La$_4$TX ($T$ = Ru, Rh, Ir; $X$ = Al, In): A family of noncentrosymmetric superconductors with tunable antisymmetric spin-orbit coupling

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ABSTRACT We report the discovery of superconductivity in a series of noncentrosymmetric compounds La$_4$TX ($T$ = Ru, Rh, Ir; $X$ = Al, In), which have a cubic crystal structure with the space group $Fm3m$. La$_4$RuAl, La$_4$RhAl, La$_4$IrAl, La$_4$RuIn and La$_4$IrIn exhibit bulk superconducting transitions with critical temperatures ($T_c$) of 0.61–3.35 K, while La$_4$RhIn was not successfully synthesized. The specific heats of La$_4$RuAl and La$_4$RhAl are best accounted for by an s-wave model with a fully open superconducting gap, while a nodal gap cannot be excluded for La$_4$IrAl, which has a stronger antisymmetric spin-orbit coupling (ASOC). In all cases, the upper critical fields are well described by the Werthamer-Helfand-Hohenberg model, and the values are well below the Pauli limit, indicating that orbital limiting is the dominant pair-breaking mechanism. Density functional theory (DFT) calculations reveal that the degree of band splitting by the ASOC shows considerable variation between the different compounds. This indicates that the strength of the ASOC is highly tunable across this series of superconductors, suggesting that they are good candidates for examining the relationship between ASOC and superconducting properties in noncentrosymmetric superconductors.

Keywords: noncentrosymmetric superconductivity, superconducting order parameter, spin-orbit coupling

INTRODUCTION

Noncentrosymmetric superconductors (NCSs), where the crystal structure lacks an inversion center, have been identified as prime candidates for realizing unconventional superconducting pairing states [1], following the discovery of unconventional superconductivity in the heavy fermion antiferromagnet CePt$_3$Si [2]. When inversion symmetry is broken, an antisymmetric spin-orbit coupling (ASOC) can lift the degeneracy of the electrons near the Fermi level, allowing for superconductivity with a mixture of spin-singlet and spin-triplet pairing [3]. Subsequently, pressure-induced superconductivity was realized in the noncentrosymmetric heavy fermion systems Ce(Rh, Ir)Si$_3$ [4,5], Ce(Co, Ir, Rh)Ge$_3$ [6–8], and UIr [9], where large and anisotropic upper critical fields have been observed well in excess of the Pauli limit [10–12], but disentangling the influence of the superconductivity of the inversion symmetry breaking from the strong electronic correlations and magnetism has proved challenging. As such, weakly correlated NCSs have also been investigated. For instance, in the Li$_x$(Pd$_{1-x}$Pt$_x$)$_3$B system, Li$_x$Pd$_3$B has two nodeless superconducting gaps, while in Li$_x$Pt$_3$B there is evidence for one of the gaps having line nodes, which has been ascribed to stronger singlet-triplet mixing upon increasing the ASOC, by replacing Pd with the heavier element Pt [13]. These findings stimulated interest in weakly correlated NCS where there is strong band-splitting by the ASOC due to the presence of heavy elements [1,14–17]. On the other hand, the properties of many reported weakly correlated NCSs are consistent with fully gapped superconductivity, including La(Ni, Pt)Si$_3$ [18–21], La(Rh, Pt, Pd, Ir)Si$_3$ [22–25], (Rh, Ir)Ga$_5$ [26,27], Re-T (T = transition metal) [28–32], and BiPd [33,34], despite a number of these systems exhibiting an appreciable band splitting due to the ASOC [1]. As such, the relationship between the ASOC and nature of the superconducting order parameter, as well as the necessary conditions for significant singlet-triplet mixing, still remains to be determined, requiring the study of additional classes of NCS where the ASOC can be tuned.

