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# Superconductivity in $LaPd_2As_2$ with a collapsed 122 structure

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ABSTRACT

The superconducting properties of $LaPd_2As_2$ with a collapsed tetragonal structure are reported. DC magnetization and resistivity measurements reveal that the compound is a type-II bulk superconductor below 1 K. The electronic specific heat coefficient $\gamma$ is found to be 5.56 mJ $mol^{-1}$ $K^{-2}$. The specific heat change at the superconducting transition is 1.17, which is relatively low compared to the BCS weak coupling limit of 1.43. The density of states at the Fermi level calculated from electronic specific heat data is about 0.84 states/(eV f.u.), which may explain the low $T_c$ of this material. These results, together with previous work on $A^{2+}M_2X_2$ compounds, imply that the superconducting transition temperature can be tailored by proper chemical substitution.



## 1. Introduction

Ternary intermetallic compounds with the $ThCr_2Si_2$ ($AM_2X_2$) structure are well known for accommodating a superconducting ground state. Since the discovery of superconductivity in $LaFeAsO_{1-x}F_x$ at $T_c = 26$ K, Fe-based compounds having the $ThCr_2Si_2$ structure, that is $AFe_2As_2$ (A = Ba, Ca, Sr and Eu), have been found to be superconducting either with carrier doping or under pressure [1–4]. The superconductivity in these compounds emerges upon the suppression of a spin density wave (SDW) transition [5]. The $ThCr_2Si_2$-type structure can also accommodate trivalent rare earth ions at the A site, paving the way for the synthesis of new compounds with additional electrons. For instance, $LaRu_2P_2$ is superconducting with a $T_c$ of 4.1 K [6]. However, no superconductivity was observed in $ARu_2P_2$ (A = Ca, Sr, Ba) [6].

The $ThCr_2Si_2$-type structure (Fig. 1) contains stacked layers along the $c$ axis in the order A–[X–$M_2$–X]–A, providing a quasi-two-dimensional (2D) MX network. However, as pointed out by Hoffmann and Zheng [7], interlayer X–X bonding sometimes forms to give a 3D network, called a collapsed tetragonal (cT) structure. The Ba, Sr and Ca-based series of iron arsenides remain in the un-collapsed tetragonal (ucT) structure at ambient pressure, while $SrCu_2As_2$, $CaCu_{1.7}As_2$, $CaPd_2As_2$, $SrPd_2As_2$ and $LaNi_2As_2$ crystallize in the cT structure [8–10].

Superconductivity in the collapsed Fe–As phases is rather rare and is often attained under high pressure. For example, the application of pressure on $A^{2+}Fe_2As_2$ (A = Ca, Sr, Ba, Eu) induces both superconducting and collapsed transitions [11–14]. Recently, Anand et al. [8] reported ambient pressure superconductivity in $A^{2+}Pd_2As_2$ (A = Ca, Sr) with a cT structure, with a $T_c$ of 1.27 K and 0.92 K, respectively. However, so far, the observed superconducting materials in the cT structure are exclusively limited to those containing a divalent A cation.

In the present article, we report the discovery of superconductivity in $LaPd_2As_2$ with the cT structure. $LaPd_2As_2$, the rare earth analogue of $A^{2+}Pd_2As_2$, was first reported by Hofmann and Jeitschko in 1985 [15]. Although no statement was given as to which phase (cT or ucT) is formed, the obtained interlayer As–As distance of 2.318 Å, slightly shorter than the covalent single bond distance of 2.38 Å for As, indicating that $LaPd_2As_2$ has a cT structure. The collapsed phase is generally stable compared to the un-collapsed phase at low temperatures. The decreasing temperature decreases the As–As bond length, and the shorter As–As distance destabilizes the ucT structure. This results in the formation of the cT structure at low temperature or high pressure. Hence, once the structure is collapsed, the collapsed phase is seen even at the lowest temperature. $LaPd_2As_2$ contains strong ionic covalent Pd–As bonding inside the $Pd_2As_2$ blocks and covalent As–As bonding between the adjacent $Pd_2As_2$ layers, combined with ionic bonding between $Pd_2As_2$ blocks and La cations. Within the ionic description the valence of As is $-2$ (compared to $-3$ in ucT structure). In

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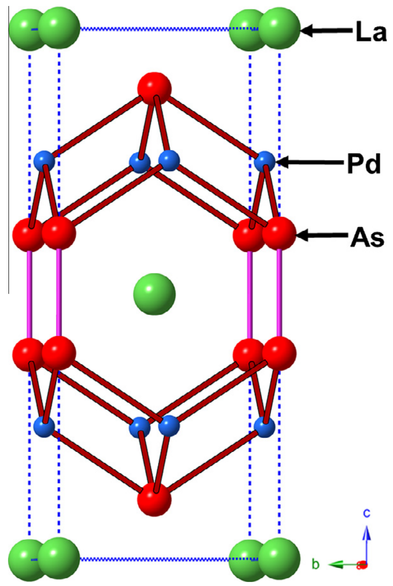


**Fig. 1.** Crystal structure of $LaPd_2As_2$, where green, blue and red spheres represent La (2*a*), Pd (4*d*), As (4*e*) respectively; the blue dotted line indicates the unit cell. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$A^{2+}Pd_2As_2$, the formal Pd valence is +1, while in $LaPd_2As_2$ it is in a subvalent state.

**Table 1**
Refined room temperature synchrotron XRD parameters for $LaPd_2As_2$. $R_p = 2.303$, $R_{wp} = 3.995$, Occ = 1 for all sites.

