Robust Nodal Superconductivity Induced by Isovalent Doping in $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ and $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$

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We present the ultra-low-temperature heat-transport study of iron-based superconductors $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ and $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. For optimally doped $\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$, a large residual κ_0/T at zero field and a $\sqrt{H}$ dependence of $\kappa_0(H)/T$ are observed, which provide strong evidences for nodes in the superconducting gap. This result demonstrates one more nodal superconductor in iron pnictides. The similarities between isovalent Fe and P dopings strongly suggest that the nodal superconductivity in $\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$ may have the same origin as in $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$. Furthermore, in underdoped $\text{Ba}(\text{Fe}_{0.77}\text{Ru}_{0.23})_2\text{As}_2$ and strongly underdoped $\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$, κ_0/T manifests similar nodal behavior, which result shows the robustness of nodal superconductivity in the underdoped regime and puts constraint on theoretical models.

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Since the discovery of high- T_c superconductivity in iron pnictides [1,2], the issue of what mechanisms underlie the electron pairing in these systems has been a central one [3]. One key step in resolving it is to clarify the symmetry and structure of the superconducting gap [4]. However, even for the most studied (Ba, Sr, Ca, Eu) Fe_2As_2 (122) system, the situation is still fairly complex [4].

Near optimal doping where the T_c is the highest, for both hole- and electron-doped 122 compounds, the angle-resolved photon-emission-spectroscopy (ARPES) experiments have clearly demonstrated multiple nodeless superconducting gaps [5,6]. Those experiments have been further supported by measurements of bulk properties such as thermal conductivity [7–9]. On the overdoped (with respect to the optimal doping) side, nodal superconductivity has been found in the extremely hole-doped KFe_2As_2 [10,11], while a strongly anisotropic nodeless gap [9] or isotropic nodeless gaps with significantly different magnitudes [12,13] have been suggested in heavily electron-doped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$. On the underdoped side, recent heat-transport measurements have claimed possible nodes in the superconducting gap of hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ with $x < 0.16$ [14], in contrast to the nodeless gaps that have been found in electron-doped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [9]. It is hard to get a simple pairing mechanism from such complex situation of the superconducting gap structure.

More intriguingly, nodal superconductivity has also been found in optimally doped $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ ($T_c = 30$ K) [15,16], in which the superconductivity is induced by isovalent P doping. Moreover, LaFePO ($T_c \sim 6$ K) was found to display clear nodal behavior [17–19], and recently evidence for nodes in the superconducting gap of LiFeP ($T_c \sim 4.5$ K) has emerged from measurements of magnetic penetration depth [20]. The nodal superconductivity in these P-doped compounds is very striking, which raises the puzzling questions of whether, and why, the P doping is unique among iron-based superconductors. Although various theoretical explanations have been offered for this puzzle, investigators are far from reaching consensus [21–25].

A recent empirical proposal is that the nodal state in iron-pnictide superconductors, except for KFe_2As_2 , is induced when the pnictogen height h_{pn} from the iron plane decreases below a threshold value of approximately $1.33 \text{ \AA}$ [20]. According to this proposal, there may exist a transition from nodal to nodeless state as h_{pn} is tuned, for example, in underdoped $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. Therefore, it is important to investigate the doping evolution of the superconducting-gap structure in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. In another aspect, since isovalent substitution of Fe with Ru in BaFe_2As_2 , as shown in Fig. 1, can also decrease h_{pn} and result in a similar phase diagram [26–28], it will be very interesting to check whether the gap of $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ has nodes.