In recent years, time-reversal symmetry breaking (TRSB) has also been detected in the superconducting states of a number of NCSs [35], including LaNiC$_2$ [36], La$_x$(Ir, Rh)$_3$ [37,38], Re-T [28,29,39,40] and CaPdAs [17,41], but in most cases the relationship between the broken time reversal and inversion symmetries is not resolved. In systems such as orthorhombic LaNiC$_2$, the low symmetry of the crystal structure excludes there being both TRSB and significant singlet triplet mixing [42], which led to the proposal of an internally-antisymmetric, non-unitary triplet state [43]. On the other hand, in higher symmetry structures such as the cubic α-Mn type structure of several Re-based NCSs, there are symmetry-allowed mixed parity states with TRSB [28], but the actual origin of the TRSB in these materials is yet to be determined. As such, it is of considerable interest to search for more families of NCSs, in particular those...
crystallizing in cubic structures.

The La₄TX (T = Ru, Rh, Ir; X = Al, In) compounds belong to a large family of rare-earth-based materials [44], which have the cubic Gd₄RhIn-type structure with the noncentrosymmetric space group Fm̅3m [45]. The Gd₄RhIn-type structure is a ternary ordered variant of the centrosymmetric Ti₂Ni-type structure (space group Fd̅3m) [46,47]. The crystal structure of La₄TX is displayed in Fig. 1a [44]. Slightly distorted La₆T trigonal prisms form a rigid three-dimensional network sharing corners and edges, with cavities that are occupied by La octahedra and X tetrahedra, where the T and X atoms are located on non-centrosymmetric sites. There are three inequivalent La sites, among which only the La(1) is centrosymmetric. Superconductivity has been reported in systems with a different structure but the same space group as the Gd₄RhIn-type, namely in the equiatomic half-Heusler compounds including non-magnetic (Y, Lu)(Pd, Pt)Bi with topological electronic structures [48–51] and the magnetic superconductors RPdB (R: magnetic rare earth) [52,53], among which evidence for unconventional pairing states is also reported [54–56].

In this study, we report the discovery of superconductivity in five La₄TX compounds using resistivity, magnetization and specific heat measurements. Electronic band structures and density of states are also calculated. The occurrence of superconductivity in several systems with different atoms on the T and X sites suggests that the La₄TX superconductors are good candidates for examining the effects of tuning the ASOC on the superconducting and normal state properties.

METHODS

Experimental techniques
Polycrystalline samples of La₄TX (T = Ru, Rh, Ir; X = Al, In) were synthesized by arc-melting stoichiometric amounts of the constituent elements. In order to improve the sample quality, La and T were first melted together and the resulting boule was subsequently melted with X. After being turned over and remelted several times to ensure homogeneity, the samples were sealed in evacuated quartz ampoules and annealed for three weeks at 350 and 700°C for X = Al and In, respectively, before being quenched in water. Note that the attempted synthesis of La₄RhIn by the above method was unsuccessful, where only a mixture of binary compounds was obtained. The crystal structures at room temperature were confirmed by powder X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with Cu Kα radiation. Resistivity measurements were performed using a standard four-probe method on a physical property measurement system (PPMS, Quantum Design) with a 3He option as well as an Oxford Instruments 3He refrigerator. The specific heat was also measured down to 0.4 K using the relaxation method in a PPMS. The alternating current (ac) magnetic susceptibility was measured down to 0.3 K using the mutual-inductance method with an ac magnetometer in a 3He refrigerator (Oxford Instruments), to characterize the superconducting transitions. Direct current (dc) magnetization measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer (MPMS) down to 2 K.

Theoretical calculations
Density functional theory (DFT) calculations were performed using the Vienna ab-initio simulation package (VASP) to obtain the electronic band structure and density of states. The projected augmented wave (PAW) and Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) was
applied \[57,58\]. The Brillouin zone was sampled with 12 × 12 × 12 k-mesh to ensure convergence and the energy-cutoff was 450 eV. The lattice parameters and the atomic internal coordinates were optimized, and therefore forces on each atom were smaller than 0.01 eV Å\(^{-1}\) and internal stress was less than 0.1 kbar.