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ (Å$^2$) |
|---|---|---|---|---|---|
| La | 2*a* | 0 | 0 | 0 | 0.00271(1) |
| Pd | 4*d* | 0 | 1/2 | 1/4 | 0.02036(6) |
| As | 4*e* | 0 | 0 | 0.38077(7) | 0.00430(8) |

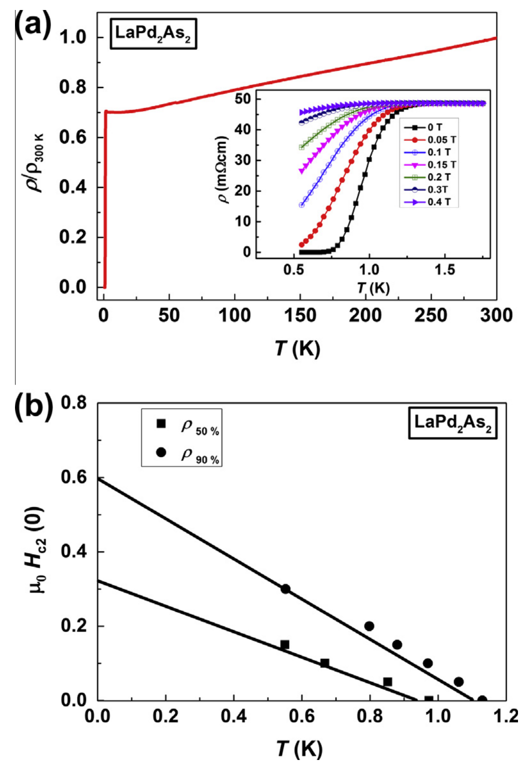


**Fig. 3.** (a) The temperature dependence of electrical resistivity $\rho$ for $LaPd_2As_2$ in zero field. The inset shows the variation of resistivity with respect to the magnetising field. (b) Temperature dependence of upper critical field $H_{c2}$ deduced from the midpoint of the resistive transition for $\rho_{50\%}$ and $\rho_{90\%}$ conditions. The solid line indicates linear fit to the data.

## 2. Experimental details

Polycrystalline samples of $LaPd_2As_2$ were synthesised at high temperature in an evacuated silica ampule. The starting materials used were La (99.9%), As (99.9%) and Pd (99.9%). Stoichiometric amounts of these elements were mixed inside a nitrogen-filled glove box, pelletized, heat-treated at 850 °C for 20 h. Then, the obtained specimen was ground, pelletized and heated again at 850 °C for 40 h before cooling down to room temperature. The light grey material is stable in air. The crystal structure of $LaPd_2As_2$ was investigated by synchrotron X-ray diffraction (SXRD) at SPring-8 BL02B2, where a wavelength of 0.420032 Å was used. A standard DC four terminal method was employed for measuring the resistivity of the specimen using a physical property measuring system (Quantum Design, PPMS) equipped with a $^3$He refrigerator. The pellet dimensions were $4 \times 2 \times 2$ mm$^3$. Magnetization measurements were carried out using a SQUID Magnetometer (Quantum Design, MPMS), with a $^3$He refrigerator. A disc-shaped sample with diameter of 2 mm and thickness of 1 mm was used for the specific heat capacity measurement by the relaxation method in the PPMS.

## 3. Results and discussion

Fig. 2 shows the SXRD pattern of $LaPd_2As_2$ at room temperature, which demonstrates formation of $LaPd_2As_2$. An unidentified impurity phase (<5%) is also present in the SXRD pattern. A Rietveld refinement using JANA2006 [16] confirms the previous structural analysis with the *I*4/*mmm* space group and the refined atomic coordinates and lattice parameters ($a = 4.3027(27)$ Å, $c = 10.268(14)$ Å) are similar to those reported in the literature [15]. The refined structural parameters are given in Table 1. The observed Pd–As and interlayer As–As distances are found to be 2.567 Å and 2.318 Å, respectively. Iso-structural $CaPd_2As_2$ and $SrPd_2As_2$ have slightly longer interlayer As–As distances of 2.433 Å and 2.541 Å, indicating that the trivalent La cation in $LaPd_2As_2$ shortens the interlayer As–As bonding. The As–Pd–As angle, where the two As atoms are on the same layer, is about 113.615°, which is larger than 109.5° (i.e. the ideal angle of a tetrahedron). In general, in collapsed $AM_2X_2$ structures this angle deviates from the ideal 109.5°. For instance, isostructural compounds $CaPd_2As_2$ and $SrPd_2As_2$ possess higher tetrahedral angles of 117.31° and 119.07° respectively [8]. However, compared with its alkaline earth counterparts, $LaPd_2As_2$ has an angle much closer to the ideal angle. It is worth to note that the ideal angle is responsible for high-$T_c$ in ucT iron arsenide superconductors [4,5].

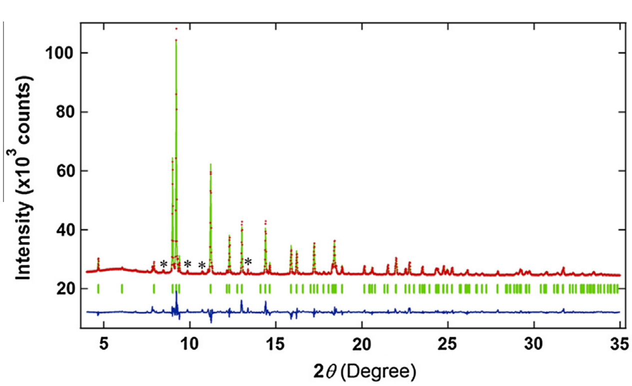


**Fig. 2.** Refined synchrotron XRD pattern of $LaPd_2As_2$, showing observed (red cross) calculated (green line) and difference (blue line) profiles. The symbol $*$ indicates impurity phases. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)