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Electron-Phonon Coupling and Superconducting Critical Temperature of the YIr$_2$Si$_2$ and LaIr$_2$Si$_2$ High-Temperature Polymorphs from First-Principles

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Ab initio calculations of the electronic structure and lattice-vibrational properties were performed on the superconducting high-temperature polymorphs of YIr$_2$Si$_2$ and LaIr$_2$Si$_2$. The electron-phonon coupling constants λ_{ep} were found to be 0.61 and 0.56 for YIr$_2$Si$_2$ and LaIr$_2$Si$_2$, respectively. The superconducting critical temperatures estimated from the Allen-Dynes formula agree well with the available experimental data and indicate that the superconductivity in these compounds can be explained by intermediate electron-phonon coupling.

I. INTRODUCTION

Ternary intermetallic compounds have been shown to display a rich spectrum of novel phases such as magnetism, heavy-fermion behaviour and superconductivity and have therefore been the subject of many studies in recent years [1]. Much of this research has focused on materials which contain rare-earth elements that have localised $4f$ electrons. These exhibit complicated interactions with one another which are mediated by the delocalised valence electrons [2]. As the presence of $4f$ electrons can complicate the understanding of these compounds, analogues containing Y, La or Lu are desirable in order to elucidate the f-electron independent properties.

Other compounds of interest are those in which the atoms are arranged in layers, perhaps some of the most notable being the iron-pnictide superconductors [3, 4]. Within this family, particular attention has been paid to the tetragonal *122* group with the ThCr$_2$Si$_2$ structure. Since many of the properties of these compounds depend upon the symmetry and chemical environment of the constituent atoms, it is often useful to study structural and chemical analogues. One such family are the *122* rare-earth iridium silicides, some of which are found to display the remarkable property of polymorphism where the material can appear in more than one crystal struture but with the same stoichiometry. YIr$_2$Si$_2$ and LaIr$_2$Si$_2$ belong to this family and have superconducting phases. The low-temperature polymorphs (LTP) have the ThCr$_2$Si$_2$ structure (space group $I4/mmm$) and are thermodynamically stable at room temperature whilst the high-temperature polymorphs (HTP) have the CaBe$_2$Ge$_2$ structure (space group $P4/nmm$) and can be studied at room temperature by quenching from above the transition temperature [5–7]. Thus, YIr$_2$Si$_2$ and LaIr$_2$Si$_2$ provide a rare and unique opportunity to study the *122*-type structure, free from f-electron influences. The aim of this study is to understand the role of electron-phonon coupling in the superconductivity in the HTP of both compounds.

Previous studies on the two polymorphs of LaIr$_2$Si$_2$ agree that only the HTP has a superconducting phase, with a T_c in the range 1.52-1.6 K [5–7]. For YIr$_2$Si$_2$, some

report that both polymorphs show superconductivity in slightly different temperature ranges ($T_c = 2.45 - 2.6$ K and $T_c = 2.6 - 2.7$ K for the LTP and HTP, respectively) [8–10], whilst Shelton *et al.* report that superconductivity only occurs in the HTP with $T_c = 2.72 - 2.83$ K [6]. More recently, Vališka *et al.* found that in both compounds only the HTP shows superconductivity, at $T_c = 2.52$ K in YIr$_2$Si$_2$ and $T_c = 1.24$ K in LaIr$_2$Si$_2$, and claim that careful control of the annealing temperature and cooling rate are essential for obtaining a single phase material which they argue can explain the controversial findings in previous work [11]. Through the use of density functional theory (DFT) calculations and their measured Debye temperature, $\theta_{\mathrm{D}} = 145$ K for YIr$_2$Si$_2$, they were also able to estimate $T_c = 0.45$ K from the McMillan formula [12]. This is much smaller than their measured value leading them to propose that the observed superconductivity may result from the coupling of electrons to special phonon modes.

II. COMPUTATIONAL DETAILS

Two separate sets of calulations were performed, the first using a highly accurate all-electron full-potential linearized augmented plane-wave (FP-LAPW) method in order to determine the ground state electronic structure, whilst a plane-wave pseudopotential method was used to calculate the phonons and electron-phonon coupling by linear response. From these calculations, it is shown that electron-phonon coupling is capable of producing the observed superconductivity in the HTP of both compounds.