RESULTS AND DISCUSSION

Crystal structure

XRD patterns of La\(_4\)TAl (T = Ru, Rh, Ir) and La\(_4\)TIn (T = Ru, Ir) are shown in Fig. 1b–f. All the experimental patterns are well indexed by the noncentrosymmetric Gd\(_4\)RhIn-type cubic structure \[45\], and they can be well-refined using this structural model. The results are displayed in Table 1, where the fitted lattice parameters are in good agreement with the reported values \[44\]. The atomic positions are displayed in the Supplementary information. We note that although the Gd\(_4\)RhIn-type structure is an ordered variant of the Ti\(_2\)Ni-type structure, the latter leads to very different peak intensities, and therefore our XRD data cannot be refined with a Ti\(_2\)Ni-type model. The small additional peaks in the La\(_4\)TAl patterns may correspond to the binary phases La\(_5\)Al\(_4\) or La\(_{16}\)Al\(_{13}\), likely as a result of the incongruent melting of the ternary phases. On the other hand, the synthesis of La\(_4\)RhIn by arc-melting was not successful.

Zero-field superconducting properties

The temperature dependences of the electrical resistivity of La\(_4\)TAl (T = Ru, Rh and Ir) are shown in Fig. 2a–c, in the vicinity of the superconducting transition temperature (\(T_c\)). The insets show the resistivity across the whole temperature range, and all the samples exhibit metallic behavior. The relatively large residual resistivity in the normal state \(\rho (77–155 \mu \Omega \text{ cm})\) and the small residual resistivity ratio \(\text{RRR} = \rho (300 K)/\rho (2 K) = 1.4–2.0\) are possibly due to the atomic disorder on the nominal Al \(16\) site \[44\]. At low temperatures, the resistivity drops to zero. We define the superconducting \(T_c\) as the temperature where the resistivity is 10% of the normal state value, namely 1.88, 3.35 and 1.75 K for La\(_4\)RuAl, La\(_4\)RhAl, and La\(_4\)IrAl, respectively. For La\(_4\)IrAl, the transition width is relatively broad, and there is a

![Figure 2](image)

**Figure 2** Characterization of the superconducting transitions of La\(_4\)RuAl, La\(_4\)RhAl, and La\(_4\)IrAl in zero field. (a–c) The respective temperature dependences of the resistivity near the transition, while the insets show the data up to room temperature. (d–f) The corresponding real and imaginary parts of the ac susceptibility. (g–i) The electronic specific heat after subtracting the phonon contribution. The red, green and blue lines show the results from fitting, respectively, with s-wave, p-wave, and d-wave models described in the text. The insets display \(C_p / T\) versus \(T^2\) at low temperatures, where the red solid lines show the results from fitting to \(C_p / T = \gamma_n + \beta T^2\).
kink in the resistivity data, which could be due to sample inhomogeneity. The temperature dependences of the ac susceptibility are shown in Fig. 2d–f. An abrupt decrease of the real part and a peak in the imaginary part indicate the presence of a superconducting transition, with $T_c$ values similar to those determined from the resistivity.

The low-temperature electronic specific heat $C_e/T$ for each compound is displayed in Fig. 2g–i, after subtracting the phonon contribution $\beta T^2$, which was determined from fitting the total specific heat ($C_t$) in the normal state with $C_t/T = \gamma_n + \beta T^2$, where $\gamma_n$ denotes the Sommerfeld coefficient. The fitting yields $\gamma_n = 20.1(1), 29.3(2)$, and $21.3(1)$ mJ mol$^{-1}$ K$^{-2}$, $\beta = 1.35(3), 1.29(3)$ and $1.68(2)$ mJ mol$^{-1}$ K$^{-4}$ for La$_4$RuAl, La$_4$RhAl, and La$_4$IrAl, respectively. The relatively low values of $\gamma_n$ suggest weak electronic correlations. The Debye temperature ($\theta_D$) is estimated from $\beta$ using $\theta_D^2 = (12\pi^4 R_0/5\beta)^{1/3}$, with the number of atoms per formula unit $n = 6$ and the molar gas constant $R = 8.314$ J mol$^{-1}$ K$^{-1}$, yielding $204(2), 208(2)$ and $191(1)$ K for the respective materials.

