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Superconductivity without Fe or Ni in the phosphides BaIr_2P_2 and BaRh_2P_2

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Heat capacity, resistivity, and magnetic susceptibility measurements confirm bulk superconductivity in single crystals of BaIr_2P_2 ($T_c=2.1$ K) and BaRh_2P_2 ($T_c=1.0$ K). These compounds form in the ThCr_2Si_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.

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Rare-earth intermetallics in the ThCr_2Si_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.^{1,2} The recent discovery of superconductivity in iron pnictides, first in LaFeAsO at 26 K³ and soon after in the AFe_2As_2 (A =alkali metal) family,⁴ has ignited new interest in non-Cu-based high- T_c SC. The ternary compounds AFe_2As_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.^{4,5} Band-structure calculations show a Fermi surface almost exclusively formed by $\text{Fe } d$ bands.⁶ Fe pnictides are also very tunable with pressure or chemical substitution, and critical temperatures (T_c) have reached as high as 55 K in $\text{SmFeAs}(\text{O},\text{F})$ ⁷ and 38 K in $(\text{Ba},\text{K})\text{Fe}_2\text{As}_2$.⁴ In both families of compounds, SC is seen to emerge from the suppression of a commensurate antiferromagnetic order with pressure or doping.^{8–10} Moreover, the long-range magnetic order is preceded by (concomitant to) a structural transition in the 1111 (122) compounds.⁶ 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_2Si_2 structure. The mechanism for SC^{11,12} 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 Reehius¹³ and Jeitschko *et al.*¹⁴ While SC has not been reported in stoichiometric Fe-based ternary phosphides at ambient pressure, it has been observed in LaRu_2P_2 ,¹⁴ BaNi_2P_2 ,¹⁵ and SrNi_2P_2 ,¹⁶ with T_c 's $\lesssim 4$ K. Most ternary phosphides grown with Co exhibit local moment magnetic order unlike their Fe or Ni counterparts.¹⁷ Isostructural transitions (tetragonal to collapsed tetragonal) have also been reported in the ternary phosphides under pressure.^{18,19} Unlike their As counterparts, these compounds do not show a concomitant magnetic transition,¹⁶ except EuCo_2P_2 with its Eu moment ordering.²⁰

This Rapid Communication reports on single-crystal SC in the Co column for the 122 phosphides, namely, in BaIr_2P_2 and BaRh_2P_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.²¹ The single crystals of BaRh_2P_2 and CaRh_2P_2 were grown in Pb flux with a ratio of 1.3:2:2:40. For BaIr_2P_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 (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_2P_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 Θ for BaRh_2P_2 single crystals and for polycrystalline BaIr_2P_2 powder. The polycrystalline powder has a composition of 85% BaIr_2P_2 , 10% $\text{Ba}_3(\text{PO}_4)_2$, and only a few percent of Ir_2P and IrP_2 binaries. Additional peaks in the BaRh_2P_2 spectra are from the Pb flux. Single crystals of both BaRh_2P_2 and BaIr_2P_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.^{23,24} Moreover, the correct composition and stoichiometry have been confirmed for all single crystals with energy dispersive x-ray analysis. Magnetic properties are measured using a commercial superconducting quantum interference device (SQUID) vibrating sample magnetometer. Heat capacity (C) has been measured using a quasiadiabatic heat pulse technique in a physical properties measurement system (PPMS). The resistivity is measured on a LR700 ac resistance bridge using Pt wires

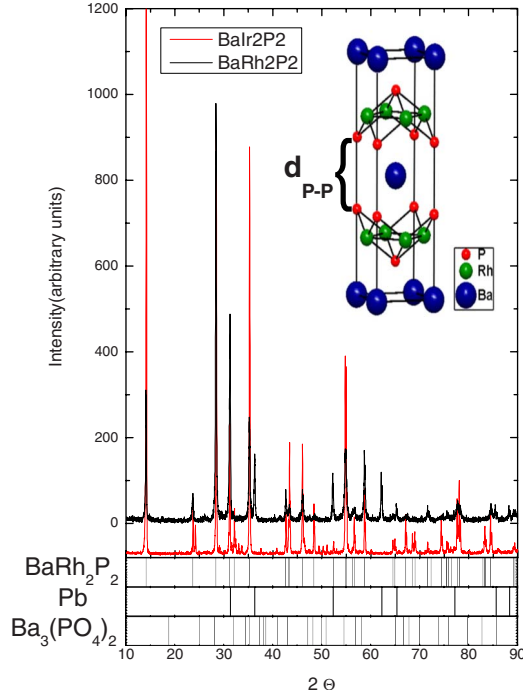


FIG. 1. (Color online) Intensity vs scattering angle Θ obtained in powder x-ray diffraction for BaRh_2P_2 (single crystals) and BaIr_2P_2 (polycrystals). The vertical lines correspond to the reference pattern of BaRh_2P_2 , Pb, and $\text{Ba}_3(\text{PO}_4)_2$ ²². The inset represents the tetragonal unit cell of BaRh_2P_2 .

