition in $\rho(T)$ remains rather sharp, even under magnetic fields as high as 200 Oe. This suggests a rather strongly pinned vortex lattice. The specific-heat anomaly also remains sharp for the BaRh$_2$P$_2$ single crystals up to 150 Oe [see Fig. 3(b)] but broadens with field for the polycrystalline BaIr$_2$P$_2$ [see Fig. 3(a)]. The possible anisotropy of the upper critical field has not been investigated and might be responsible for this broadening. The corresponding $H-T$ phase diagram is shown in Fig. 4. There is a good agreement between the values obtained from resistivity and specific heat for both compounds. The use of the approximation $H_{c2}(0) = -0.71 \frac{\rho_{\rho c}}{\rho(T)} T_c$ yields $H_{c2}(0) = 410$ and 370 Oe in BaIr$_2$P$_2$ and BaRh$_2$P$_2$. These values of $H_{c2}(0)$ are comparable to SrNi$_2$P$_2$(390 Oe)15 and BaNi$_2$P$_2$(550 Oe)15 but

FIG. 2. (Color online) (a) Resistivity (normalized) vs temperature in the range of 0.5–300 K in single crystals of BaIr$_2$P$_2$ and BaRh$_2$P$_2$. (b) Magnetization vs temperature in polycrystalline BaIr$_2$P$_2$ showing a diamagnetic jump at $T_c$ = 2.1 K in a field of 10 G. (c) Magnetization vs magnetic field ($H$) at $T$ = 1.8 K for the same sample.

### Table I. Structural parameters and physical properties.

| Compound     | $a$ (Å)  | $c$ (Å)  | $d_{P-P}$ (Å) | $T_c$ (K) | $\gamma$ (mJ/mol K$^2$) |
|--------------|----------|----------|---------------|-----------|-------------------------|
| BaIr$_2$P$_2$| 3.9469(8)| 12.559(5)| 3.688(2)      | 2.1 ± 0.04| 9.3 ± 0.6               |
| BaRh$_2$P$_2$| 3.9308(3)| 12.574(2)| 3.725(1)      | 1.0 ± 0.04| 9.2 ± 0.3               |
| CaRh$_2$P$_2$| 4.0179(3)| 9.655(1) | 2.241(1)      |           | 10.7 ± 0.2              |
smaller than those cited in the study of Hirai et al.\textsuperscript{25} The broadness of the transitions in polycrystals\textsuperscript{25} may be the source of the discrepancies. From our values of $H_{c2}(0)$ we estimate the coherence lengths to be 80 and 95 nm for BaIr$_2$P$_2$ and BaRh$_2$P$_2$, respectively.

Figure 3(d) shows a pronounced upturn in $\rho(T)$ preceding the onset of the superconducting jump in BaRh$_2$P$_2$. The resistivity rises about 100% in the temperature interval 1.35–1 K at zero field. The onset of the upturn is suppressed with magnetic field but its amplitude is unaffected. Moreover, this suppression does not appear to be correlated with the upper critical field $H_{c2}(T)$, as seen in Fig. 4, suggesting separate phenomena. We have verified that the upturn is present in a second crystal of BaRh$_2$P$_2$ of similar RRR, as well as in a polycrystalline pellet, but found that the amplitude of the upturn is sample dependent. A smaller upturn is also observed in single crystal BaIr$_2$P$_2$ above 700 Oe, but it is absent at zero field in this sample. Such an upturn is also reported in SrNi$_2$P$_2$\textsuperscript{16} and LaFePO.\textsuperscript{26} In addition, a sample-dependent Curie tail has been frequently observed in the low-temperature susceptibility, with an associated Brillouin-type behavior in $M$ vs $H$ for single crystals of both compounds (not shown). The sample-to-sample variation in this magnetic behavior is suggestive of an extrinsic origin, although the corresponding concentration of spin 1/2 is far in excess of the level of magnetic impurities contained in the starting materials ($\leq20$ ppm). Their origin remains unclear and is beyond the scope of this Rapid Communication.

We now turn to the relationship between the 122 structure and SC in pnictides. BaFe$_2$As$_2$ is a prime example of the flexibility of this structure on the route to SC: it has been shown that pressure and doping on all three atomic sites have independently induced SC.\textsuperscript{4,9,10,27} However, in the isoelectronic CaFe$_2$As$_2$ the existence of SC is highly controversial.\textsuperscript{28,29} Moreover, in CaFe$_2$As$_2$, recent theoretical calculations show an intimate connection between the Fe-spin state and the interlayer As-As bonding.\textsuperscript{30} Future studies should clarify the effect of the Fe moments on $T_c$. In addition, BaRh$_2$As$_2$ exhibits no superconductivity down to 1.8 K.\textsuperscript{31} Thus, the relationship between the tetragonal structure and SC is not clear at present in the 122 arsenides. The present phosphides allow the investigation of the relationship between SC and structure without the interference of magnetism since neither Rh nor Ir is intrinsically magnetic.