The presence of transitions in the electronic specific heat indicates bulk superconductivity, with $T_c$ values close to those found in the resistivity and ac susceptibility. The normalized specific heat jumps at $T_c$, $\Delta C/\gamma_n T_c$, are $1.23, 0.93$ and 1.09 for the Ru, Rh and Ir variants, respectively, which are smaller than the Bardeen-Cooper-Schrieffer (BCS) weak coupling limit value of 1.43. The deviation may be ascribed to the broad nature of the transitions, as well as reduced or anisotropic gap magnitudes. The electron-phonon coupling constant $\lambda_{el-ph}$ can be estimated from McMillan's theory [59] by

$$\lambda_{el-ph} = \frac{1.04 + \mu \ln(\theta_D/1.45T_c)}{(1 - 0.62\mu)\ln(\theta_D/1.45T_c) - 1.04},$$

yielding 0.45–0.54, 0.52–0.62 and 0.44–0.53, for a screened Coulomb parameter of $\mu = 0.1–0.15$. The relatively small values of $\lambda_{el-ph}$ suggest weak electron-phonon coupling. Among the three samples, a comparatively larger value of $\lambda_{el-ph}$ is correlated with a higher value of $T_c$.

The temperature dependence of the electronic specific heat can be expressed as $C_e/T = dS/dT$, where $S(T)$ is the superconducting contribution to the entropy. $S(T)$ can be calculated using [60]

$$S(T) = \frac{3\mu}{k_Bn\pi^3} \int_0^{\theta_D/\gamma_n} [(1-f)\ln(1-f) + f \ln f] d\ln f,$$

$$f = \left[1 + \exp\left(\frac{\sqrt{\epsilon + \Delta^2(T)/k_B T}}{k_B T}\right)\right]^{-1},$$

$$\Delta(T) = g_\epsilon \Delta(0) \tanh 1.82[0.1018(\theta_D/T_c - 1)]^{0.31},$$

where $f$ is the Fermi function, $\epsilon$ is the relative electronic energy, and $\Delta(0)$ is the superconducting gap at zero temperature. For the angle-dependent component $g_\epsilon$, values of 1, $\sin \theta$, and $\cos 2\theta$ are used for the s-wave, p-wave, and d-wave models, respectively, where $\theta$ is the polar angle and $\phi$ is the azimuthal angle. The experimental data for La$_4$RuAl and La$_4$IrAl are well fitted by the weak-coupling s-wave model shown by the red lines in Fig. 2, with $\Delta(0) = 1.78 k_BT_c$ for La$_4$RuAl, and $1.57 k_BT_c$ for La$_4$IrAl, but are not well described by the p-wave and d-wave models, and therefore the data are more consistent with a nodeless s-wave model, rather than the two models with nodal gaps. Here the $T_c$ is the bulk $T_c$ determined from the fitting, with values of 1.77 and 3.05 K for La$_4$RuAl and La$_4$IrAl, respectively. In the case of La$_4$IrAl, both the s-wave model and the nodal p-wave model can reasonably account for the data. Furthermore, while $C_e/T$ for La$_4$RuAl and La$_4$IrAl begins to flatten at low temperatures, this is not observed for La$_4$IrAl, and hence nodal superconductivity cannot be excluded for the latter. We note that there are a large range of additional possible scenarios for the superconducting order parameter besides those considered above, such as anisotropic s-wave and extended s-wave pairings, and moreover sample inhomogeneity can also hinder a reliable determination of the gap structure from the specific heat. As such, in order to confirm the nature of the gap structure of all three compounds, further measurements on high-quality samples to lower temperatures are necessary.

