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## Enhanced thermoelectric properties of heavy-fermion compounds

$$\left( \text{Yb}_x\text{Ce}_y\text{Sm}_z\text{Ir}_{mn} \right)_{20}$$
$$\text{Zn}_{20}$$
$$\left( \text{Yb}_x\text{Ce}_y\text{Sm}_z \right)_{mn}^{-1}$$

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# Enhanced Thermoelectric Properties of Heavy-fermion Compounds



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Thermoelectric materials hold tremendous promise for advances in fundamental science and practical applications; particularly for robust electricity generation in extreme and remote environments. Despite this, for most materials the energy conversion efficiency is limited by the proportionality between the electrical and thermal conductivities and small values of the Seebeck coefficient for metals. It was previously reported that the heavy-fermion compound  $\text{YbIr}_2\text{Zn}_{20}$  exhibits a large Seebeck coefficient [Mun et al., *Phys. Rev. B* **86**, 115110 (2012)] and thermoelectric figure of merit,  $ZT$ , at 35 K [Wei et al., *Sci. Adv.*, **5**, eaaw6183 (2019)]. This behavior is primarily associated with strong hybridization between the  $f$ - and conduction electron states. Here we seek to improve the thermoelectric properties through chemical substitution on the Yb site using Ce and Sm. By surveying different levels of substitution, we find that the thermoelectric properties vary strongly with the  $f$ -element ratio. This confirms that electronic hybridization dominates the thermoelectric properties and clarifies directions for optimizing these materials for applications. We also investigate the impact of the disorder on the thermal conductivity, where we find only weak variation with lanthanide content.

## I. INTRODUCTION

During the past several decades it has been recognized that refrigerant fluids have substantial environmental impacts [1], even as demand for cooling operations (e.g., for electronics) has increased [2]. A possible solution is found in thermoelectric materials, where electrical voltages are transformed into temperature gradients (and vice versa), but most such materials do not exhibit high efficiencies for power conversion. This is due to intrinsic limitations of standard metals and semiconductors, where the electrical ( $\sigma$ ) and thermal ( $\kappa$ ) conductivities are proportional to each other [3]. A strategy to overcome this is offered by the “phonon-glass electron-crystal” concept presented by Slack [4]. Here, the crystal structure is optimized to suppress the lattice component of the thermal conductivity ( $\kappa_L$ ), while the electronic properties are tuned to promote electrical conduction and conversion of temperature gradients to electrical voltage [5–7]. Amongst such materials, it is especially useful to find examples that also exhibit enhanced Seebeck coefficients ( $S = \Delta V/\Delta T$ ), where strongly correlated electron metals are promising candidates [8–10]. For these systems, the hybridization between the  $f$ - and conduction electron states results in Kondo-lattice hybridization, which renormalizes the Fermi surface such that there is a large and rapidly changing density of states near the Fermi energy [11–13]. This distinctive behavior not only produces enhanced Seebeck coefficients, but also is highly tunable

using chemical substitution, applied pressure, and magnetic fields [12]. Thus, there is a long-standing interest in cage-like structures with unconventional phonon scattering (e.g., filled skutterudites) that also host  $f$ -electron elements that encourage Kondo lattice formation (e.g., Ce, Yb, and U) [11, 14–17].

The compounds  $\text{YbTM}_2\text{Zn}_{20}$  ( $TM = \text{Co, Rh, Ir}$ ) have been investigated in this context because they feature cage-like structures with large unit cells and Kondo lattice physics [8, 9, 18]. They form in cubic structures with large lattice constants ( $a = 14.165 \text{ \AA}$  for  $TM = \text{Ir}$ ) where the Yb ions are separated at a distance of 6.14  $\text{\AA}$  [19]. Measurements of their bulk thermodynamic and electrical transport properties reveal that the Yb ions adopt the 3+ valence state and that electronic hybridization produces mass enhanced charge carrier quasiparticles [9, 14, 19]. Amongst them,  $\text{YbIr}_2\text{Zn}_{20}$  has attracted close interest owing to its metamagnetic behavior [18–20] and for having a large thermoelectric figure of merit ( $ZT = S^2\sigma T/\kappa = 0.07$ ) at 35 K [9]. To our knowledge, this is only second to  $\text{Bi}_{1-x}\text{Sb}_x$  at this temperature ( $ZT = 0.15$ ) [21, 22]. This motivated us to continue the investigations of this system by tuning the electronic state, the thermal conductivity, and the lattice anharmonicity through the substitution of Yb with Ce or Sm. While  $\text{CeIr}_2\text{Zn}_{20}$  exhibits intermediate valence behavior [23], the behavior of  $\text{SmIr}_2\text{Zn}_{20}$  is unknown but would be expected to resemble that of the weakly correlated antiferromagnet  $\text{SmRh}_2\text{Zn}_{20}$  [24]. Also important is that while  $\text{YbIr}_2\text{Zn}_{20}$  features a Fermi surface that is net electron-like [9],  $\text{CeIr}_2\text{Zn}_{20}$  is likely to be net hole-like [23]. Thus, it can be anticipated that  $\text{Yb} \rightarrow \text{Ce}$  chemical substitution may simultaneously tune the charge carrier balance

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and the hybridization strength while  $\text{Yb} \rightarrow \text{Sm}$  would dilute the Kondo lattice, weaken the hybridization, and introduce magnetic fluctuations. The ability to tune between n-type and p-type opens up novel possibilities for these materials in terms of applications, finding the p-type counterparts for n-type  $\text{Bi}_{1-x}\text{Sb}_x$  for instance. In addition, the introduction of multiple lanthanides with differing masses may suppress the phonon contribution to the thermal conductivity. Finally, the different size of Ce, Sm, and Yb allows us to explore the effects of local lattice strain and deformation of the underlying framework of Zn atoms. In this study we synthesized five different compositions of high-quality single crystals of  $\text{Yb}_x\text{Ce}_y\text{Sm}_z\text{Ir}_2\text{Zn}_{20}$  ( $x + y + z = 1$ ), listed in Table I (numbers 2-6).

