Journal of Physics: Conference Series **500** (2014) 032007 doi:10.1088/1742-6596/500/3/032007

Hydrostatic high-pressure studies to 25 GPa on the model superconducting pnictide $LaRu_2P_2$

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Abstract. Prior to the discovery of the Fe-pnictides in 2008, the ruthenium phosphide $LaRu_2P_2$ possessed the highest value of the superconducting transition temperature, $T_c \approx 4$ K, in the entire pnictide family. Recently, there has been renewed interest in this compound in an effort to better understand why the Fe-pnictides have much higher values of T_c. In related phosphides superconductivity appears to only be present if the separation between the phosphor ions d_{p-p} in neighboring Ru_2P_2 planes is greater than the critical value 2.8 Å, too great for a P-P covalent bond to be formed. For example, in superconducting $LaRu_2P_2$, the value of d_{p-p} is 3.0 Å. To test these ideas directly, we have carried out hydrostatic high-pressure studies on single-crystalline $LaRu_2P_2$ in a diamond-anvil cell using He pressure medium to pressures as high as 25 GPa and temperatures as low as 1.5 K. We find that T_c initially increases under pressure, but suddenly disappears above 2.1 GPa. Since d_{p-p} decreases under pressure, the sudden disappearance of superconductivity is likely due to the formation of a covalent P-P bond between adjacent Ru_2P_2 planes and a possible structural phase transition.

1. Introduction

Since the discovery of the fluorine-doped iron- and arsenic-based 1111 superconductors with $T_c \approx 26$ K in 2008 [1], many more related superconductors with tetragonal structure have been reported, among them the 122 family, such as (Ca, Sr, Ba)Fe_2As_2, consisting of more than 450 members, including K-doped $BaFe_2As_2$ with $T_c \approx 40$ K. The isoelectronic pnictides (Ca, Sr, Ba)Fe_2P_2 are free of arsenic, but none were found to be superconducting at ambient pressure. The substitution of nonmagnetic transition metals for Fe in these phosphides resulted in the stoichiometric compounds $LaRu_2P_2$, $BaNi_2P_2$, $SrNi_2P_2$, $BaIr_2P_2$, and $BaRh_2P_2$, all of which are superconducting with $T_c \approx 4$ K. These phosphides are of particular interest with respect to superconductivity since, unlike their arsenic counterparts, no magnetic order is present to possibly weaken or interfere with the superconducting state.

In the tetragonal 122 pnictide $LaRu_2P_2$, the superconductivity originates in the quasi-2D Ru_2P_2 planes, in analogy with the CuO_2 planes in the cuprates. The distance between the phosphor ions d_{p-p} in neighboring planes is believed to be of particular importance. Electronic structure calculations by Hoffmann and Zheng [2] reveal that the bonding or antibonding nature of the P-P bond is responsible for the wide variation in bond length [3]. It has been inferred

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from structural analysis that the interlayer P-P bond distance d_{p-p} is a relevant parameter to identify when superconductivity occurs in the 122 phosphides and when it does not [4]. From theoretical considerations the critical distance for covalent P-P bond formation is $d_{p-p} \approx 2.8$ Å (see figure 1) [2]. The calculated energy bands and electronic charge density of $CaRh_2P_2$, $SrRh_2P_2$ and $BaRh_2P_2$ show that a covalent P-P bond is only formed for $CaRh_2P_2$ where $d_{p-p} \approx 2.25$ Å, but not for $SrRh_2P_2$ and $BaRh_2P_2$ where $d_{p-p} \approx 3.3$ Å and 3.7 Å, respectively [5]. In contrast to $BaRh_2P_2$, $CaRh_2P_2$ is not superconducting. This suggests that a covalent P-P bond between adjacent planes is detrimental to the appearance of superconductivity.