We also investigated the superconducting properties of the X = In compounds, La$_4$RuIn and La$_4$IrIn. The temperature dependences of the resistivity, ac susceptibility and electronic specific heat are shown in Fig. 3. Both exhibit metallic behavior, as shown in the insets, with respective residual resistivities of 134 and 100 µΩ cm, and RRR of 1.9 and 1.6. La$_4$RuIn has a superconducting transition at around 0.61 K, with a relatively wide transition width, while La$_4$IrIn becomes superconducting below around 0.93 K. As shown in the insets, fitting the low-temperature specific heat above $T_c$ yields $\gamma_n$ of 15.9(1) and 21.1(2) mJ mol$^{-1}$ K$^{-2}$ for La$_4$RuIn and La$_4$IrIn, together with $\beta$ of 2.51(2) and 2.09(2) mJ mol$^{-1}$ K$^{-4}$. These correspond to $\theta_D$ of 169(1) and 177(1) K, which are lower than those of the X = Al compounds described above, consistent with the lower values of $T_c$. Using Equation (1), $\lambda_{el-ph}$ values were estimated to be 0.36–0.45 and 0.39–0.48, implying weaker electron-phonon coupling strengths compared with the X = Al compounds. The electronic specific heat jumps $\Delta C/\gamma_n T_c$ of 0.82 for La$_4$RuIn and 1.01 for La$_4$IrIn are much smaller than the BCS value of 1.43. Polycrystalline samples of isostructural Lu$_4$RhAl and Lu$_4$RhIn were also successfully synthesized, and no superconductivity was observed from measurements down to 0.4 K.

In-field superconducting properties

Measurements of the dc magnetic susceptibility were carried out only for La$_4$RhAl as its $T_c$ is higher than the low-temperature limit 2 K of the available MPMS. Fig. 4a displays the low-temperature dc magnetic susceptibility of La$_4$RhAl upon both zero-field cooling (ZFC) and field-cooling (FC) in an applied field of 1 mT, where the data are corrected for demagnetization effects. Here a demagnetization factor of $N = 0.18$ is estimated, considering a cuboid sample of dimensions $0.81$ mm $\times 0.55$ mm $\times 1.45$ mm, with the field applied along the longest side [61]. A clear transition at around 3.1 K and a saturated diamagnetic signal value of $4\pi \chi$ close to $-1$ in the ZFC curve provide evidence for full diamagnetic shielding in La$_4$RhAl. The large difference between the FC and ZFC curves is due to trapping of the magnetic flux, which is frequently observed in polycrystalline samples of type-II superconductors. Fig. 4b displays the field dependence of the magnetization $M(H)$ measured at various temperatures below $T_c$ using a ZFC protocol, which shows the typical behavior expected for a type-II superconductor. A linear fitting of the low-field region, $M_{iso}$ is shown by the solid line. The lower critical field $\mu_0 H_{c1}$ was determined from the field where the magnetization deviates from the linear response by a small value of 0.1 emu cm$^{-3}$, as displayed in the inset of Fig. 4c. Fig. 4c displays the temperature dependence of the obtained $\mu_0 H_{c1}$ after correcting for demagnetization effects, which were
fitted with
\[ \mu_0 H_{c2}(T) = \mu_0 H_{c2}(0) \left[ \frac{T}{T_c} \right]^2 \] 

yielding a zero-temperature value of \( \mu_0 H_{c2}(0) = 10.1(2) \) mT.

Fig. 5 displays the temperature dependence of \( \rho(T) \) and \( C_v/T(T) \) of La₄TAl under various applied fields. The superconducting transitions are gradually shifted to lower temperatures and become slightly broadened with increasing magnetic field. The specific heat jump becomes smaller, suggesting second-order transitions in field for the three materials, which is characteristic of type-II superconductivity. The upper critical fields \( \mu_0 H_{c2} \) plotted as a function of temperature are shown in Fig. 5g–i. Here \( T_c \) is determined from where resistivity is 10% of the normal state value (blue) and the midpoints of the specific heat jump (red). The upper critical fields \( \mu_0 H_{c2}(T) \) can be fitted by the Werthamer-Helfand-Hohenberg (WHH) model [62], from solving
\[
\ln t = 1 + \left( 1 + \frac{\nu_0 H_{c2}(0)}{2} \right) + \left( 1 - \frac{\nu_0 H_{c2}(0)}{2} \right) \psi \left( 1 + \frac{h + 0.5 \delta_{v0} + i \delta}{2t} \right),
\]