In section III A, we survey the electrical transport and thermoelectric properties in this series to establish the impact of  $f$ -block chemical substitution. In section III B we examine the impact of chemical substitution on the magnetic properties, which provides insights into the  $f$ -electron valence and hybridization between the  $f$ - and conduction electron states. In section III C we investigate the atomic structure using high-energy XRD coupled to atomic pair distribution function (PDF) analysis. These measurements collectively clarify the parameters that control the behavior of  $\text{YbIr}_2\text{Zn}_{20}$ , and provide guidance for optimizing its thermoelectric properties.

## II. EXPERIMENTAL METHODS

Single-crystal specimens were synthesized by the molten metal flux technique using the growth protocols described by Torikachvili *et al.* [14] and Jia *et al.* [25, 26]. Elements with purities >99.9% were loaded into 2-mL Canfield alumina crucibles [27] with the molar ratio of 1(Ce,Yb):2(Ir):60(Zn) and 1(Ce,Sm,Yb):2(Ir):60(Zn). The crucibles were sealed under vacuum in 2-mm thick quartz tubes (18 mm outer diameter and 14 mm inner diameter), heated to 1050°C at a rate of 50°C/hr, and held at that temperature for 72 hours. The quartz tubes were then cooled down to 700°C at a rate of 2°C/hr, and held at that temperature for another 72 hours. At 700°C, the excess flux was removed by centrifuging, after which crystals with dimensions of several millimeters were collected.

Elemental analysis was done using an FEI NOVA 400 nanoSEM scanning electron microscope (SEM) with electron-dispersive spectroscopy (EDS) capabilities using an Oxford UltimMAX SDD (silicon drift detector). The structure and unit cell parameters of the single crystals were characterized by single-crystal X-ray diffraction (XRD) using an Oxford-Diffraction Xcalibur2 CCD system with graphite monochromated  $\text{Mo K}\alpha$  radiation. High-energy XRD data were collected using synchrotron X-rays with energy of 110 keV ( $\lambda=0.1126$  Å). Scattered intensities were collected with a point detector (Ge solid state detector) coupled with a multi-channel analyzer to

remove unwanted background scattering. Scattered intensities were collected to  $Q$  values of  $30 \text{ \AA}^{-1}$  to achieve high resolution in real space, where the wave vector  $Q$  is defined as  $Q = 4\pi \sin(\theta)/\lambda$  and  $\theta$  is the Bragg angle. The intensities were converted into atomic pair distribution functions (PDF) which have proven useful in structure studies on complex materials exhibiting local structural distortions.

Temperature-dependent magnetic susceptibility  $\chi(T)$  and isothermal magnetization  $M(H)$  measurements were done for single crystals using a Quantum Design VSM Magnetic Property Measurement System (MPMS).  $M(H)$  measurements were performed at a constant temperature  $T = 1.8$  K under applied magnetic fields  $H$  from -7 T to 7 T.  $\chi(T)$  measurements were done under a constant magnetic field  $H = 0.1$  T for a range of temperatures from 1.8 K to 300 K. For both cases, single crystals were mounted such that the magnetic fields were parallel to the (111) planes. Heat Capacity ( $C_p$ ) was measured from 1.8 K to 250 K using a Quantum Design Physical Property Measurement System (PPMS). The temperature-dependent Seebeck coefficient  $S$ , thermal conductivity  $\kappa$ , and electrical resistivity  $\rho$  were measured using the PPMS Thermal Transport Option (TTO). For these measurements, single crystals were cut into rectangular bars with a general dimension of 7 mm by 2 mm by 1 mm. All surfaces were polished in order to reduce surface scattering. TTO measurements were performed from 3 K to 400 K, obtaining  $\rho$ ,  $\kappa$ , and  $S$  simultaneously as a function of  $T$  in order to assess both  $ZT$  and the power factor  $PF = S^2\sigma$ . Both  $C_p$  and TTO measurements were performed under high vacuum ( $\approx 10^{-4}$  Torr) with no magnetic field being applied to the specimens.

## III. RESULTS AND DISCUSSION

### A. Electrical Transport and Thermoelectric Properties

Fig. 1A shows the temperature dependent electrical resistivities  $\rho(T)$  of all specimens of  $\text{Yb}_x\text{Ce}_y\text{Sm}_z\text{Ir}_2\text{Zn}_{20}$  ( $x + y + z = 1$ ). Consistent with earlier reports [9, 14, 20], the parent compound ( $\text{YbIr}_2\text{Zn}_{20}$ ) exhibits metallic behavior at high temperatures that is followed by a broad minimum near 50 K and a broad maximum near 20 K that are due to hybridization between the  $f$ - and conduction electron states [9, 14]. The introduction of even small amounts of Ce strongly modifies this behavior: e.g.,  $\rho(T)$  for  $\text{Yb}_{0.87}\text{Ce}_{0.08}\text{Sm}_{0.05}\text{Ir}_2\text{Zn}_{20}$  develops a shoulder that is centered around 50 K, which is typical for Kondo lattice systems [28]. This behavior persists for the other specimens where Ce is the main substituent, including for  $\text{Yb}_{0.6}\text{Ce}_{0.4}\text{Ir}_2\text{Zn}_{20}$ , and resembles what is seen for  $\text{CeIr}_2\text{Zn}_{20}$  [23]. On the other hand, the presence of large amounts of Sm (e.g.,  $\text{Yb}_{0.43}\text{Ce}_{0.13}\text{Sm}_{0.44}\text{Ir}_2\text{Zn}_{20}$  and  $\text{Yb}_{0.33}\text{Ce}_{0.44}\text{Sm}_{0.23}\text{Ir}_2\text{Zn}_{20}$ ) suppresses the Kondo lattice behavior and strongly drives the system to a more