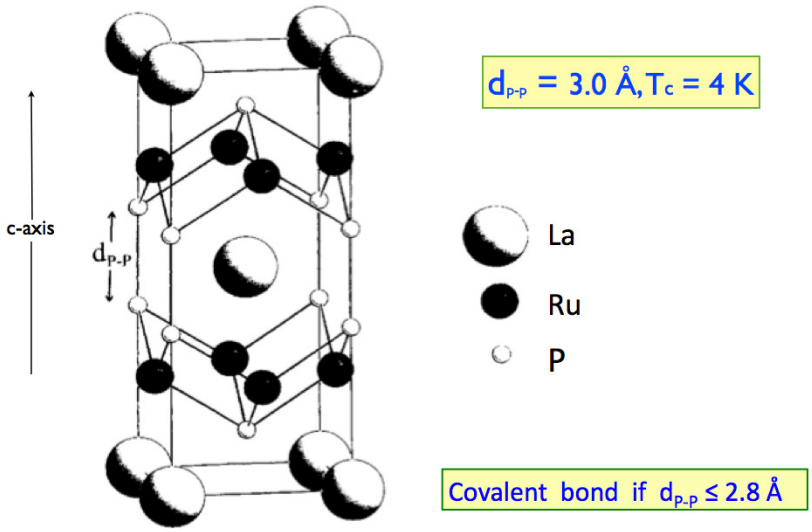

Figure 1. Tetragonal unit cell of $LaRu_2P_2$. The P-P separation at ambient pressure is $d_{p-p} \approx 3.0$ Å .

To test these ideas, it would be interesting to take a superconducting 122 compound where $d_{p-p} > 2.8$ Å and apply pressure to decrease d_{p-p} to a value below 2.8 Å. The superconductor $LaRu_2P_2$ is the ideal candidate for such an experiment since its value of $d_{p-p} = 3.0$ Å lies only slightly above the critical value 2.8 Å. In this paper we report the results of ac susceptibility measurements on $LaRu_2P_2$ to hydrostatic pressures as high as 25 GPa and to temperatures as low as 1.5 K. T_c is found to increase with pressure at the rate +0.67(5) K/GPa to 2.1 GPa pressure, but to suddenly disappear at higher pressures, presumably due to the formation of a covalent P-P bond. A more detailed account of these and further results will be given elsewhere [6].

2. Experimental details

Single crystals (mm in size) of $LaRu_2P_2$ were grown by a tin flux method. One gram of elemental La (filed into powder), Ru (powder), and P (pieces) were thoroughly mixed in 1:2:2 molar ratio together with 11 g of Sn (powder) in an argon filled glove box. The mixture was transferred to a tantalum tube, sealed under vacuum and heated to 1050°C for 24 days in a computer-controlled furnace. The sample was cooled down naturally by turning off the furnace. The Sn flux was removed by soaking the sample in 6M HCl overnight. Many metallic rectangular crystals were observed (see figure 2), and their composition was confirmed to be in the 1:2:2 ratio by a TESCAN VEGA II energy dispersive X-ray microanalyzer.

AC susceptibility measurements to hydrostatic pressures as high as 25 GPa were carried out in a diamond-anvil pressure cell [7] with two opposing 1/6-carat, type-Ia diamonds with either

0.5 mm or 0.9 mm diameter culets. The primary ac field was 3 Oe (rms) at 1023 Hz. The signal from two calibrated, compensated secondary coils, one surrounding the gasket containing the sample and the other surrounding a "dummy" gasket, was fed into a Stanford Research SR830 digital lock-in amplifier via an SR554 transformer preamplifier. Temperatures were measured using a calibrated Cernox resistor from Lake Shore Cryotronics located close to the sample.

Three experiments were carried out. In the first, diamond anvils with 0.5 mm culets were used and a 250 μm diameter hole drilled through the center of a gold-plated Re gasket (3 mm in diameter, 250 μm thick), preindented to a thickness of $\sim$72 μm. The pressure was determined *in situ* by placing small ruby spheres [8] in the sample space. In the second and third experiments anvils with 0.5 mm and 0.9 mm culets were used with gold-plated CuBe gaskets. The $LaRu_2P_2$ crystal was placed in a 260-μm diameter hole (for 0.5 mm culets) and a 450-μm diameter hole (for 0.9 mm culets) drilled through the center of a CuBe gasket (3 mm in diameter, 250 μm thick), preindented to a thickness of $\sim$100 μm (see figure 3). AC susceptibility data were obtained at the following pressures: first experiment (0.8, 1.1, 1.6, 2.1, 2.5, 5.5, 9.4 GPa), second experiment (0, 3.2, 4.8, 7, 20, 25 GPa), third experiment (0, 0.81, 0.9, 1.86, 2.05, 2.4, 3.2, 5 GPa).