where \( \psi(x) \) is the digamma function, \( t = T/T_c \),
\[
h = \frac{4H_{c2}}{\pi^2} \left( \frac{dH_{c2}}{dT} \right)^{-1}
\]
and \( \delta = \sqrt{\left( \alpha_v h \right)^2 - 0.25 \delta_{v0}^2} \). Since here the orbital limiting fields are much less than the Pauli paramagnetic limit, we used \( \alpha_v = 0 \), and as such the spin-orbit scattering parameter \( \lambda_{so} \) does not affect \( H_{c2} \). Using the slope of the upper critical field near \( T_c \), \( (d\nu_0 H_{c2}/dT = -1.06, -1.49, \) and \( 1.17 \) \( T^{-1} \), for the Ru, Rh, and Ir variants, respectively), we can obtain zero-temperature values \( \nu_0 H_{c2}(0) = 1.34(1), 3.34(2), \) and \( 1.39(1) \) \( T \), respectively. All of these are significantly below the Pauli limit \( (\nu_0 H_{c2}^{Pauli} = 1.86T_c) \). The Ginzburg-Landau coherence length \( \xi_{GL} \) was calculated to be \( 15.6(1) \) \( nm \) for \( La_{4}RuAl, 9.9(1) \) \( nm \) for \( La_{4}RhAl \) and \( 15.3(1) \) \( nm \) for \( La_{4}IrAl \), using
\[
\nu_0 H_{c2}(0) = \frac{\Phi_0}{2\pi \xi_{GL}}.
\]

Therefore, the Ginzburg-Landau parameter \( \kappa_{GL} = \lambda_{GL}/\xi_{GL} \) is \( 22.7(3) \), which is much larger than \( 1/\sqrt{2} \), indicating type-II superconductivity in \( La_{4}RhAl \). The thermodynamic critical field \( \nu_0 H_{c2}(0) \) can be estimated from
\[
\mu_0 H_{c2}(0) = \left( \frac{\Phi_0}{4\pi \xi_{GL}} \right)^2
\]
yielding \( 105(3) \) \( mT \) for \( La_{4}RhAl \).

The residual electronic specific heat coefficient \( \gamma_0(H) \) can give information about low-energy quasi-particle excitations near vortex cores and hence can characterize the superconducting pairing state. The magnetic field dependences of the normalized residual Sommerfeld coefficient \( \gamma_0(0)/\gamma_n \) are shown in the insets of Fig. 5g, h, where the linear behaviors are consistent with nodeless superconductivity.

The upper critical fields of \( La_{4}RuIn \) and \( La_{4}IrIn \) were determined from \( \rho(T) \) and \( C/T \) in various magnetic fields, as shown in Fig. 6. The \( \mu_0 H_{c2} \) values are displayed in Fig. 6e, f. The WHH model can be used to fit the data, yielding \( \mu_0 H_{c2}(0) \) of \( 0.24(1) \) and \( 0.52(1) \) \( T \) for \( La_{4}RuIn \) and \( La_{4}IrIn \), respectively, where both...
values are much smaller than the Pauli limit. The coherence length $\xi_{GL}$ are calculated via Equation (7) to be 37.0(1) nm (La$_4$RuIn) and 25.1(1) nm (La$_4$IrIn). The corresponding data are summarized in Table 2.