TABLE I. Magnetization parameters from Curie-Weiss fit, fitting parameters for  $C_p$  and  $C_p/T$  curves, relevant characteristic temperatures, and lattice parameters  $a$  of  $\text{Yb}_x\text{Ce}_y\text{Sm}_z\text{Ir}_2\text{Zn}_{20}$  ( $x + y + z = 1$ ), where  $\mu_{\text{eff}}$  and  $\mu_{\text{eff,Th}}$  have units in  $\mu_B$ ,  $\beta$  has units in  $\text{mJmol}^{-1}\text{K}^{-4}$ ,  $a$  in  $\text{\AA}$ , and all other variables shown in the table have units in Kelvin.

Number	Composition	$\theta_W$	$\mu_{\text{eff}}$	$\mu_{\text{eff,Th}}$	$\beta$	$\theta_D$	$\theta_E$	$T_{\text{min}}^S$	$T_{\text{max}}^p$	$a$
1	$\text{YbIr}_2\text{Zn}_{20}$	-7.6	4.1	4.5	4.0	240	110	26.0	19.4	14.140
2	$\text{Yb}_{0.6}\text{Ce}_{0.4}\text{Ir}_2\text{Zn}_{20}$	-6.5	3.4	3.7	4.2	307.8	102.1	19.2	56.4	14.165
3	$\text{Yb}_{0.87}\text{Ce}_{0.08}\text{Sm}_{0.05}\text{Ir}_2\text{Zn}_{20}$	-32.4	4.0	4.2	3.7	291.6	97.1	19.8	50.2	14.162
4	$\text{Yb}_{0.77}\text{Ce}_{0.21}\text{Sm}_{0.02}\text{Ir}_2\text{Zn}_{20}$	-12.6	3.6	4.0	4.2	276.8	93.8	22.5	73.7	14.292
5	$\text{Yb}_{0.43}\text{Ce}_{0.13}\text{Sm}_{0.44}\text{Ir}_2\text{Zn}_{20}$	-16.7	2.7	2.7	3.5	302.7	102.4	18.7	68.9	14.274
6	$\text{Yb}_{0.33}\text{Ce}_{0.44}\text{Sm}_{0.23}\text{Ir}_2\text{Zn}_{20}$	-18.2	1.8	1.7	3.6	300.2	102.9	14.5	44.3	14.276

typical metallic behavior [28]. Taken together, these data indicate that increased Ce content tunes the Kondo hybridization temperature towards higher values than those seen for the pure Yb compound, while Sm substitution tends to weaken the hybridization.

The temperature dependent thermopower,  $S(T)$ , is presented in Fig.1B. Similar to earlier reports [8, 9],  $S(T)$  for the parent compound decreases with decreasing  $T$  and reaches a value of  $-64 \mu\text{V/K}$  at  $T \approx 20$  K. This was earlier interpreted as being due to Kondo lattice hybridization, where the negative value shows that the

charge carriers are mainly electron-like. By introducing 8% Ce and 5% Sm on the Yb site, the peak value is enhanced to  $-70 \mu\text{V/K}$ . Further increase of Ce content reduces the magnitude of the negative peak and produces a positive peak at  $T \approx 100$  K, which is as a result of Ce-dominated hybridization [29] and resembles what is seen for  $\text{CeIr}_2\text{Zn}_{20}$  [23]. Here, the evolution from positive to negative values demonstrates that while Yb favors an electron-like Fermi surface, Ce produces a hole like Fermi surface. Additional Sm substitution preserves the overall shape of the Ce substituted samples, but results in further fine-tuning of  $S$ . Taken together, these results indicate that the mixing of Yb and Ce results in distinct hybridization for the separate sets of  $f$ -electrons, as well as competition between the electron-like and hole-like Fermi surfaces.

The total thermal conductivity,  $\kappa(T)$ , for all the specimens is presented in Fig.2A, which is a combination of a lattice term  $\kappa_L$  and an electronic term  $\kappa_E$ . For  $\kappa_L$ , a correction for radiation loss effects has been made following the procedure described in Pope *et al.* [30]. Fig.2B shows  $\kappa_L(T)$  after the correction.  $\kappa_E$  was obtained through the Wiedemann-Franz relation [31]:

$$\kappa_E(T) = \frac{L_0 T}{\rho(T)}, \quad L_0 = 2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2 \quad (1)$$

where  $L_0$  represents the Lorentz number. These results will be discussed in detail in section III C, but are presented here in order to calculate the thermoelectric figure of merit  $ZT$ .

