Enhanced Thermoelectric Power and Electronic Correlations in RuSe$_2$

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We report the electronic structure, electric and thermal transport properties of Ru$_{1-x}$Ir$_x$Se$_2$ ($x \leq 0.2$). RuSe$_2$ is a semiconductor that crystallizes in a cubic pyrite unit cell. The Seebeck coefficient of RuSe$_2$ exceeds -200 $\mu$V/K around 730 K. Ir substitution results in the suppression of the resistivity and the Seebeck coefficient, suggesting the removal of the peaks in density of states near the Fermi level. Ru$_{0.8}$Ir$_{0.2}$Se$_2$ shows a semiconductor-metal crossover at about 30 K. The magnetic field restores the semiconducting behavior. Our results indicate the importance of the electronic correlations in enhanced thermoelectricity of RuSb$_2$.

Recent interest in thermoelectric energy conversion induces a wide interest in the materials with high thermoelectric performance. A narrow distribution or a large peak in the electronic density of states (DOS) close to the Fermi level has long been considered favorable for a high Seebeck coefficient. Such peak could be induced by the resonant level dopants in semiconductors or by the magnetic interaction between the local magnetic moment and itinerant electrons in many f- and d-electron based materials. It has been reported that some strongly correlated metals (such as heavy fermion metals) and correlated semiconductors (such as Kondo insulators) show significant enhanced Seebeck coefficient and power factor. For example, large peaks in Seebeck coefficient up to 800 $\mu$V/K were observed in heavy fermion metal CePd$_3$, Kondo insulator FeS$_2$, Ce$_3$Pt$_3$Sb$_4$ and CeFe$_3$P$_{12}$.

More recently, a very large Seebeck coefficient ($\sim 4 \times 10^4$V/K) and huge power factor ($\sim 2 \times 10^5$W/K$^2$cm) was observed in FeSb$_2$. This makes the mechanism of thermopower enhancement in FeSb$_2$ of high interest. The results from density functional theory without electron correlation effect can only qualitatively reproduce the temperature dependence of the Seebeck coefficient. The predicted peak value of $S$ is only one tenth of the experimental value, suggesting the importance of strong electronic correlations.

Pyrrhotite FeS$_2$ is a semiconductor with a band gap of (0.8 - 0.95) eV and a high light absorption. FeS$_2$ shows a Seebeck coefficient up to $\sim 300 \mu$V/K at 300 K. The Seebeck coefficient of iron dichalcogenides FeX$_2$ [X=(S,Se,Te)] decreases for heavier chalcogens due to decreasing energy gap, but retains relatively large values of $\sim (2 - 3) \times 10^2 \mu$V/K above 200 K.

Here we report the detailed electronic structure, electric and thermal transport properties of pure and Ir-doped RuSe$_2$. RuSe$_2$ shows a semiconducting behavior with an indirect gap from resistivity $\sim 1.5$ eV. The band structure calculation shows a pileup of states near the Fermi level suggesting correlation effects. The Seebeck coefficient of RuSe$_2$ exceeds -200 $\mu$V/K at 730 K, showing the electron-type carriers. Ir doping introduces lattice expansion and extra electrons, which results in the significant suppression of the resistivity and the Seebeck coefficient. The sample with 20% Ir doping shows a semiconductor-metal transition at about 20 K, while the magnetic field restores the semiconducting behavior.