The ELK code [13], a highly accurate all-electron FP-LAPW method, was used to determine the ground state electronic structure. The HTP of YIr$_2$Si$_2$ and LaIr$_2$Si$_2$ crystallise in the CaBe$_2$Ge$_2$ structure (space group $P4/nmm$). The lattice constants and internal atomic coordinates were fixed at the experimental values (see tables I and II) [11] and calculations were made with a cutoff for plane-waves (in the interstitial region) determined by $|\mathbf{G} + \mathbf{k}|_{\max} = 7.5/R_{\mathrm{mt}}$, where R_{mt} is the average muffin-tin radius. In YIr$_2$Si$_2$ the muffin-tin radii for Y, Ir1, Ir2, Si1 and Si2 were 2.6000, 2.2817, 2.5000,

TABLE I: Comparison of the experimental lattice constants [11] of YIr_2Si_2-HTP and $LaIr_2Si_2$-HTP and those calculated in this work.

YIr_2Si_2	Experiment [11]	Calculation
a [Å]	4.0938(2)	4.132
c [Å]	9.6856(7)	9.858
c/a	2.3659(2)	2.386
$LaIr_2Si_2$		
a [Å]	4.1873(1)	4.214
c [Å]	9.9380(3)	10.009
c/a	2.3734(1)	2.375

TABLE II: Comparison of the experimental Wyckoff positions [11] of YIr_2Si_2-HTP and $LaIr_2Si_2$-HTP and those calculated in this work.

YIr_2Si_2	Experiment [11]			Calculation		
Atom	x	y	z	x	y	z
Y	1/4	1/4	0.742(8)	1/4	1/4	0.754
Ir1	3/4	1/4	1/2	3/4	1/4	1/2
Ir2	1/4	1/4	0.127(5)	1/4	1/4	0.128
Si1	3/4	1/4	0	3/4	1/4	0
Si2	1/4	1/4	0.422(9)	1/4	1/4	0.369
$LaIr_2Si_2$						
La	1/4	1/4	0.742(8)	1/4	1/4	0.744
Ir1	3/4	1/4	0	3/4	1/4	0
Ir2	1/4	1/4	0.374(4)	1/4	1/4	0.374
Si1	3/4	1/4	1/2	3/4	1/4	1/2
Si2	1/4	1/4	0.140(8)	1/4	1/4	0.129

1.9643 and 1.7928 a.u., respectively, and in $LaIr_2Si_2$ the muffin-tin radii for La, Ir1, Ir2, Si1 and Si2 were 2.8000, 2.7736, 2.3959, 2.1657 and 1.9122 a.u., respectively. Convergence was obtained for both compounds on 1331 k-points in the irreducible Brillouin zone and the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) exchange-correlation functional was used [14].

In order to investigate electron-phonon mediated superconductivity, the QUANTUM ESPRESSO package was used to calculate, by linear response, the phonon dispersions and the electron-phonon coupling [15]. Scalar relativistic ultrasoft pseudopotentials were chosen and convergence was checked with respect to the k-point density and the plane-wave cutoffs. Subsequent calculations were made with wavefunction and charge-density cutoffs of 40 Ry and 400 Ry, respectively. Phonons were calculated on a $4 \times 4 \times 2$ Monkhorst-Pack q-point grid with Brillouin zone integrations on a $16 \times 16 \times 8$ mesh, while the electron-phonon coupling was evaluated on a denser $(32 \times 32 \times 16)$ mesh.