Fig.3 shows the power factors,  $PF = S^2/\rho$ , and the thermoelectric figures of merit,  $ZT = S^2 T/(\rho\kappa)$ , where  $S$  is the Seebeck coefficient,  $\rho$  is the electrical resistivity, and  $\kappa$  is the thermal conductivity. The specimen that presents the highest  $PF$  is  $\text{Yb}_{0.87}\text{Ce}_{0.08}\text{Sm}_{0.05}\text{Ir}_2\text{Zn}_{20}$ , with a peak value of  $100.55 \mu\text{W}/(\text{cmK}^2)$  at 16.8 K. This value represents an improvement of approximately 35% as compared to the previous reported value for  $\text{YbIr}_2\text{Zn}_{20}$  [9]. This large  $PF$  and small  $\kappa$  value result in a large  $ZT$  value for this specimen (Fig.3B), with a peak value of 0.076 at 18.63 K. It can also be observed that for several specimens the  $ZT$  peaks are shifted to higher temperatures. Between 100 K and 200 K, the specimen  $\text{Yb}_{0.33}\text{Ce}_{0.44}\text{Sm}_{0.23}\text{Ir}_2\text{Zn}_{20}$  presented the highest  $ZT$  peak, with a value of 0.02 at 140.67 K. This spec-

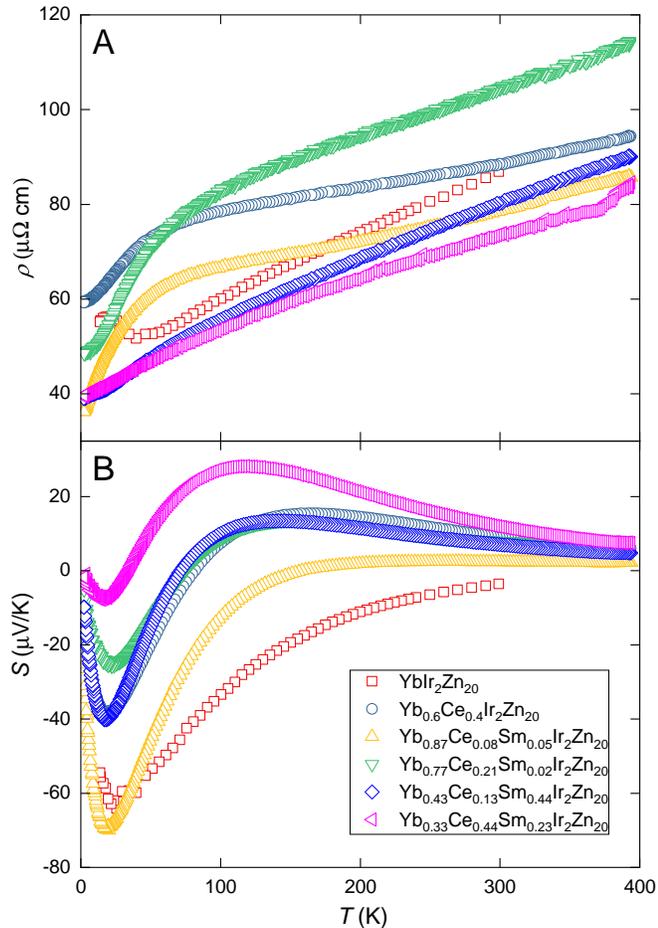


FIG. 1. Temperature-dependent (A) electrical resistivity  $\rho(T)$ , and (B) Seebeck coefficient  $S(T)$  for  $\text{Yb}_x\text{Ce}_y\text{Sm}_z\text{Ir}_2\text{Zn}_{20}$  ( $x + y + z = 1$ ).

imen also contains triple fillers (Yb, Ce, and Sm) with the highest concentration of Ce among other specimens.

### B. Magnetic and Heat Capacity Properties

To better understand the effect of introducing Ce and Sm on the Yb site, the temperature-dependent magnetization was measured, which provides insights into the  $f$ -electron valence states and the hybridization strength [32–34]. Fig.4A presents the temperature-dependent magnetic susceptibility,  $\chi(T)$ , for all specimens, where paramagnetic behavior is observed at elevated temperatures in all cases. Curie-Weiss fits were performed at high temperatures ( $T > 150$  K) to the inverse of the magnetic susceptibility (Fig.4B) using the expression [35],

$$\chi(T) + \chi_0(T) = \frac{c}{T - \theta_W} \quad (2)$$

where  $c$  is the Curie constant (calculated as a fitting pa-

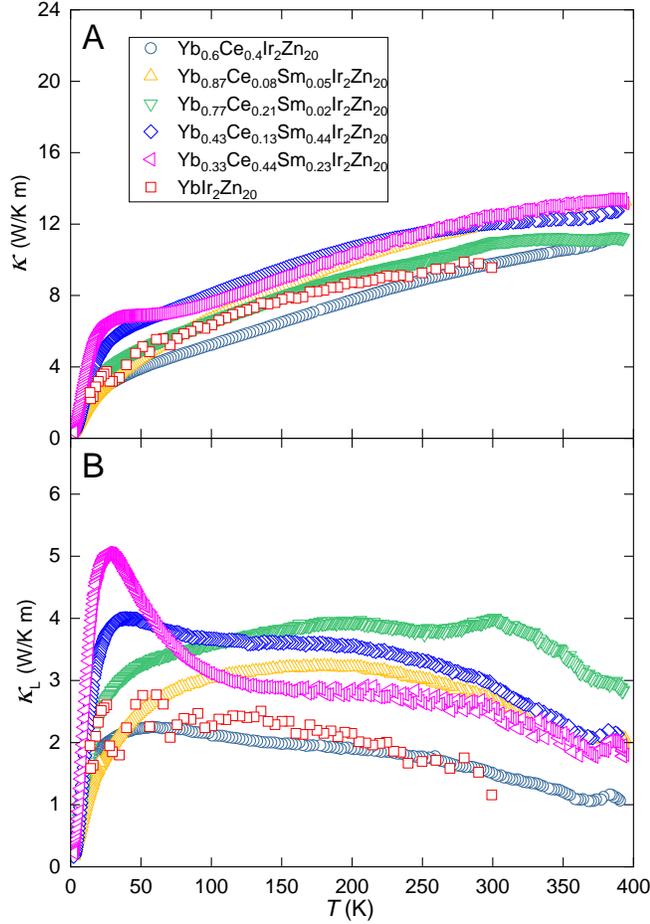


FIG. 2. (A) Total thermal conductivity  $\kappa$  vs  $T$ , and (B) Lattice thermal conductivity  $\kappa_L$  vs  $T$  for  $\text{Yb}_x\text{Ce}_y\text{Sm}_z\text{Ir}_2\text{Zn}_{20}$  ( $x + y + z = 1$ ).