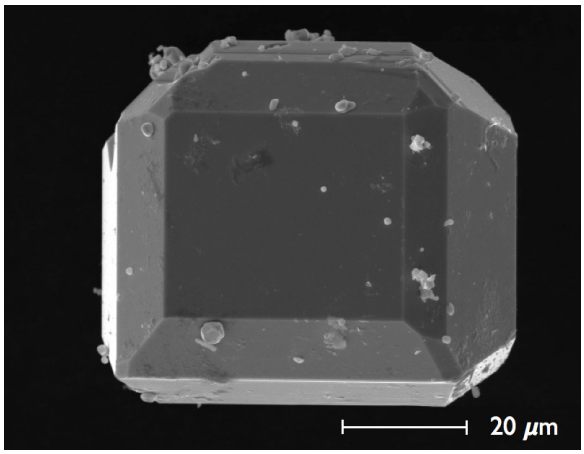

Figure 2. High quality $LaRu_2P_2$ single crystal.

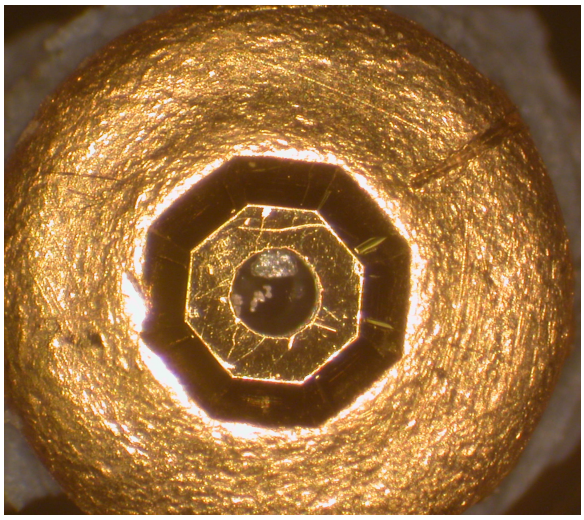

Figure 3. Pre-indented CuBe gasket with single-crystal sample and ruby spheres seen in 450 μm diameter gasket hole.

The pressure was determined at a temperature of 5 -10 K to within $\pm$0.2 GPa using the revised ruby pressure scale of Chijioke *et al* [9]. Hydrostatic pressure conditions were assured by using He as pressure medium since it remains fluid to a higher pressure and lower temperature than any other substance. Even when He solidifies, it is a relatively soft solid and can only exert weak shear stresses on the sample it surrounds. Further details of the DAC pressure techniques are given elsewhere [7, 10].

3. Results and discussions

In figure 4 the real part of the ac susceptibility of $LaRu_2P_2$ from the first experiment is plotted versus temperature to 10 K for hydrostatic pressures to 2.5 GPa. Two superconducting transitions are seen in the data at 1.1, 1.6 and 2.1 GPa. The large transition near 4 K arises from the superconductivity of the Re gasket; the smaller transition at a somewhat higher temperature is from the sample. The T_c value of the sample shifts to higher temperatures with pressure, but suddenly disappears above 2.1 GPa. The pressure dependence of T_c is found to be reversible

upon release of pressure. In the second and third experiments non-superconducting CuBe gaskets were used, allowing the search for superconductivity in the sample to temperatures as low as 1.5 K.

In figure 5 the values of T_c obtained in all experiments from the transition midpoint are plotted versus hydrostatic pressure. T_c is seen to initially increase with pressure at the rate +0.67(5) K/GPa to 2.1 GPa, but to suddenly disappear to the highest pressure measured, namely 25 GPa. The initial dependence of T_c on pressure agrees well with parallel experiments to 0.44 GPa in a He-gas apparatus [6].