In the ternary phosphides there is an isostructural transition into a collapsed tetragonal structure,\textsuperscript{18} similar to CaFe$_2$As$_2$.\textsuperscript{28,29} except that it does not appear to be associated with any magnetic order.\textsuperscript{16} Previous investigations in BaRh$_2$P$_2$ did not show any structural transition up to 11 GPa and down to low temperatures\textsuperscript{18} (no reports for BaIr$_2$P$_2$). In the phoshpides, unlike the arsenides, proximity to a structural transition is not a prerequisite for SC. It is known that this isostructural transition corresponds to the formation or breaking of a bond between the interlayer P atoms.\textsuperscript{32} In the absence of P-P bond, the cohesion of the layers is due to the Coulomb attraction through the intermediate A$^{2+}$ cation.\textsuperscript{33} The critical distance for bond formation obtained theoretically is about $d_c \approx 2.8$ Å between the interlayer P atoms, labeled $d_{P-P}$ in the inset of Fig. 1.\textsuperscript{33} We found that both BaRh$_2$P$_2$ and BaIr$_2$P$_2$ have a $d_{P-P}$ of $\approx 3.7$ Å (see Table I) indicating the absence of interlayer bonding between the P atoms, which is consistent with structural calculations.\textsuperscript{32} In contrast, CaRh$_2$P$_2$ has a $d_{P-P}$ of only 2.25 Å, which is below the critical distance for bond formation. We have also grown single crystals of CaRh$_2$P$_2$ and found no evidence of SC down to 0.55 K. This suggests that the absence of bonds favors SC.

The absence of P-P bonds is also found in other superconducting phosphides, such as BaNi$_2$P$_2$ which has $d_{P-P}=3.71$ Å.\textsuperscript{34} In fact, none of the known ternary phosphides [BaIr$_2$P$_2$, BaRh$_2$P$_2$, BaNi$_2$P$_2$,\textsuperscript{15} and LaRu$_2$P$_2$\textsuperscript{14}] that exhibit ambient pressure SC in the tetragonal structure are bonded between the interlayer P atoms. Nevertheless, it is interesting that LaRu$_2$P$_2$, with the highest $T_c$, at 4.1 K, lies closest (3.00 Å) to the theoretical structural instability while
still being in the nonbonding state.\textsuperscript{14} However, SrNi$_2$P$_2$ shows SC in the collapsed tetragonal phase under pressure where a bond exists between the layers.\textsuperscript{16} Since the ambient pressure orthorhombic phase is also superconducting, it is hard to assess the importance of the structure for SC in this case. De Haas—van Alphen results of BaNi$_2$P$_2$ show a three-dimensional (3D) Fermi surface dominated by the Ni $d$ bands, indicating that the effect of interlayer coupling on the electronic dimensionality is small.\textsuperscript{35} Our results lay the groundwork for more theoretical investigations in order to clarify the relationship between the interlayer bonding and the mechanism for SC in the nonmagnetic 122 phosphides.

In conclusion, we have shown the existence of bulk weak coupling SC in 122 pnictides in the Co column of the periodic table with nonmagnetic transition metals Rh and Ir. This emphasizes the importance of the 122 structure and the robustness of SC with respect to changes in the electronic configuration, opening the door for SC in other non-Fe-based compounds. Also, these findings suggest that the lack of interlayer bonding favors SC. It is important to understand how the structure affects SC in the ternary and quaternary pnictides in the absence of competing magnetic order. Due to the apparent lack of magnetism, BaIr$_2$P$_2$ and BaRh$_2$P$_2$ provide convenient systems in which to study the interplay between structure and SC.

This research was supported with funding from NSF (Contract No. DMR 0854781). A.D.B. received support from Natural Sciences and Engineering Research Council of Canada, Fonds Québécois de la Recherche sur la Nature et les Technologies, and Canada Research Chair Foundation.