rameter), and  $\theta_W$  is the Weiss temperature. In some cases, an additional  $\chi_0$  term was needed to fit the data, which may be due to a Van Vleck contribution that originates from the Sm ions [36]. Table I shows  $\theta_W$  for all the specimens, together with the experimental effective magnetic moment,  $\mu_{\text{eff}} = 2.82\sqrt{c/n}$ , where  $n$  represents the number of magnetic elements per formula unit [31]. These values are compared to the theoretical effective magnetic moment for trivalent ions [35],  $\mu_{\text{eff,Th}} = x \cdot \mu_{\text{eff(Ce)}} + y \cdot \mu_{\text{eff(Sm)}} + z \cdot \mu_{\text{eff(Yb)}}$ , where  $x + y + z = 1$ . The parent compound,  $\text{YbIr}_2\text{Zn}_{20}$ , has also been included for comparison. By comparing the theoretical and experimental total effective magnetic moments of all the specimens (Table I), it is seen that the values are in good agreement, which indicates that the ions remain trivalent for all substitutions.

Heat capacity measurements (Fig.5) provide further insights about the evolution of the electronic hybridization and the lattice behavior. Starting with the parent compound ( $\text{YbIr}_2\text{Zn}_{20}$ ), it is seen that there is a Fermi liquid dependence [37],  $C_p/T = \gamma + \beta T^2$  for  $10 \text{ K} < T < 14 \text{ K}$ , where  $\gamma$  and  $\beta$  represent the electronic and lattice contri-

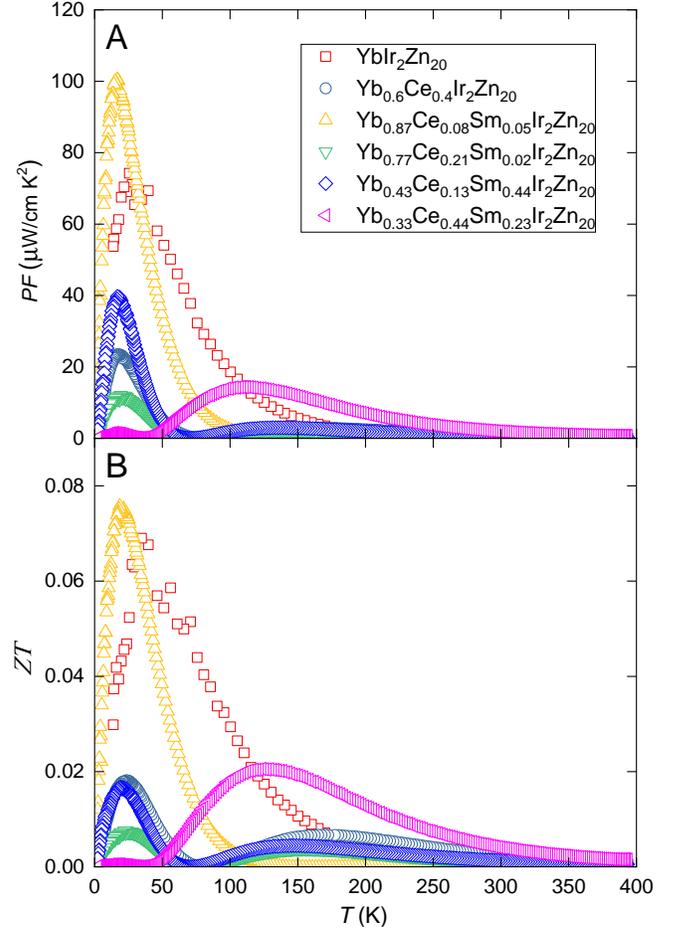


FIG. 3. Temperature-dependent (A) power factor  $PF$  and (B) dimensionless figure of merit  $ZT$  of  $\text{Yb}_x\text{Ce}_y\text{Sm}_z\text{Ir}_2\text{Zn}_{20}$  ( $x + y + z = 1$ ).

butions to the heat capacity. But this dependence is interrupted by a broad hump at low temperatures (Fig. 5B), which indicates the presence of additional electronic degrees of freedom at low temperatures. Despite this, it can be seen that over this temperature range chemical substitution has only a weak effect on the electronic contribution to the heat capacity. However, a stronger evolution is seen at lower temperatures. Focusing first on the samples that primarily substitute Ce, it can be observed that the low-temperature value is suppressed with increasing Ce content, which is consistent with earlier results showing that for  $\text{CeIr}_2\text{Zn}_{20}$  there is simple Fermi liquid behavior with  $\gamma = 87 \text{ mJmol}^{-1}\text{K}^{-2}$  [23]. The Sm case is potentially more complex given that  $\text{SmIr}_2\text{Zn}_{20}$  exhibits a low-temperature hump that originates from magnetic fluctuations of the Sm ions that eventually resolves into an ordered magnetic state [38]. The temperatures at which all these broad humps appear agree with the magnetic ordering observed in  $\chi(T)$  (Figure 4A). Therefore, we suspect these humps are associated with the magnetic contribution due to the Yb, Ce, and Sm ions. However, we cannot rule out the possibility that