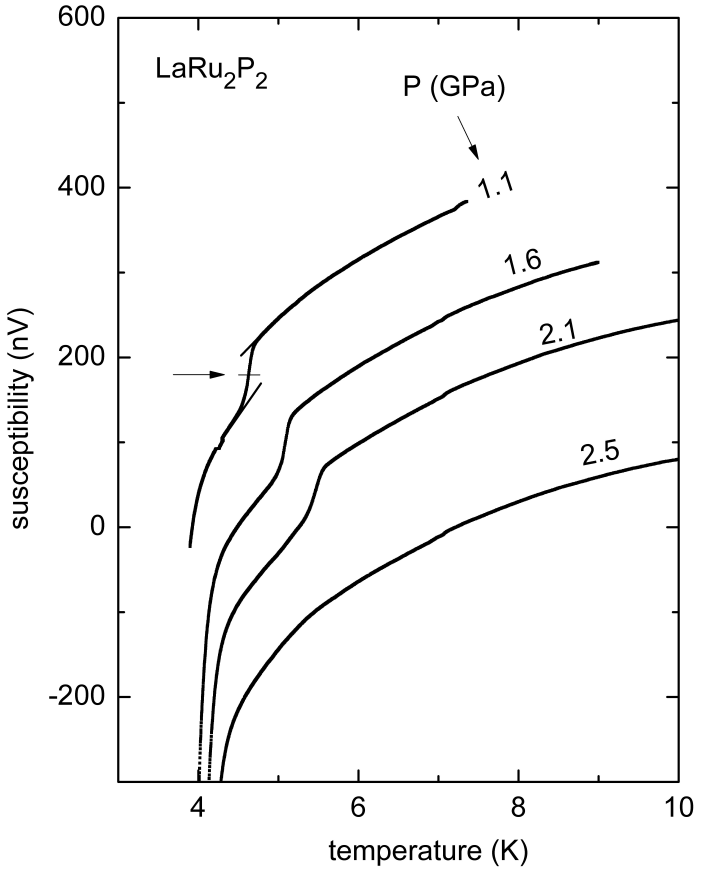

Figure 4. Real part of ac susceptibility versus temperature at several hydrostatic (DAC) pressures for $LaRu_2P_2$. T_c is determined from transition midpoint (see data at 1.1 GPa). T_c clearly increases as pressure is applied. The order of measurement is 1.1, 1.6, 2.1, and 2.5 GPa. Steep susceptibility drop near 4 K is from superconductivity of Re gasket.

The principal result of the present experiments is that the superconducting state in $LaRu_2P_2$ abruptly disappears for hydrostatic pressures above 2.1 GPa. Since the value of d_{p-p} for this compound is only 0.2 Å greater than the critical value 2.8 Å, we suggest that at 2 GPa the P-P separation has decreased sufficiently that a covalent P-P bond forms, resulting in the loss of superconductivity. In addition, when a covalent P-P bond is formed, one would expect a sudden decrease in the lattice parameter along the c-axis, in analogy with previous x-ray studies on $SrRh_2P_2$ where the c-axis is observed to decrease abruptly at 5 GPa [3]. Single crystal x-ray diffraction studies under pressure on $LaRu_2P_2$ would resolve this issue.

For $SrRh_2P_2$ the P-P separation is $d_{p-p} = 3.3$ Å at ambient pressure. Using the known c-axis

compressibility $\kappa_c = 5.2\times10^{-3}$ GPa^{-1}, where $c = 11.7$ Å, a pressure of 5 GPa would decrease c by approximately 0.3 Å [3]. If all of this reduction in c comes from a reduction in the P-P separation d_{p-p}, then at 5 GPa one would expect d_{p-p} to be reduced from 3.3 Å to 3.0 Å which is quite close to the critical value of 2.8 Å. If one assumes that $LaRu_2P_2$ (where $c = 10.7$ Å) has a c-axis compressibility comparable to that of $SrRh_2P_2$, then a pressure of 2 GPa would lead to a reduction in c of approximately 0.1 Å, placing d_{p-p} close to the critical value of 2.8 Å. It thus seems quite likely that the sudden disappearance of superconductivity at 2 GPa in $LaRu_2P_2$ is the result of the formation of strong covalent P-P bonds between adjacent planes.