DFT calculations

Calculations of the band structure of La$_4$TX ($T = $ Ru, Rh, Ir; $X = $ Al, In) were performed. These are displayed in Fig. 7, both with and without the inclusion of SOC. Since the crystal structure contains four formula units per unit cell, the band structure is very complex and highly metallic, consistent with resistivity measurements. The electronic bands are clearly split due to the ASOC and the splitting magnitude near the Fermi level $E_{ASOC}$ for each compound is listed in Table 2, where the splitting values at the high symmetry K-points are taken as representative values. The values are between 13 and 40 meV, which are moderately large compared with those of other NCSs [1]. As the SOC is related to the atomic number $Z$ [63,64], the compounds with the heavier elements Ir and In have larger $E_{ASOC}$ splitting than those with Ru, Rh, and Al. In addition, overall the Rh/Ir compounds can be regarded as electron doped compared to the Ru compounds. This effect is most prominent in the states around $\Gamma$, where the electron pockets in the Ru compounds are absent in Rh/Ir compounds. It is noted that numerous band-crossing-like

Table 2  Superconducting and normal state properties of La$_4$TX. Here $N_{DFT}(E_F)$ and $\gamma_n^{cal}$ correspond to the calculated values of the DOS at the Fermi level and the Sommerfeld coefficient, respectively, from DFT calculations.

| Compound     | $T_c$ (K) | $\mu_0 H_{c2}$ (T) | $\xi$ (nm) | $\gamma_n^{cal}$ (meV) | $\lambda_{d-ph}$ (K) | $N_{DFT}(E_F)$ (states eV$^{-1}$ f.u.$^{-1}$) | $\gamma_n^{cal}$ (mJ mol$^{-1}$ K$^{-2}$) | $E_{ASOC}$ (meV) | $\frac{E_{ASOC}}{\lambda_{d-ph}}$ |
|--------------|-----------|--------------------|------------|------------------------|---------------------|---------------------------------------------|----------------------------------------|------------------|---------------------------|
| La$_4$RuAl   | 1.88      | 1.34(1)            | 15.6(1)    | 20.1(1)                | 204(2)              | 0.45–0.54                                    | 5.51                                   | 20.0             | 13                         |
| La$_4$RhAl   | 3.35      | 3.34(2)            | 9.9(1)     | 29.3(2)                | 208(2)              | 0.52–0.62                                    | 6.35                                   | 24.3             | 16                         |
| La$_4$IrAl   | 1.75      | 1.39(1)            | 15.3(1)    | 21.3(1)                | 191(1)              | 0.44–0.53                                    | 5.18                                   | 18.7             | 37                         |
| La$_4$RuIn   | 0.61      | 0.24(1)            | 37.0(1)    | 15.9(1)                | 169(1)              | 0.36–0.45                                    | 2.53                                   | 8.7              | 17                         |
| La$_4$IrIn   | 0.96      | 0.52(1)            | 25.1(1)    | 21.1(2)                | 177(1)              | 0.39–0.48                                    | 4.90                                   | 17.2             | 40                         |

DFT calculations

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features between X-W and U-L exist near the Fermi level in this compound. The band topology and its relation with the superconductivity in this family require further study.

The partial densities of states (DOS) are shown in the Supplementary information. The contributions to the DOS at the Fermi level $N(E_F)$ are dominated by La d orbitals for all the materials, with smaller contributions from T d, La p and In p orbitals. In La$_4$RhAl, the quasi-flat bands near the W point at $\sim E_F -30$ meV and $\sim E_F + 10$ meV result in two van-Hove singularity like peaks in the DOS, which disappear in La$_4$IrIn as the SOC is enhanced. The values of the total $N(E_F)$ are summarized in Table 2, where it can be seen that the compounds with relatively higher $T_c$ have comparatively larger $N(E_F)$. The relatively lower $T_c$ values and larger band splitting of La$_4$TIn may point to the influence from the ASOC on $N(E_F)$ and $T_c$. The electronic specific heat coefficient can be estimated using

$$\gamma_n = \frac{1}{T} \lambda_{el-ph} \frac{N(E_F)}{1 + \lambda_{el-ph}}.$$  

where $\lambda_{el-ph}$ is experimentally determined as described above. The resulting values $\gamma_n = 20.0$ mJ mol$^{-1}$ K$^{-2}$ (La$_4$RuAl), 24.3 mJ mol$^{-1}$ K$^{-2}$ (La$_4$RhAl), 18.7 mJ mol$^{-1}$ K$^{-2}$ (La$_4$IrAl), 8.7 mJ mol$^{-1}$ K$^{-2}$ (La$_4$RuIn), and 17.2 mJ mol$^{-1}$ K$^{-2}$ (La$_4$IrIn) are slightly smaller than the observed $\gamma_n$ (Table 2), suggesting a small effective-mass enhancement due to electronic correlations.