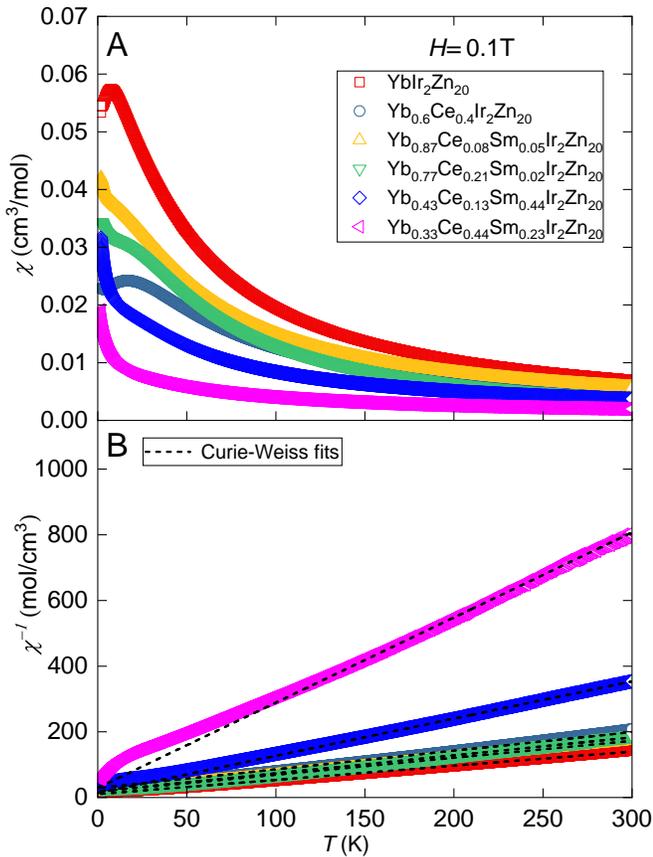


FIG. 4. Temperature-dependent (A) magnetic susceptibility  $\chi(T)$  with an applied magnetic field  $H = 0.1 \text{ T}$ , and (B) inverse of the magnetic susceptibility  $\chi^{-1}(T)$  for  $\text{Yb}_x\text{Ce}_y\text{Sm}_z\text{Ir}_2\text{Zn}_{20}$  ( $x + y + z = 1$ ). The dashed lines represent the Curie-Weiss fits mentioned in the text.

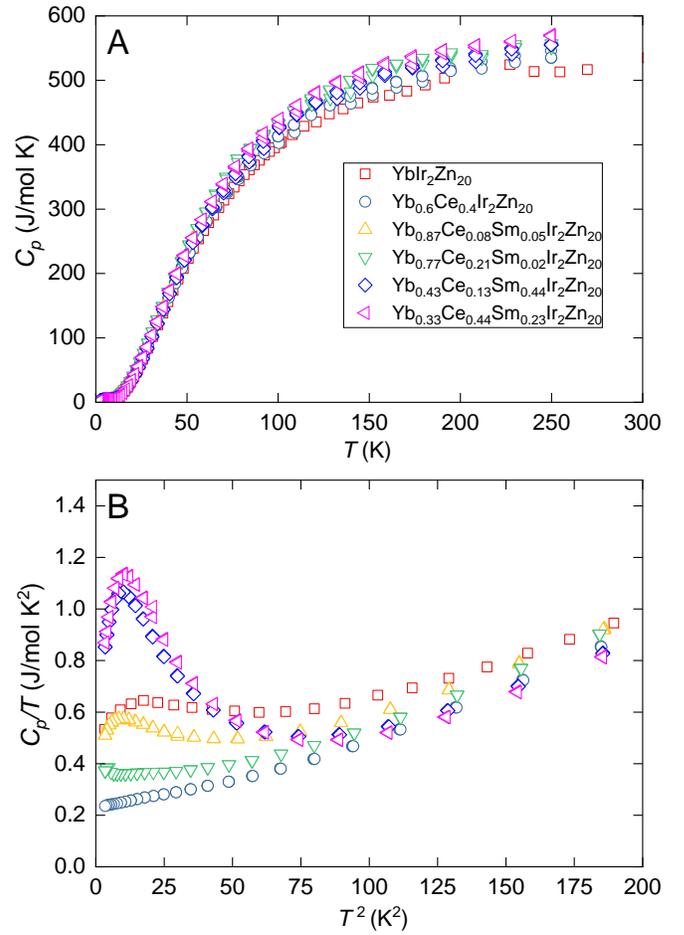


FIG. 5. (A)  $C_p$  vs  $T$  and (B)  $C_p/T$  vs  $T^2$  for  $\text{Yb}_x\text{Ce}_y\text{Sm}_z\text{Ir}_2\text{Zn}_{20}$  ( $x + y + z = 1$ ).

the Schottky anomaly also contributes to this behavior, as described by Torikachvili *et al.* [14]. As a result, it is very challenging to extract an accurate  $\gamma$  from a low temperature fit, so only  $\beta$  is being reported for all samples (Table I). To better understand the lattice dynamic, full temperature range of the heat capacity has been fitted using the combined Debye-Einstein model, where  $C_p(T)$  can be expressed as [39]

$$C_p = C_D \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx + C_E \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad (3)$$

where  $x = \hbar\omega/\kappa_B T$ ,  $\omega$  is the Debye frequency,  $\theta_D$  and  $\theta_E$  are the Debye and Einstein temperatures, respectively, and  $C_D$  and  $C_E$  are constants containing numbers of oscillators and degrees of freedom. All calculated parameters are listed in Table I, where  $\theta_D$  and  $\theta_E$  vary little for different concentrations.