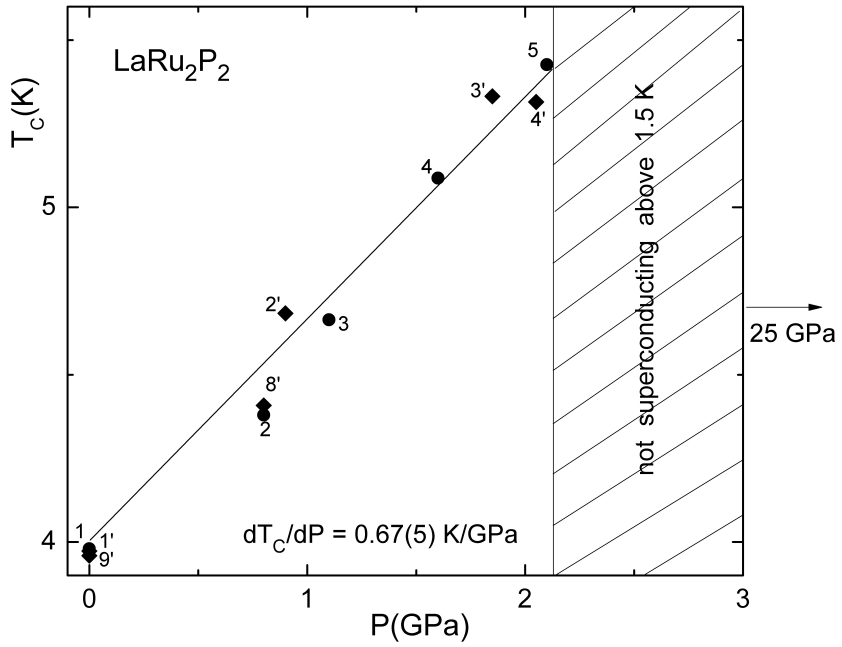

Figure 5. Dependence of the superconducting transition temperature T_c on pressure for single crystalline $LaRu_2P_2$ determined by measurements of ac susceptibility up to 25 GPa. Numbers give order of measurement. Primed numbers give T_c values from Fig. 4 (first experiment). Unprimed numbers give T_c values from third experiment. No superconducting transition was observed for pressures above 2.1 GPa.

In conclusion, the present ac susceptibility studies on $LaRu_2P_2$ to 25 GPa hydrostatic pressure demonstrate that the superconducting transition temperature increases with pressure at the rate of +0.67(5) K/GPa to 2 GPa but disappears abruptly at higher pressures, 25 GPa being the highest pressure measured and 1.5 K the lowest temperature. The separation between P-P atoms in $LaRu_2P_2$ is close to the critical value 2.8 Å at ambient pressure. When 2 GPa pressure is applied, the P-P separation likely decreases to the critical value and a strong covalent bond is formed, significantly altering the electronic properties in the Ru_2P_2 planes of the compound and destroying its superconductivity. The present experiments thus provide further evidence for the sensitivity of the superconducting properties of the 122 pnictides to the interplanar separation.

Acknowledgments
Research at Washington University is gratefully supported by the National Science Foundation under DMR-1104742.

References

[1] Kamihara Y, Watanabe T, Hirano M, and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296
[2] Hoffmann R and Zheng C 1985 *J. Phys. Chem.* **89** 4175 and refrences cited therein
[3] Huhnt C, Michels G, Roepke M, Schlabitz W, Wurth A, Johrendt D and Mewis A 1997 *Physica* B **240** 26
[4] Berry N, Capan C, Seyfarth G, Bianchi A D, Ziller J and Fisk Z 2009 *Phys. Rev.* B **79** 180502
[5] Shameem Banu I B, Rajagopalan M and Vaitheeswaran G 2000 *Solid State Commun.* **116** 451
[6] Fotovat R, Foroozani N, Wang L, Lim J, Xiao Zh, Schlueter J, Schilling J S, Zheng C and Hoffmann R (unpublished)
[7] Schilling J S 1984 *Mat. Res. Symp. Proc.* **22** 79
[8] Chervin J C, Canny B and Mancinelli M 2001 *High Pressure Res.* **21** 305
[9] Chijioke A D, Nellis W J, Soldatov A and Silvera I F 2005 *J. Appl. Phys.* **98** 114905
[10] Hamlin J J, Tissen V G and Schilling J S 2006 *Phys. Rev.* B **73** 094522