It is well known that phonon calculations at the experimental lattice constants and internal atomic coordinates lead to softer (lower) frequencies than those calculated at
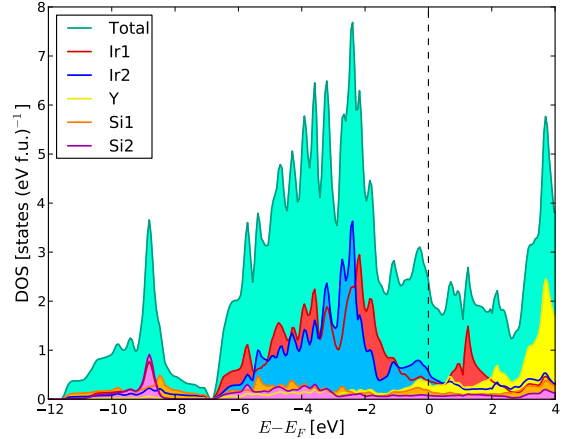

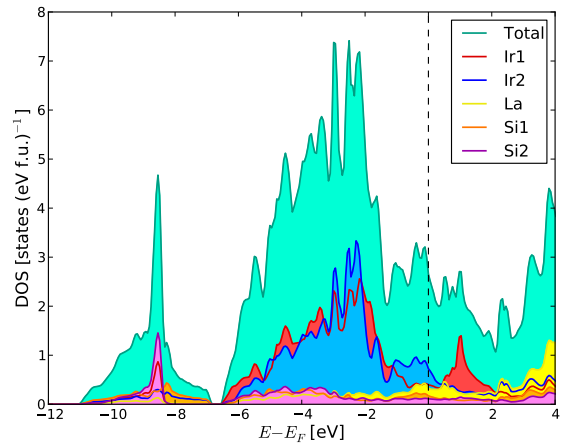FIG. 1: (Color online) DOS of YIr_2Si_2 in the relaxed structure.

FIG. 2: (Color online) DOS of $LaIr_2Si_2$ in the relaxed structure.

the relaxed positions [16]. Therefore, the relaxed structure was determined within the pseudopotential code (as this code is used for the phonon calculation) by minimising the total energy with respect to the lattice constants and by minimising the forces on the atoms with respect to the internal coordinates. The results are summarised in tables I and II and show good agreement with experimental data and previous calculations [6, 11, 17, 18]. In both compounds the relaxed cell volume is larger (by 3.7% in YIr_2Si_2 and 2.0% in $LaIr_2Si_2$). This is a well known inherent problem of GGA functionals which tend to underbind structures in contrast to LDA functionals which tend to overbind. The atomic positions changed very little except for the Si2 atoms which, in the Y-based compound, move further from, and in the La-based compound move closer to, the Ir1 square nets. It is interesting to note that for both compounds in the relaxed geometry the Si2 atoms sit approximately the same fractional distance from the Ir1 square nets ($0.131c$ for YIr_2Si_2 and
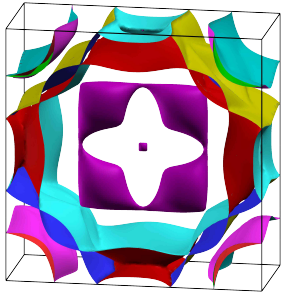
FIG. 3: (Color online) The Fermi surface of YIr$_2$Si$_2$ in the relaxed structure.
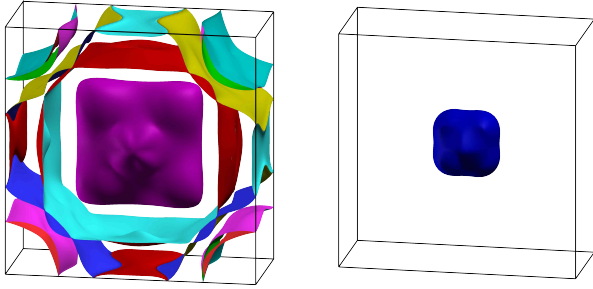

FIG. 4: (Color online) The Fermi surface of LaIr$_2$Si$_2$ in the relaxed structure (left) and band 75 (right) which is hidden by the other sheets.

0.129c for LaIr$_2$Si$_2$).