To explore the relationship between superconducting properties and the ASOC strength, the ratios $E_{\text{S SOC}}/k_B T_c$ for the five superconductors are listed in Table 2. In each panel, the band structures without (red) and with (blue) SOC are presented. (f) Total density of states of the five superconductors near the Fermi level.

SUMMARY

We report superconductivity in a series of noncentrosymmetric compounds La$_4$TX (T = Ru, Rh, Ir; X = Al, In) with the cubic Gd$_4$RhIn-type structure (space group $F m\overline{4}3m$), and characterize the superconducting properties by means of electrical resistivity, magnetization and specific heat measurements, as well as electronic structure calculations. Bulk superconductivity was found with $T_c$ values of 1.88, 3.35, 1.75, 0.61 and 0.96 K for La$_4$RuAl, La$_4$RhAl, La$_4$IrAl, La$_4$RuIn, and La$_4$IrIn, respectively. Both the temperature and field dependences of the specific heat of La$_4$RuAl and La$_4$RhAl are consistent with nodeless superconductivity, while a nodal gap cannot be excluded from the analysis of $C_e/T$ of La$_4$IrAl, which has a significantly stronger ASOC. This opens up the possibility that the ASOC can tune the superconducting pairing states of the La$_4$TX series, and examination of this scenario requires systematic studies of the gap structures at lower temperatures, to look for unconventional superconducting properties. Furthermore, the calculated partial DOS of La$_4$TX indicates that there is a dominant contribution from La orbitals near $E_F$, and hence substitution on the La-site may allow for a wider range of ASOC splitting to be realized.
elemental substitution, and therefore they are good candidates for examining the relationship between the ASOC and superconducting properties. As such, it is of particular interest to characterize the superconducting pairing states of these compounds, via both measurements to lower temperatures which are sensitive to the superconducting gap structure, as well as probing for broken time reversal symmetry using muon-spin relaxation or the Kerr effect.

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Author contributions Smidman M and Yuan H conceived the study and led the project. Samples were synthesized by Su H, Xie W, Takakabate T and Smidman M. Measurements of the properties were performed by Su H, Luo S, Nie Z, Li R, Shen B, Wang Y, and Smidman M. The experimental data were analyzed by Su H, Nie Z, Wang A, Takakabate T, Smidman M, and Yuan H. Theoretical calculations were performed by Du F and Cao C. The manuscript was written by Su H, Cao C, Smidman M, and Yuan H. All authors participated in discussions.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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La$_8$TX (T = Ru, Rh, Ir; X = Al, In): 一个具有可调节反对称自旋轨道耦合强度的新型非中心对称超导体系

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摘要 本文报道了非中心对称化合物家族La$_8$TX (T = Ru, Rh, Ir; X = Al, In)中的超导电性。该系列超导体具有立方晶体结构，空间群为$Pmar{3}m$。La$_8$RuAl, La$_8$RhAl, La$_8$IrAl, La$_8$RuIn和La$_8$RhIn的超导转变温度在0.61–3.35 K之间，而La$_8$In和La$_8$AlIn的低温比热可由无超导能隙节点的$e$波超导描述。这些超导体的上临界磁场可通过Werthamer-Helfand-Hohenberg模型描述，且上临界场$H_{c2}(0)$远低于饱和流动。说明轨道效应在库伯对拆对机制中占据主导，密度泛函理论计算表明，对于该超导家族的不同化合物，其反对称自旋-轨道耦合导致的能带劈裂在明显区别。有助于进一步探究超导配对态与反对称自旋-轨道耦合强度之间的联系。