In this paper, we report the demonstration of nodal superconductivity in optimally doped $\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$, underdoped $\text{Ba}(\text{Fe}_{0.77}\text{Ru}_{0.23})_2\text{As}_2$, and strongly underdoped $\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$ by thermal-conductivity measurements down to 50 mK. Our finding of a nodal gap in $\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$ suggests a common origin for the nodal superconductivity induced by isovalent P and Ru

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FIG. 1. Isovalent doping in the Fe_2As_2 slabs of BaFe_2As_2 , by substituting As with P, or Fe with Ru. Both ways can induce superconductivity, and both result in similar phase diagrams.

doping. The nodal gaps in both $\text{Ba}(\text{Fe}_{0.77}\text{Ru}_{0.23})_2\text{As}_2$ and $\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$ show no transition from a nodal to a nodeless state in the underdoped regime.

Single crystals of $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ and $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ are grown according to the methods described in Refs. [29,30]. The Ru- and P-doping levels are determined by energy-dispersive X-ray spectroscopy. The sample is cleaved to a rectangular shape with typical dimensions of $1.50 \times 0.7 \text{ mm}^2$ in the ab plane, and from 40 to $80 \mu\text{m}$ in the c axis. In-plane thermal conductivity is measured in a dilution refrigerator using a standard four-wire steady-state method with two RuO_2 chip thermometers, calibrated *in situ* against a reference RuO_2 thermometer. Magnetic fields are applied along the c axis. To ensure a homogeneous field distribution in the samples, all fields are applied at a temperature above T_c .

Figure 2 shows the in-plane resistivity $\rho(T)$ of $\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$, $\text{Ba}(\text{Fe}_{0.77}\text{Ru}_{0.23})_2\text{As}_2$, and $\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$ single crystals. The transition temperatures defined by $\rho = 0$ are $T_c = 20$, 17, and 4 K; correspondingly, we name these three samples OP20K, UD17K, and UD4K, respectively. One can see clear resistivity anomalies in UD4K and UD17K, but not in OP20K. The decrease of the anomaly temperature manifests the gradual suppression of spin-density-wave (SDW) order upon P or Ru doping [27,28,31]. For OP20K, the resistivity data between 30 and 90 K are fitted to $\rho(T) = \rho_0 + AT^n$, which gives a residual resistivity of $\rho_0 = 43.7 \pm 0.1 \mu\Omega \text{ cm}$ and $n = 1.31 \pm 0.1$. Such a non-Fermi-liquid temperature dependence of $\rho(T)$ is similar to that observed in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ near optimal doping, which may reflect the presence of antiferromagnetic spin fluctuations near a quantum critical point [31].

FIG. 2. In-plane electronic resistivity of $\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$, $\text{Ba}(\text{Fe}_{0.77}\text{Ru}_{0.23})_2\text{As}_2$, and $\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$ single crystals. The low-temperature superconducting transitions are shown in the inset. Defined by $\rho = 0$, the transition temperatures $T_c = 20$, 17, and 4 K are obtained; correspondingly, these three samples are named OP20K, UD17K, and UD4K, respectively. The solid line is a fit of the data between 30 and 90 K to $\rho(T) = \rho_0 + AT^n$ for the OP20K sample.

To determine their upper critical field H_{c2} and normal-state ρ_0 , we have also measured the resistivity of these samples in the presence of magnetic fields, the highest of which reaches up to 14.5 T. For OP20K, UD17K, and UD4K, our estimates are $H_{c2} = 23$, 19, and 5 T, and normal-state $\rho_0 = 44$, 115, and $74 \mu\Omega \text{ cm}$, respectively.

Figure 3 shows the temperature dependence of the in-plane thermal conductivity for OP20K, UD17K, and UD4K in zero and finite magnetic fields, plotted as κ/T vs T . All the curves are roughly linear, as previously observed in $\text{BaFe}_{1.9}\text{Ni}_{0.1}\text{As}_2$ [8], KFe_2As_2 [10], and overdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ single crystals [9,12]. Therefore, we fit all the curves to $\kappa/T = a + bT^{\alpha-1}$, with α fixed at 2. The two terms aT and bT^{α} represent contributions from electrons and phonons, respectively. Here, we focus only on the electronic term.