III.   RESULTS AND DISCUSSION

The density-of-states (DOS) of the relaxed structures of YIr$_2$Si$_2$ and LaIr$_2$Si$_2$ are shown in figs. 1 and 2, respectively, and the corresponding Fermi surfaces are shown in figs. 3 and 4, respectively. Both compounds have similar electronic structures with six bands crossing the Fermi level, two of which are three dimensional whilst the remaining four are quasi-two dimensional. In both compounds, the main contribution to the Fermi level DOS $N(E_F)$ comes from the Ir d electrons which have a slight degree of hybridization with Y/La d and Si p states. In both compounds, the Ir2 atoms (which surround the Si1 square nets) contribute more states at the Fermi level than the Ir1 atoms (which are arranged in square nets surrounded by the Si2 atoms).

In order to confirm the validity of the pseudopotential-based structural relaxation, the calculated electronic structure was compared with the all-electron FP-LAPW calculation at both the experimental and relaxed structure. In YIr$_2$Si$_2$ the muffin-tin radii for Y, Ir1, Ir2, Si1 and Si2 were now 2.6000, 2.6869, 2.4005, 2.1275 and 1.8716 a.u., respectively, and in LaIr$_2$Si$_2$ the muffin-tin radii for La, Ir1, Ir2, Si1 and Si2 were now 2.8000, 2.5862, 2.5651, 2.0203 and 2.0271 a.u., respectively. In LaIr$_2$Si$_2$, the DOS, band structure and Fermi surface were found
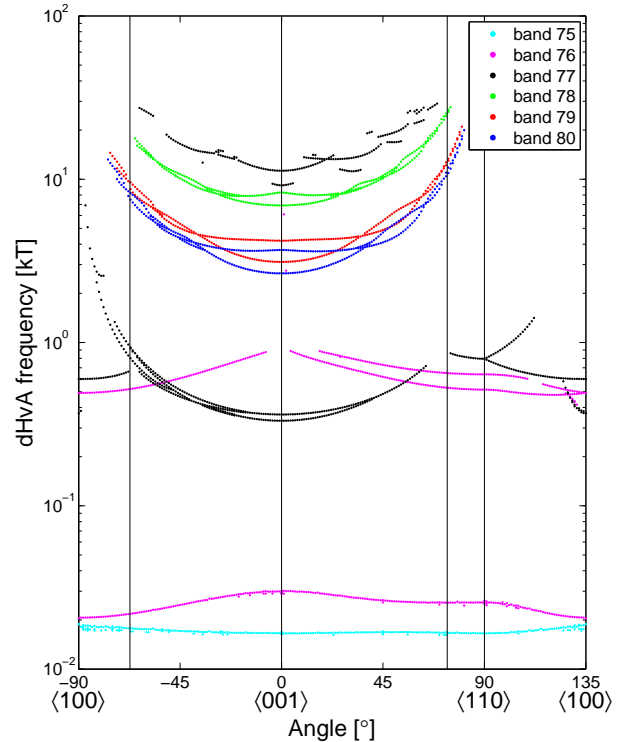

FIG. 5: (Color online) Predicted angular dependences of the calculated dHvA frequencies for YIr$_2$Si$_2$ in the relaxed structure.

to be almost indistinguishable, however, the calculated $N(E_F) = 2.65$ states (eV f.u.)$^{-1}$ was slightly higher than $N(E_F) = 2.26$ states (eV f.u.)$^{-1}$ for the experimental structure. In YIr$_2$Si$_2$, the calculation with the experimental structure converged to a solution 5.87 eV higher in energy than the relaxed structure. For the experimental structure, the calculated $N(E_F) = 4.84$ states (eV f.u.)$^{-1}$ was much higher than $N(E_F) = 2.42$ states (eV f.u.)$^{-1}$ for the relaxed structrue. By calculating the linear electronic specific heat coefficient γ^{calc} from,

$$\gamma^{\text{calc}} = \frac{\pi^2}{3} k_B^2 N(E_F), \tag{1}$$

we find that $\gamma^{\text{calc}} = 11.39$ mJ K^{-2} mol^{-1} and $\gamma^{\text{calc}} = 5.69$ mJ K^{-2} mol^{-1} for the experimental and relaxed structures, respectively. Since the calculation explicitly neglects any many-body effects which would increase γ^{exp} relative to γ^{calc}, the mass renormalisation λ can be evaluated through the relationship,