(Ru$_{1-x}$Ir$_x$)$_2$Se$_2$ (with $x = 0, 0.1, 0.2$) polycrystals were made using a high-temperature solid state reaction method. Stoichiometric Ru (99.99%), Ir (99.99%) and Se (99.9999%) were ground, pelletized, sealed in a quartz
tube, heated to 1000 °C, kept for about 20 hours and then the furnace was turned off. Next, the material was ground, pelletized again and heated with the similar temperature profile at 1100 °C. Medium resolution room temperature X-ray diffraction measurements were carried out using a (0.25-0.25) mm² 48 keV (λ = 0.02487 nm) focused (on the detector) X-ray beam at 28-ID-C beam line at National Synchrotron Light Source II at Brookhaven National Laboratory. The X-ray energy was selected using a horizontally focused double crystal Laue monochromator, with vertical focusing achieved using 1 m long Si mirror. Finely pulverized samples were filled into 1 mm diameter cylindrical polyimide capillaries, and the data collection was carried out in transmission geometry using Perkin Elmer amorphous silicon area detector mounted orthogonal to the beam path 1272.6 mm away from the sample. The raw 2D data were integrated and converted to intensity versus scattering angle using the software Fit2D. The average structure was assessed through Rietveld refinements to the raw diffraction data using the General Structure Analysis System (GSAS) operated under EXPANGL utilizing Pa-3 model from the literature. Electrical transport measurements were conducted on polished samples in Quantum Design PPMS-9 with conventional four-wire method. Thermal transport properties were measured in Quantum Design PPMS-9 from 2 K to 350 K, and in Ulvac ZEM-3 system at higher temperatures, both using one-heater-two-thermometer method. The relative error of each measurement was ∆ρ/ρ ~5% and ∆σ/σ ~10% based on standard, however at 350 K the discrepancy in measured values was 25%. As opposed to ULVAC ZEM-3, PPMS S and ρ were obtained in separate measurements using TTO and ACT option on the same sample. Hence, ULVAC ZEM-3 data were normalized to PPMS values at 300 K. First principle electronic structure calculation were performed using experimental lattice parameters within the full-potential linearized augmented plane wave (LAPW) method implemented in WIEN2k package. The general gradient approximation (GGA) of Perdew et al. was used for exchange-correlation potential. The LAPW sphere radius were set to 2.5 Bohr for all atoms. The converged basis corresponding to Rminkmax = 7 with additional local orbital were used where Rmin is the minimum LAPW sphere radius and kmax is the plane wave cutoff.

Diffraction data for all three compositions are well explained within pyrite-type Pa-3 structure, comprised of 3D network of distorted (squashed) Se6 octahedra that coordinate Ru/Ir. Irregularity of the octahedra is reflected in principal axes deviating from 90 degrees (see Figure 1). Refined structural parameters are summarized in Table 1. Lattice parameter increases on substituting Ru with larger Ir. Average Ru-Se near neighbor distance decreases slightly with doping, whereas departure for regularity in octahedral angles increases slightly. Debye-Waller factors increase slightly with doping as well, consistent with presence of quenched disorder introduced by chemical substitution. The Ir doping limit is 20% and above that the synthesis resulted in mixed phases of Pa-3 space group of pure RuSe2 and Pnma space group of pure IrSe2.

![Figure 2](image)

**FIG. 2.** (Color online) The Resistivity ρ (a), the log ρ vs 1/T relationship for pure RuSe2 and the solid line is the linear fitting result using thermal activation theory (b), Seebeck coefficient S (c) and thermal conductivity κ (d) for (Ru1−xIrx)Se2 with x = 0, 0.1 and 0.2.

The resistivity of RuSe2 [Fig. 2(a)] shows typical semiconducting behavior. The fitting for thermal activation conductivity [the solid line in Fig. 2(b)] estimates that the main band gap is ~ 1.5 eV. The slope of the resistivity or the energy gap changes in the low temperature range, possibly due to the native d-states or impurity states within the main band gap, similar to Fe1−xRu2Sb2. The Seebeck coefficient [Fig. 2(c)] approaches 180 µV/K at 350 K and shows a peak of about 247 µV/K at about 730 K. The thermal conductivity of RuSe2 [Fig. 2(d)] is rather high in the whole range of measured temperatures.

The semiconducting behavior of RuSe2 is consistent with the first principle calculation results (Fig. 3). The density of states [Fig. 3(a)] shows a gap with size of 0.4 eV, whereas the band structure [Fig. 3(b)] indicates that RuSe2 is a indirect-gap semiconductor. However, the gap size from the density functional theory (0.4 eV) is much smaller than the transport gap (about 1.5 eV), suggesting that the electron correlations may be important. There are several narrow bands just below the Fermi level with Ru 4d orbital character [the heavy lines in Fig 3(b)].
there is also significant hybridization between Ru $4d$ and Se $p$ orbitals indicated by the overlap between the peaks from Ru and Se below and above the Fermi level.

The high Seebeck coefficient of RuSe$_2$ should come from the peaks in density of states just below the Fermi level [Fig. 3(a)], with major contribution from the narrow $d$-bands. Although the Seebeck coefficient of RuSe$_2$ is high, its power factor is small because of the high resistivity.