In Fig. 3(a), for OP20K in zero magnetic field, the fitting gives a residual $\kappa_0/T = 0.266 \pm 0.002 \text{ mW K}^{-2} \text{ cm}^{-1}$. This value is more than 40% of what is expected based on the normal-state Wiedemann-Franz law, which is $\kappa_{N0}/T = L_0/\rho_0 = 0.56 \text{ mW K}^{-2} \text{ cm}^{-1}$, where L_0 is the Lorenz number $2.45 \times 10^{-8} \text{ W}\Omega \text{ K}^{-2}$ and $\rho_0 = 44 \mu\Omega \text{ cm}$ is the normal-state resistivity. In nodeless superconductors, there are no fermionic quasiparticles to conduct heat as $T \rightarrow 0$, since all electrons become Cooper pairs. Therefore there is no residual linear term of κ , i.e., $\kappa_0/T = 0$. However, for unconventional superconductors with nodes in the superconducting gap, the nodal quasiparticles will

FIG. 3. Low-temperature in-plane thermal conductivity of (a) $\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$ (called sample OP20K in the paper), (b) $\text{Ba}(\text{Fe}_{0.77}\text{Ru}_{0.23})_2\text{As}_2$ (sample UD17K), and (c) $\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$ (sample UD4K) in zero and finite magnetic fields applied along the c axis. The solid lines are $\kappa/T = a + bT$ fit to all the curves, respectively. The dashed horizontal lines are the normal-state Wiedemann-Franz law expectation L_0/ρ_0 , where L_0 is the Lorenz number, $2.45 \times 10^{-8} \text{ W}\Omega \text{ K}^{-2}$, and normal-state $\rho_0 = 44, 115$, and $74 \mu\Omega \text{ cm}$, respectively.

contribute a finite κ_0/T in zero field [32]. For example, $\kappa_0/T = 1.41 \text{ mW K}^{-2} \text{ cm}^{-1}$ for the overdoped cuprate $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ (Ti-2201), a d -wave superconductor with $T_c = 15 \text{ K}$ [33]. For optimally doped $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ single crystal, $\kappa_0/T \approx 0.25 \text{ mW K}^{-2} \text{ cm}^{-1}$ is obtained, which is about 30% of its normal-state κ_{N0}/T [16]. Therefore, the significant κ_0/T of our $\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$ in zero field is strong evidence for nodes in the superconducting gap [32].

With a decreasing doping level, for UD17K and UD4K, $\kappa_0/T = 35 \pm 1$ and $69 \pm 1 \mu\text{W K}^{-2} \text{ cm}^{-1}$ are obtained, as seen in Figs. 3(b) and 3(c). These values are about 17% and 22% of their normal-state κ_{N0}/T , respectively. We

note that Hashimoto *et al.* have already mentioned that the superconducting gaps in overdoped $\text{SrFe}_2(\text{As}_{0.6}\text{P}_{0.4})_2$ and $\text{BaFe}_2(\text{As}_{0.36}\text{P}_{0.64})_2$ have nodes [20]. Therefore, our observation of significant κ_0/T in the underdoped regime, particularly in the strongly underdoped $\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$, further shows the robustness of nodal superconductivity against doping in P- and Ru-doped 122 iron pnictides.

The field dependence of κ_0/T can provide further support for the gap nodes [32]. In Fig. 4, the normalized $(\kappa_0/T)/(\kappa_{N0}/T)$ of OP20K ($\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$), UD17K ($\text{Ba}(\text{Fe}_{0.77}\text{Ru}_{0.23})_2\text{As}_2$), and UD4K ($\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$) are plotted as a function of H/H_{c2} . For UD4K, κ/T saturates above $H = 3 \text{ T}$, as shown in Fig. 3(c), which is determined as its bulk H_{c2} . For OP20K and UD17K, we use their H_{c2} estimated from resistivity measurements. Choosing a slightly different H_{c2} does not affect our discussion of the field dependence of κ_0/T . Similar data on Ti-2201 [33] and $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ [16] are also plotted for comparison.