$$\frac{\gamma^{\text{exp}}}{\gamma^{\text{calc}}} = 1 + \lambda. \tag{2}$$

Given the experimentally determined $\gamma^{\text{exp}} = 8.0$ mJ K^{-2} mol^{-1} [11] this would imply that the calculation with the experimental structure would have a negative (unphysical) mass renormalisation.
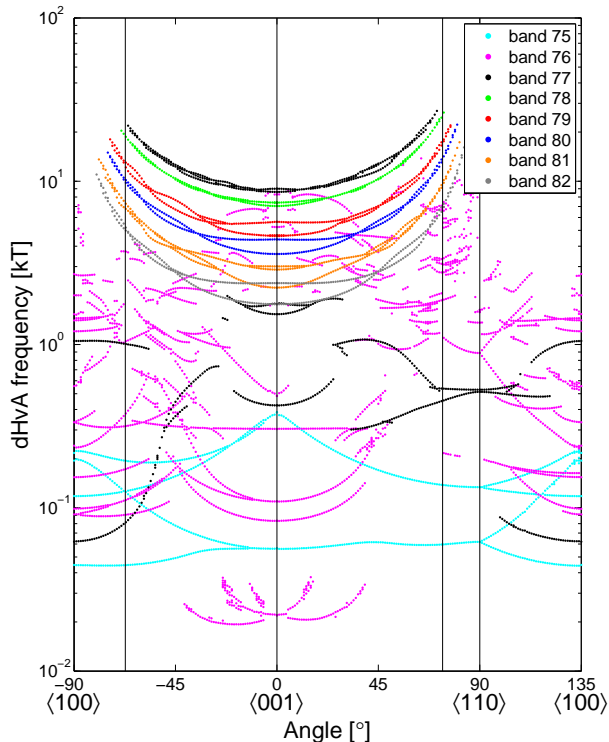
FIG. 6: (Color online) Predicted angular dependences of the calculated dHvA frequencies for YIr$_2$Si$_2$ in the experimental structure.

FIG. 7: Phonon dispersion of YIr$_2$Si$_2$ along selected high-symmetry directions. The size of the points indicates the relative size of the electron-phonon coupling of that mode at that q-point.

Further support for using the relaxed structure comes from comparison with the DFT calculations by Shein [17] and Vališka *et al.* [11] who find $\gamma^{\text{calc}} = 5.459$ mJ K^{-2} mol^{-1} and $\gamma^{\text{calc}} = 5.64$ mJ K^{-2} mol^{-1}, respectively. It therefore seems unlikely that the calculation at the experimental coordinates is the true ground state of this system. This situation is highly reminiscent of the iron-pnictide superconductors where it has been shown that the calculated electronic structure is heavily dependent on the internal pnictogen position and, in the case of optimally doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, requires the relaxation of the internal As position in order to bring the Fermi surface into agreement with experiment [19, 20].

The predicted angular dependences of the calculated de Haas-van Alphen (dHvA) frequencies [21] for the relaxed (and, for completeness, the experimental) structure of YIr$_2$Si$_2$ are presented in figs. 5 and 6, respectively. Since the electron-phonon coupling is heavily dependent on the electronic structure near the Fermi level and considering the arguments above and the agreement of the calculated electronic structure with previous reports [11, 17], the relaxed structure has been adopted for the remainder of this study.