attached with silver paint. The single crystals of BaIr_2P_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 (ρ) in single crystals of BaIr_2P_2 and BaRh_2P_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 ($\text{RRR} = \rho(300 \text{ K})/\rho(3 \text{ K}) = 16.5$ in BaIr_2P_2 and 7.5 in BaRh_2P_2) as well as by the low values of the residual resistivities (8.7 and 1.2 $\mu\Omega \text{ cm}$ 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 ρ up to 300 K. At low temperatures, a sharp drop to $\rho=0$ indicates the onset of SC at $T_c = 2.1 \text{ K}$ in BaIr_2P_2 and 1 K in BaRh_2P_2 .

The temperature and magnetic field dependence of magnetization (M) are shown in Figs. 2(b) and 2(c) for polycrystalline BaIr_2P_2 . The diamagnetic jump in $M(T)$ corresponds

TABLE I. Structural parameters and physical properties.

	a (Å)	c (Å)	$d_{\text{p-p}}$ (Å)	T_c (K)	γ (mJ/mol K ²)
BaIr_2P_2	3.9469(8)	12.559(5)	3.688(2)	2.1 ± 0.04	9.3 ± 0.6
BaRh_2P_2	3.9308(3)	12.574(2)	3.725(1)	1.0 ± 0.04	9.2 ± 0.3
CaRh_2P_2	4.0179(3)	9.655(1)	2.241(1)		10.7 ± 0.2

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_2P_2 and BaRh_2P_2 , consistent with Bardeen-Cooper-Schrieffer (BCS) theory. The values of the electronic specific heat coefficient γ are obtained from a linear fit to $\frac{C}{T}$ vs T^2 in the range 0.4–2.4 K (BaIr_2P_2) and 0.5–1.0 K (BaRh_2P_2) (see Table I). The γ and T_c shown here are consistent with those reported on polycrystals.²⁵

The suppression of T_c with magnetic field is seen in $\frac{C}{T}(T)$ [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 $\approx \frac{H_{c2}}{2}$. This suggests a rather strongly pinned vortex lattice. The specific-heat anomaly also remains sharp for the BaRh_2P_2 single crystals up to 150 Oe [see Fig. 3(b)] but broadens with field for the polycrystalline BaIr_2P_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 $H_{c2}(0) \approx -0.7T_c \frac{\partial H_{c2}}{\partial T} \Big|_{T_c}$ yields $H_{c2}(0) = 410$ and 370 Oe in BaIr_2P_2 and BaRh_2P_2 . These values of $H_{c2}(0)$ are comparable to SrNi_2P_2 (390 Oe)¹⁶ and BaNi_2P_2 (550 Oe)¹⁵ but

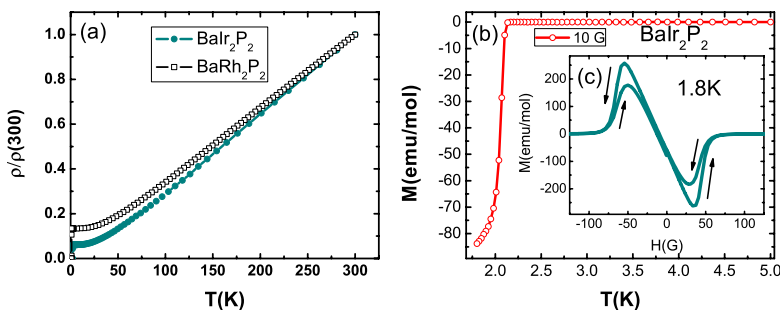


FIG. 2. (Color online) (a) Resistivity (normalized) vs temperature in the range of 0.5–300 K in single crystals of BaIr_2P_2 and BaRh_2P_2 . (b) Magnetization vs temperature in polycrystalline BaIr_2P_2 showing a diamagnetic jump at $T_c = 2.1 \text{ K}$ in a field of 10 G. (c) Magnetization vs magnetic field (H) at $T = 1.8 \text{ K}$ for the same sample.