For a nodal superconductor such as Ti-2201 in a magnetic field, delocalized electronic states exist outside the vortex cores and dominate the heat transport in the vortex state, in contrast to the s -wave superconductor. At low magnetic fields, the Doppler shift due to superfluid flow around the vortices will yield an $H^{1/2}$ growth in quasiparticle density of states (the Volovik effect [34]), which gives the $H^{1/2}$ field dependence of κ_0/T . From Fig. 4, the

FIG. 4. Normalized residual κ_0/T of $\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$ (called sample OP20K in the paper), $\text{Ba}(\text{Fe}_{0.77}\text{Ru}_{0.23})_2\text{As}_2$ (sample UD17K), and $\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$ (sample UD4K) as a function of H/H_{c2} . Similar data of an overdoped d -wave cuprate superconductor Ti-2201 [33], and $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$ [16] are also shown for comparison. The behaviors of $\kappa_0(H)/T$ in OP20K, UD17K, and UD4K clearly mimic the behaviors in Ti-2201 and $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$. Inset: the same data points for OP20K, UD17K, UD4K, and Ti-2201 are plotted against $(H/H_{c2})^{1/2}$. The lines represent the $H^{1/2}$ dependence.

behavior of $\kappa_0(H)/T$ in OP20K, UD17K, and UD4K clearly mimics that in Tl-2201 and $\text{BaFe}_2(\text{As}_{0.67}\text{P}_{0.33})_2$. In the inset of Fig. 4, the $\kappa_0(H)/T$ of OP20K, UD17K, and UD4K obey the $H^{1/2}$ dependence at low field, which supports the existence of gap nodes.

To our knowledge, so far, five iron-based superconductors display nodal superconductivity: KFe_2As_2 [10,11], underdoped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($x < 0.16$) [14], $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ [15,16], LaFePO [17–19], and LiFeP [20]. In this paper, we consider only the “in-plane” nodes, and do not count the “*c*-axis nodes” in underdoped and overdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ as suggested by *c*-axis heat-transport experiments [35]. For the extremely hole-doped KFe_2As_2 , the electron pockets are absent and the hole pockets are very large, therefore the dominant interaction is intrapocket interaction on the large hole pocket, which may result in the *d*-wave nodal gap [10,36,37]. For underdoped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, it is still not clear how the superconducting gap transforms from nodeless to nodal at $x \approx 0.16$ [14]. The remaining three compounds, $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, LaFePO , and LiFeP , have stimulated various interpretations of the effect of isovalent P doping [21–25].

Our new finding of nodal superconductivity in $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ reveals the similarity between the isovalently Ru- and P-doped iron pnictides. In this sense, the P doping does not appear to play a special role in inducing nodal superconductivity now, and the puzzle of P doping in iron-based superconductors has thus been partially solved. What is needed next is to determine concretely the common origin for the nodal superconductivity in these isovalently doped iron pnictides.

Because the P ion is smaller than the As ion, one common structural feature of the P-doped compounds $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, $\text{LaFeAs}_{1-x}\text{P}_x\text{O}$, and $\text{LiFeAs}_{1-x}\text{P}_x$ is the decrease of pnictogen height h_{Pn} and increase of the As-Fe-As angle upon P doping [20,31,38,39]. The substitution of the larger Ru ion for the Fe ion in $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ results in the increase of the lattice parameter *a* and the decrease of the lattice parameter *c*, with the concomitant decrease of pnictogen height and increase of the As-Fe-As angle [27]. Therefore, both the P and the Ru dopants cause the same trend of structure change in iron arsenides.