\begin{thebibliography}{99}
\bibitem{1} F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schafer, Phys. Rev. Lett. \textbf{43}, 1892 (1979).
\bibitem{2} O. Trovarelli, C. Geibel, S. Mederle, C. Langhammer, F. M. Grosche, P. Gegenwart, M. Lang, G. Sparn, and F. Steglich, Phys. Rev. Lett. \textbf{85}, 626 (2000).
\bibitem{3} Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. \textbf{130}, 3296 (2008).
\bibitem{4} M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. \textbf{101}, 107006 (2008).
\bibitem{5} P. Quebe, L. J. Terb"{u}chte, and W. Jeitschko, J. Alloys Compd. \textbf{302}, 70 (2000).
\bibitem{6} D. Kasinathan, A. Ormeci, K. Koch, U. Burkhardt, W. Schnelle, A. Leithe-Jasper, and H. Rosner, New J. Phys. \textbf{11}, 025023 (2009).
\bibitem{7} R. Zhi-An \textit{et al.}, Chin. Phys. Lett. \textbf{25}, 2215 (2008).
\bibitem{8} K. Sasmal, B. Lv, B. Lorenz, A. M. Guloy, F. Chen, Y.-Y. Xue, and C.-W. Chu, Phys. Rev. Lett. \textbf{101}, 107007 (2008).
\bibitem{9} A. S. Sefat, R. Jin, M. A. McGuire, B. C. Sales, D. J. Singh, and D. Mandrus, Phys. Rev. Lett. \textbf{101}, 117004 (2008).
\bibitem{10} P. L. Alireza, Y. T. C. Ko, J. Gillett, C. M. Petrone, J. M. Cole, G. G. Lonzarich, and S. E. Sebastian, J. Phys.: Condens. Matter \textbf{21}, 012208 (2009).
\bibitem{11} R. T. Gordon \textit{et al.}, Phys. Rev. Lett. \textbf{102}, 127004 (2009).
\bibitem{12} K. Nakayama \textit{et al.}, EPL \textbf{85}, 67002 (2009).
\bibitem{13} W. Jeitschko and M. Reehuis, J. Phys. Chem. Solids \textbf{48}, 667 (1987).
\bibitem{14} W. Jeitschko, R. Glauk, and L. Boonk, J. Solid State Chem. \textbf{69}, 93 (1987).
\bibitem{15} T. Mine, H. Yanagi, T. Kamiya, Y. Kamihara, M. Hirano, and H. Hosono, Solid State Commun. \textbf{147}, 111 (2008).
\bibitem{16} F. Ronning, E. Bauer, T. Park, S.-H. Baek, H. Sakai, and J. Thompson, Phys. Rev. B \textbf{79}, 134507 (2009).
\bibitem{17} M. Reehuis, W. Jeitschko, T. Ebel, and N. St"{u}sser, J. Alloys Compd. \textbf{287}, 32 (1999).
\bibitem{18} C. Huhnt, G. Michels, M. Roepke, W. Schlabitz, A. Wurth, D. Johrendt, and A. Mewis, Physica B \textbf{240}, 26 (1997).
\bibitem{19} C. Huhnt, W. Schlabitz, A. Wurth, A. Mewis, and M. Reehuis, Phys. Rev. B \textbf{56}, 13796 (1997).
\bibitem{20} M. Chefki, M. M. Abd-Elmeguid, H. Micklitz, C. Huhnt, W. Schlabitz, M. Reehuis, and W. Jeitschko, Phys. Rev. Lett. \textbf{80}, 802 (1998).
\bibitem{21} P. C. Canfield and Z. Fisk, Philos. Mag. B \textbf{65}, 1117 (1992).
\bibitem{22} P. Villars and K. Cenzual, \textit{Pearson's Crystal Data} (ASM International, Ohio, 2008).
\bibitem{23} A. Lohken, C. Lux, D. Johrendt, and A. Mewis, Z. Anorg. Allg. Chem. \textbf{628}, 1472 (2002).
\bibitem{24} A. Wurth, D. Johrendt, A. Mewis, C. Huhnt, G. Michels, M. Roepke, and W. Schlabitz, Z. Anorg. Allg. Chem. \textbf{623}, 1418 (1997).
\bibitem{25} D. Hirai, T. Takayama, R. Higashinaka, H. Aruga-Katori, and H. Takagi, J. Phys. Soc. Jpn. \textbf{78}, 023706 (2009).
\bibitem{26} J. G. Analytis, J.-H. Chu, A. S. Erickson, C. Kucharczyk, A. Serafin, A. Carrington, C. Cox, S. M. Kauzlarich, H. Hope, and I. R. Fisher, arXiv:0810.5368 (unpublished).
\bibitem{27} S. Jiang, C. Wang, Z. Ren, Y. Luo, G. Cao, and Z. Xu, arXiv:0901.3227 (unpublished).
\bibitem{28} A. Kreyssig \textit{et al.}, Phys. Rev. B \textbf{78}, 184517 (2008).
\bibitem{29} W. Yu, A. A. Aczel, T. J. Williams, S. L. Budko, N. Ni, P. C. Canfield, and G. M. Luke, Phys. Rev. B \textbf{79}, 020511(R) (2009).
\bibitem{30} Y. Yildirim, Phys. Rev. Lett. \textbf{102}, 037003 (2009).
\bibitem{31} Y. Singh, Y. Lee, S. Nandi, A. Kreyssig, A. Ellern, S. Das, R. Nath, B. N. Harmon, A. I. Goldman, and D. C. Johnston, Phys. Rev. B \textbf{78}, 104512 (2008).
\bibitem{32} I. B. Shameem Banu, M. Rajagopalan, and G. Vaitheeswaran, Solid State Commun. \textbf{116}, 451 (2000).
\bibitem{33} R. Hoffmann and C. Zheng, J. Phys. Chem. \textbf{89}, 4175 (1985).
\bibitem{34} V. Keimes, D. Johrendt, P. D. A. Mewis, and W. S. C. Huhnt, Z. Anorg. Allg. Chem. \textbf{623}, 1699 (1997).
\bibitem{35} T. Terashima \textit{et al.}, J. Phys. Soc. Jpn. \textbf{78}, 033706 (2009).
\end{thebibliography}