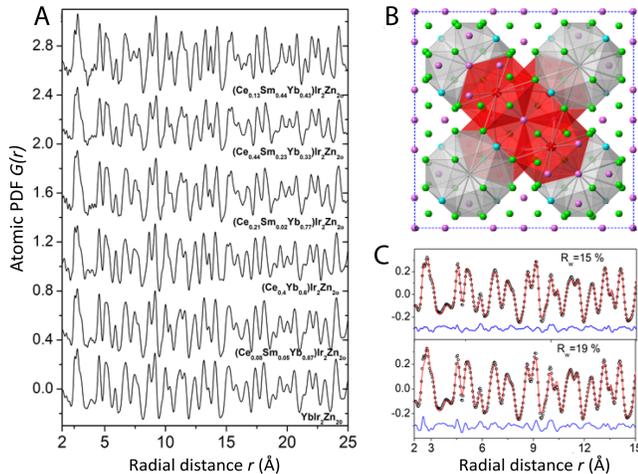


FIG. 6. (A) Experimental atomic PDFs reflecting the atomic arrangement in the respective system. Samples 2 to 6 are offset for a clear presentation. (B) Polyhedron representation of the unit cell, where  $R$  is represented in black, Ir in red,  $\text{Zn}_1$ ,  $\text{Zn}_2$ , and  $\text{Zn}_3$  in green, magenta, and blue respectively. (C) Fit (red line) to the experimental (symbols) atomic PDF for  $\text{YbIr}_2\text{Zn}_{20}$ . In the fit on top, anisotropic thermal factors are refined. In the bottom fit, the thermal factors are kept isotropic. The residual difference (blue line) is shifted by a constant factor for clarity. The goodness-of-fit indicators,  $R_w$ , are given.

### C. High-energy XRD and Atomic Pair Distribution Function (PDF) analysis

The atomic structure was studied by high-energy XRD coupled to atomic pair distribution function (PDF) analysis. The technique has proven useful in studying materials exhibiting lattice distortions, including thermoelectric materials [40–42]. Experimental atomic PDFs are shown in Fig. 6A. The PDFs show a sequence of well-defined peaks. The area under a peak is proportional to the number of atomic pairs separated by the particular interatomic vector [41]. In particular, the first PDF peak reflects the first coordination sphere in studied materials. It splits into 3 compounds reflecting distinct Zn-Zn,  $R$ -Zn, and  $TM$ -Zn bonding distances, where  $R$  and  $TM$  are rare earth and transition metal elements, respectively. In the compounds,  $R$  atoms have 16 Zn neighbors forming a Frank-Kasper polyhedron and  $TM$  atoms have 12 first neighbors, as shown in Fig. 6B. On the other hand, Zn atoms occupy 3 distinct positions  $\text{Zn}_1$  (Wyckoff position 96g),  $\text{Zn}_2$  (Wyckoff position 48f) and  $\text{Zn}_3$  (Wyckoff position 16c), where  $\text{Zn}_1$  and  $\text{Zn}_2$  atoms are 12-fold coordinated and  $\text{Zn}_3$  atom is 14-fold coordinated. Hence,  $\text{Zn}_3$  may be expected to exhibit large atomic displacements, where the displacements of  $\text{Zn}_1$  and  $\text{Zn}_2$  would be smaller. In addition, because  $\text{Zn}_1$  has both Ir and lanthanides as first neighbors, its displacements from the average position may be expected to vary with changes in the lanthanide type. The atomic PDFs were fit with a

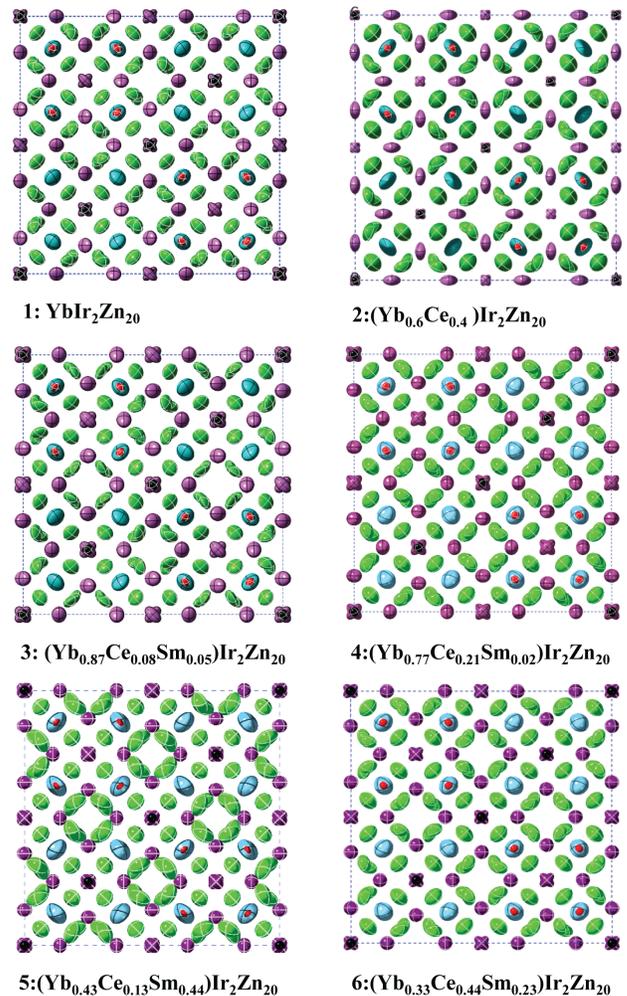


FIG. 7. Projection of the refined unit cells of  $\text{Yb}_x\text{Ce}_y\text{Sm}_z\text{Ir}_2\text{Zn}_{20}$  ( $x + y + z = 1$ ), where  $R$  is represented in black, Ir in red,  $\text{Zn}_1$ ,  $\text{Zn}_2$ , and  $\text{Zn}_3$  in green, magenta, and blue, respectively. Mean square displacements for Zn atoms are much larger and anisotropic than those for metal atoms.

structural model based on the well-known crystal structure of  $RTM_2\text{Zn}_{20}$  compounds [18]. The fit parameters included lattice parameters (Table I), coordinates of  $\text{Zn}_1$  and  $\text{Zn}_2$  atoms, and mean squared atomic displacements (MSD). A model based on isotropic displacements, however, did not fit well the first PDF peak as shown in Fig. 6C. A model based on anisotropic displacements performs much better ( $R_w$  of 15% vs 19%).