In iron pnictides, the strong Fermi-surface evolution upon hole and electron doping has given clues to understand the complex superconducting gap structures [10,12]. However, the Fermi-surface evolution upon isovalent P and Ru doping is rather delicate, mainly caused by above-described crystal structure change. The main feature—hole pockets around the Brillouin-zone center and electron pockets around the Brillouin-zone corners—remains in LaFePO [40], $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ [30], $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ [41,42], and LiFeP [43]. For LaFePO , Kuroki *et al.* have attributed the low- T_c nodal pairing to the lack of Fermi

surface γ around (π, π) in the unfolded Brillouin zone, due to the low pnictogen height [21]. For $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, Suzuki *et al.* have proposed a three-dimensional nodal structure in the largely warped hole Fermi surface and no nodes on the electron Fermi surface [24]. This proposal is supported by recent ARPES experiments that found a nodal gap in the expanded α -hole pocket at $k_z = \pi$ in $\text{BaFe}_2(\text{As}_{0.7}\text{P}_{0.3})_2$ [44]. Since ARPES experiments did not find significant changes in the shape of the Fermi surface or in the Fermi velocity over a wide range of doping levels in $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$, Dhaka *et al.* have speculated that its superconducting mechanism relies on magnetic dilution that leads to the reduction of the effective Stoner enhancement [42]. In LiFeP , the middle hole pocket has significantly lower mass enhancement than the other pockets, which implies that the electron-hole scatter rate is suppressed for this pocket and may result in the lower T_c and nodal gap [43].

More recently, Hashimoto *et al.* gathered the available data for the low-energy quasiparticle excitations in several iron-pnictide superconductors and suggested that there is a threshold value of $h_{\text{Pn}} \sim 1.33 \text{ \AA}$, below which all the superconductors exhibit a nodal-superconducting state [20]. If this is the case, there may exist a transition from nodal to nodeless state tuned by h_{Pn} in underdoped $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ and $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. To test this idea, we estimate $h_{\text{Pn}} = 1.317, 1.333$, and $1.340 \text{ \AA}$ for OP20K, UD17K, and UD4K, respectively, from the roughly linear increase of h_{Pn} with decreasing Ru or P doping [27,31].

One can see that both the h_{Pn} ’s of UD17K and UD4K are slightly larger than the proposed threshold value of $1.33 \text{ \AA}$. In particular, the h_{Pn} of UD4K is comparable to that of overdoped $\text{Ba}(\text{Fe}_{0.89}\text{Co}_{0.11})_2\text{As}_2$, which is a nodeless superconductor [20]. Since our thermal conductivity data suggest that UD17K and UD4K are nodal superconductors, h_{Pn} should not be considered as the only parameter for tuning between nodeless and nodal superconducting states. By saying this, however, we do not deny its importance, since the h_{Pn} ’s of the underdoped $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ and $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ are still very close to the threshold value of $1.33 \text{ \AA}$. More careful consideration of the structural parameters, Fermi-surface topology, and local interactions is needed to clarify the origin of the nodal superconductivity in isovalently doped iron pnictides.

In summary, we have measured the thermal conductivity of $\text{Ba}(\text{Fe}_{0.64}\text{Ru}_{0.36})_2\text{As}_2$, $\text{Ba}(\text{Fe}_{0.77}\text{Ru}_{0.23})_2\text{As}_2$, and $\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$ single crystals down to 50 mK. A significant κ_0/T at zero magnetic field and an $H^{1/2}$ -field dependence of $\kappa_0(H)/T$ at low magnetic field give strong evidences for nodal superconductivity in all three compounds. Comparing with previous P-doped iron pnictides, our new finding suggests that the nodal superconductivity induced by isovalent Ru and P doping may have the same origin. With a decreasing doping level, the nodal

superconducting state persists robustly in strongly underdoped $\text{BaFe}_2(\text{As}_{0.82}\text{P}_{0.18})_2$, suggesting that the h_{pn} is not the only tuning parameter, and thus putting constraint on theoretical models. Finding the origin of these nodal superconducting states will be a crucial step toward a complete electronic-pairing mechanism in the iron-based high- T_c superconductors.

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