The phonon dispersions of YIr$_2$Si$_2$ and LaIr$_2$Si$_2$ are shown in figs. 7 and 8, respectively, where the size of the points indicates the relative size of the mode and q-point resolved electron-phonon coupling. Both compounds ex-
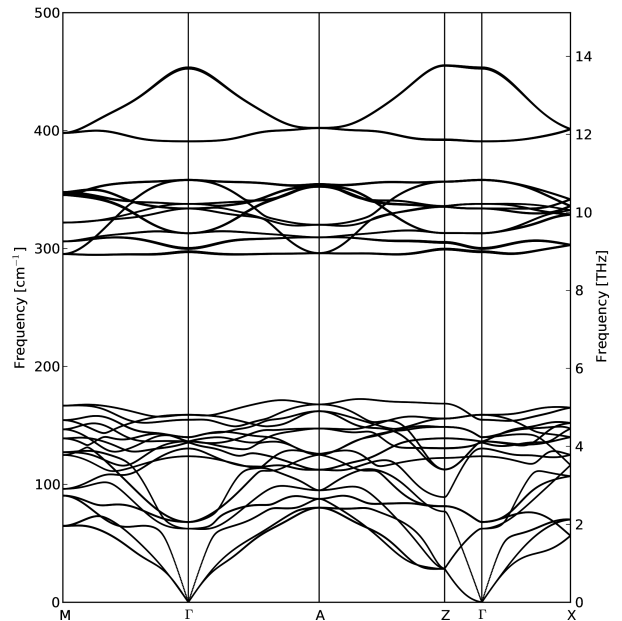

FIG. 8: (Color online) Phonon dispersion of LaIr$_2$Si$_2$ along selected high-symmetry directions. The size of the points indicates the relative size of the electron-phonon coupling of that mode at that q-point.
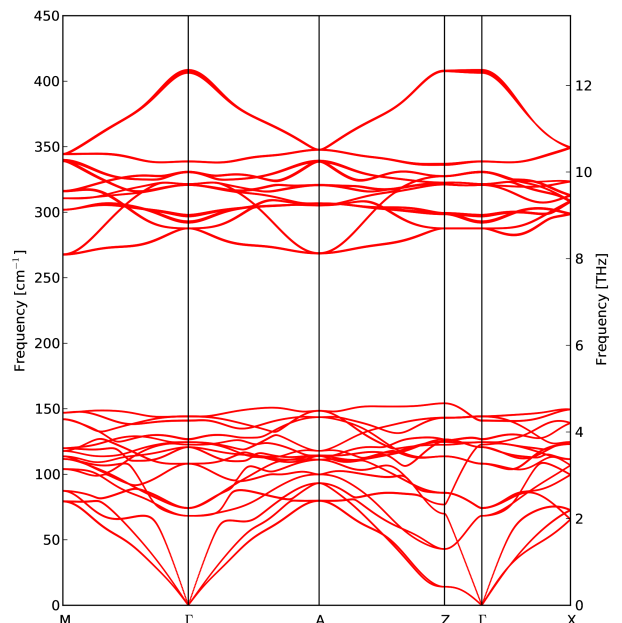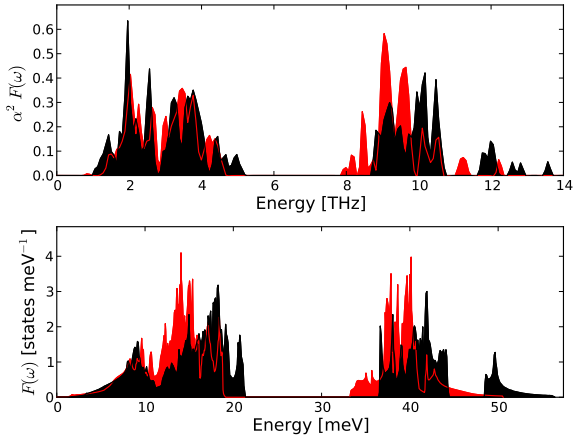
FIG. 9: (Color online) Comparison of the Eliashberg function $\alpha^2 F(\omega)$ (top) and the phonon DOS $F(\omega)$ (bottom) of YIr_2Si_2 (black) and $LaIr_2Si_2$ (red). As 1 THz is equivalent to 4.1 meV (or 33 cm^{-1}), the ranges spanned by the two separate plots are equivalent.

hibit a large gap in the frequency spectrum due to the large mass difference between the light Si atoms and the heavier Y, La and Ir atoms. YIr_2Si_2 also exhibits another gap at higher frequencies whereas $LaIr_2Si_2$ does not since the La and Ir masses are similar.