Projection of the refined unit cells are shown in Fig. 7. It can be observed that Zn atoms suffer large anisotropic displacements, where the preferred direction of the displacements and their magnitude are different for different compounds. The observed anharmonicity of the atomic vibrations of Zn atoms would lead to a diminished  $\kappa_L$ . The decrease would be different for different compounds, as illustrated in Fig. 2. Note, as the small atomic displacements indicate, the contribution of  $R$  and Ir atoms

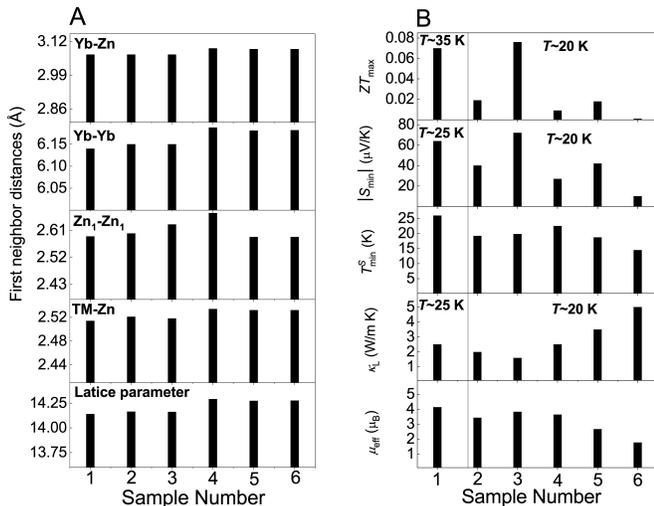


FIG. 8. (A) Lattice parameters and selected interatomic distances derived from the PDF refined models, and (B) selected property data. Specimen compositions are listed in Table I.

to the observed diminishing of  $\kappa$  would be limited.

Refined lattice parameters and selected interatomic distances derived from the PDF refined models are shown in Fig.8A. It is seen a partial replacement of Yb atoms by Ce atoms expands the lattice parameter, Yb-Yb distances, and coordination polyhedra of Yb and Ir atoms. This is because Ce atoms are larger in size than Yb atoms. Distances between nearby Zn atoms do not scale with Ce content, indicating a uniform distortion of the Zn framework upon introducing Ce. Split positions for Zn atoms were considered but proved to be non-realistic. Increased MSD did a better job, indicating that the Zn sublattice/framework is continuous and just distorted/softened. The observed expansion of unit cell volume and coordination polyhedra of R and Ir atoms, i.e. negative pressure, would affect the electronic properties of studied compounds significantly. In particular, negative pressure and coupled increase of the volume of the Yb cage would reduce partially the valence state of magnetic  $\text{Yb}^{3+}$  ions toward non-magnetic  $\text{Yb}^{2+}$  state, resulting in diminished  $\mu_{\text{eff}}$  as documented by our measurements (see Table I). The enhanced degree of hybridization would increase the density of states at the Fermi level when compared to the limiting  $\text{Yb}^{3+}$  and  $\text{Yb}^{2+}$  states. This may explain the emergence of a “negative” dip in

$S(T)$  at low temperatures (Fig.1B). The combined effect of increased (negative) Seebeck coefficient and diminished lattice conductivity would result in increased  $PF$  and  $ZT$ , as observed in Fig.3. Selected property data are also shown in Fig.8B. Inspection of the data indicates a strong correlation between the thermoelectric ( $ZT$ ,  $\kappa_L$ , and  $S$ ) and structural properties (lattice parameters and near neighbor distances) of 100% Yb and 87% Yb samples.

#### IV. CONCLUSIONS

We have investigated the effects on the magnetic, thermal, and thermoelectric properties of 1-2-20 compounds when introducing other rare-earth elements (Ce and Sm) in the compound that motivated this study ( $\text{YbIr}_2\text{Zn}_{20}$ ). The electrical resistivity data suggests that by introducing Ce and Sm, a variation in the Kondo coherence temperature can be observed. Heat capacity data shows that chemical substitution has only a weak effect on both the electronic contribution to the heat capacity and the average lattice behavior. XRD data shows strong lattice anharmonicity (the Zn sub-lattice is “soft”, i.e. phonon glass, as indicated by the observed large MSD), which, typically, reduces the lattice thermal conductivity. Overall, our results indicate that it is possible to improve the thermoelectric properties of 1-2-20 compounds by introducing multiple rare-earth as cage fillers. The specimen that has the largest  $ZT$  is  $\text{Yb}_{0.87}\text{Ce}_{0.08}\text{Sm}_{0.05}\text{Ir}_2\text{Zn}_{20}$  with an absolute value of Seebeck coefficient of  $70\mu\text{V}/\text{K}$  and a  $ZT$  of 0.076, at 20K. Finally, having  $ZT$  peaks at higher temperatures (100 K to 200 K) for the Ce-content specimens is also an interesting result. It opens up opportunities for applications under broader temperatures.

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