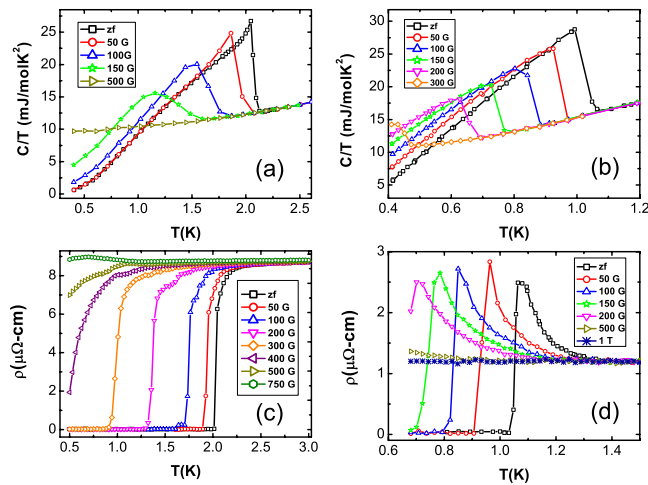


FIG. 3. (Color online) Total $\frac{C}{T}(T)$ at the indicated magnetic fields in polycrystalline BaIr_2P_2 (a) and single crystals of BaRh_2P_2 (b). Resistivity vs temperature at the indicated magnetic fields in single crystals of (c) BaIr_2P_2 and (d) BaRh_2P_2 .

smaller than those cited in the study of Hirai *et al.*²⁵ The broadness of the transitions in polycrystals²⁵ 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_2P_2 and BaRh_2P_2 , respectively.

Figure 3(d) shows a pronounced upturn in $\rho(T)$ preceding the onset of the superconducting jump in BaRh_2P_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_2P_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_2P_2 above 700 Oe, but it is absent at zero field in this case. Such an upturn is also reported in SrNi_2P_2 ¹⁶ and LaFePO .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 (≤ 20 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_2As_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.^{4,9,10,27} However, in the isoelectronic CaFe_2As_2 the existence of SC is highly controversial.^{28,29} Moreover, in CaFe_2As_2 , recent theoretical calculations show an intimate connection between the Fe-spin state and the interlayer As-As bonding.³⁰ Future studies should clarify the effect of the Fe moments on T_c . In addition,

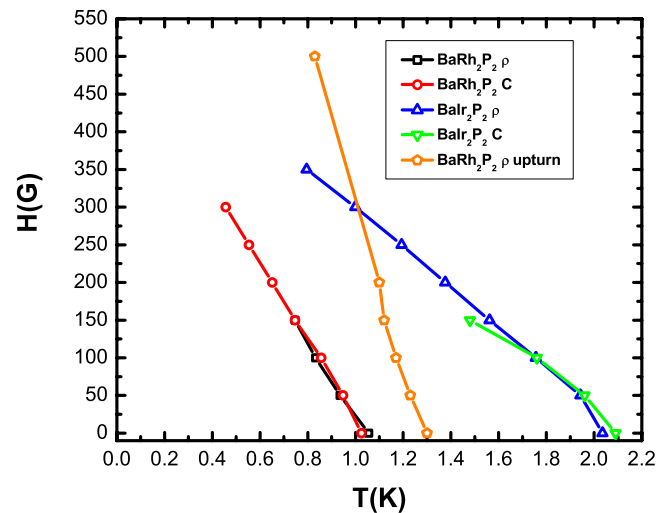


FIG. 4. (Color online) Upper critical field (H_{c2}) vs temperature in BaIr_2P_2 and in BaRh_2P_2 as determined from resistivity and specific-heat data. Also shown is the onset of the resistivity upturn in BaRh_2P_2 .

tion, BaRh_2As_2 exhibits no superconductivity down to 1.8 K.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,¹⁸ similar to CaFe_2As_2 ,^{28,29} except that it does not appear to be associated with any magnetic order.¹⁶ Previous investigations in BaRh_2P_2 did not show any structural transition up to 11 GPa and down to low temperatures¹⁸ (no reports for BaIr_2P_2). In the phosphides, 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.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.³³ The critical distance for bond formation obtained theoretically is about $d_{c} \sim 2.8$ Å between the interlayer P atoms, labeled $d_{\text{P-P}}$ in the inset of Fig. 1.³³ We found that both BaRh_2P_2 and BaIr_2P_2 have a $d_{\text{P-P}}$ of ~ 3.7 Å (see Table I) indicating the absence of interlayer bonding between the P atoms, which is consistent with structural calculations.³² In contrast, CaRh_2P_2 has a $d_{\text{P-P}}$ of only 2.25 Å, which is below the critical distance for bond formation. We have also grown single crystals of CaRh_2P_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_2P_2 which has $d_{\text{P-P}} = 3.71$ Å.³⁴ In fact, none of the known ternary phosphides [BaIr_2P_2 , BaRh_2P_2 , BaNi_2P_2 ,¹⁵ and LaRu_2P_2 ¹⁴] that exhibit ambient pressure SC in the tetragonal structure are bonded between the interlayer P atoms. Nevertheless, it is interesting that LaRu_2P_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.¹⁴ However, SrNi₂P₂ shows SC in the collapsed tetragonal phase under pressure where a bond exists between the layers.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 BaNi₂P₂ 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.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 ro-

bustness 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, BaIr₂P₂ and BaRh₂P₂ provide convenient systems in which to study the interplay between structure and SC.

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