The calculated phonon density of states $F(\omega)$ and Eliashberg function $\alpha^2 F(\omega)$ are shown in fig. 9. These yield electron-phonon coupling constants λ_{ep} of 0.61 and 0.56 for YIr_2Si_2 and $LaIr_2Si_2$, respectively. In YIr_2Si_2 the average coupling across the 30 modes is 0.0205, however the contributions from the first five modes greatly exceed this (0.0923, 0.0805, 0.0620, 0.0471 and 0.0307, respectively). For $LaIr_2Si_2$ the average coupling per mode is 0.0186 and again the contributions from the first five modes are much larger (0.0750, 0.0632, 0.0528, 0.0320 and 0.0336, respectively). These first five modes are responsible for the peaks in $\alpha^2 F(\omega)$ below about 3 THz (100 cm^{-1}) and contribute approximately half of the total λ_{ep} in both compounds.

After calculating the relevant electron and phonon quantities, the superconducting critical temperature can be estimated from the Allen-Dynes formula [22]. Here,

$$T_c = \frac{\hbar\omega_{\ln}}{1.2 k_B} \exp\left(-\frac{1.04(1+\lambda_{ep})}{\lambda_{ep} - \mu^*(1 + 0.62\lambda_{ep})}\right), \quad (3)$$

where λ_{ep} is the electron-phonon coupling, $\omega_{\ln}$ is the logarithmically averaged phonon frequency and the dimensionless μ^* is the Coulomb pseudopotential, which characterizes the strength of the (screened) electron-electron Coulomb repulsion. Using the calculated $\lambda_{ep} = 0.61$, $\omega_{\ln} = 101.12\,cm^{-1}$, and choosing $\mu^* = 0.13$ (suggested by McMillan for all transition metals and their compounds [12] although values between 0.1 and 0.2 are considered

physically reasonable [23, 24]), a T_c of 2.54 K is obtained for YIr_2Si_2 which agrees remarkably well with the experimental value of 2.52 K [11]. For $LaIr_2Si_2$, $\lambda_{ep} = 0.56$, $\omega_{\ln} = 110.62\,cm^{-1}$, and again with $\mu^* = 0.13$ this gives a T_c of 1.92 K which is reasonably close to the experimental value of 1.24 K [11].

Although our initial estimate for T_c in $LaIr_2Si_2$ is approximately 50% higher than the experimental value, it is worth considering that μ^* may not be the same for the two systems. Within Eliashberg theory, μ^* is normally considered an adjustable parameter [23]. If the Allen-Dynes formula is used for $LaIr_2Si_2$ but with $\mu^* = 0.15$ (which is reasonable) then $T_c = 1.39$ K is obtained. It is also worth noting that here the experimental situation is less clear. Firstly, the superconducting transition in the two compounds is quite different. In YIr_2Si_2 the transition is quite sharp ($\Delta T = 0.1$ K) whilst for $LaIr_2Si_2$ the transition is much broader ($\Delta T = 0.4$ K) [11]. Secondly, the authors also show that when determined from resistivity measurements, a value of $T_c = 1.4$ K is obtained (compared with $T_c = 1.24$ K from specific heat measurements). Finally, previous studies have given the measured T_c in the range 1.52-1.6 K [5–7].

IV. CONCLUSION

In conlusion, the electronic structure and lattice vibrational properties of HTP YIr_2Si_2 and $LaIr_2Si_2$ were calculated from first-principles. This allowed an evaluation of the electron-phonon coupling from which the superconducting critical temperature was estimated. The electron-phonon coupling was found to be slightly higher for YIr_2Si_2 ($\lambda_{ep} = 0.61$) compared with $LaIr_2Si_2$ ($\lambda_{ep} = 0.56$) which, despite a larger logarithmically averaged phonon frequency in the latter, explains the difference in T_c. Using the Allen-Dynes formula, we find $T_c = 2.54$ K and $T_c = 1.39$ K for the Y and La-based compounds, respectively, which is in excellent agreement with recent experimental findings. The calculations show that the electron-phonon coupling in the HTP of both compounds is dominated by the low energy phonon modes. Finally, we also note that phonon calculations for the LTP of both systems may be interesting and could reveal soft phonon modes related to the structural phase transition, but such an investigation is beyond the scope of this study.

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