Ir doping introduces carriers and is effective in enhancing the conductivity, however it also significantly suppresses Seebeck coefficient [Fig. 2(a,c)]. The 10% Ir doped sample still shows semiconducting behavior but the residual resistivity decreases by two orders of magnitude at 2 K and in half at 200 K when compared to pure RuSe$_2$. Further increase in Ir substitution suppresses the resistivity even more. The sample with 20% Ir doping shows a semiconducting-metal crossover at $\sim 30$ K; below that temperature the resistivity begins decreasing with decreasing temperature [Fig. 2(a) and Fig. 4(a)]. The thermal conductivity is also suppressed by Ir doping [Fig. 2(d)], possibly due to the lattice disorder introduced by the doping. The 10% Ir doping reduces the Seebeck coefficient to only about 2 $\mu$V/K at 300 K [inset in Fig. 2(c)].

The magnetic field has significant influence on the transport of Ru$_{0.8}$Ir$_{0.2}$Se$_2$ in the low temperature range [Fig. 4(a)]. Above the semiconducting-metal crossover at $\sim 30$ K, the application of magnetic field has minute effect on the resistivity. But below it, in the metallic regime, the magnetic field enhances the value of resistivity and changes its temperature dependence. In 4 T field, the $\rho(T)$ still undergoes the semiconductor-metal transition at the same temperature but then changes to semiconducting behavior below 4 K. The 9 T magnetic field totally smears out the semiconductor-metal transition and restores the semiconducting behavior. The MR is always positive at 2 K and tends to saturate in higher fields [Fig. 4(b)].

The clear suppression of the value and the slope of the resistivity indicates that the Ir-doping induces the decrease of the band gap. The 10% Ir doping only introduces 0.1 electrons per unit cell. This will result in a slight shift of the Fermi level toward higher energy direction [Fig. 3(a)], within the framework of the density functional theory. Since 10% Ir-doped RuSe$_2$ is still a semiconductor, it is reasonable to believe that the Fermi level is still in the gap. If so, this slight shift of the Fermi level could not induce the huge suppression of the Seebeck coefficient [Fig. 2(c)]. Since the Seebeck coefficient is related to the energy slope of the density of states near the Fermi level, this implies the effect of electronic correlations. The 5$d$ electrons of Iridium feature less localized (i.e. more extended) wave functions when compared to 4$d$ electrons of Ruthenium. Hence, Iridium substitution not only introduces extra carriers, but also reduces the electronic correlations. Furthermore, since the magnetic field restores the semiconducting behavior in sample with 20% Ir level, the original semiconducting behavior in pure RuSe$_2$ could be related to some extent to the magnetic mechanism. Taken together with enhanced thermopower, our results suggest that physical properties of RuSe$_2$ may share some similarity with the correlated electron semiconductor FeSb$_2$. The comparison of the electronic structure, electronic and magnetic cor-

FIG. 3. (Color online) (a) The density of states and (b) the band structure of RuSe$_2$. The different colors in band structure indicate different bands and the thickness of the bands represents the weight of Ru 4d orbitals.
relations of pyrite RuSe$_2$ to marcasite FeSb$_2$ could be important for studies of structural effects on correlated electron thermoelectricity and deserves further studies.

Electronic structure of pyrites such as NiS$_{2-x}$Se$_x$ is related to the occupation of $d$ orbitals which have significant influence on the band filling and correlation effect. Pyrites and marcasites both feature distorted octahedral coordination of transition metals (e.g. Fe or Ru) in the local structure. Whereas the octahedra share common corners in the cubic pyrite unit cell and the resulting crystal field at Ru in RuSe$_2$ has trigonal symmetry, the orthorhombic marcasite unit cell features linear chains of edge-sharing octahedra parallel to orthorhombic $c$-axis. In both cases $d$-electrons dominate the electronic states near the Fermi level. In RuSe$_2$ the $t_{2g}$ orbitals are completely filled as opposed to $t_{2g}$ orbitals in marcasite FeSb$_2$.

This inhibits a possibility for thermally induced anisotropic metallic states and thermally induced enhanced Pauli susceptibility. On the other hand, when comparing RuSe$_2$ to RuSb$_2$, Se($4p_3$) has an extra electron when compared to Sb ($5p_3$). So it is expected that the occupation of $d$ orbitals in RuSe$_2$ is different from RuSb$_2$ which would change correlation strength. This is reflected in the density of states: Ru $d$-states in RuSe$_2$ (Fig. 3) are more enhanced near the Fermi level when compared to RuSb$_2$. Triangular arrangement of metal (i.e. Ru) atoms in pyrite lattice of RuSe$_2$ (Fig. 1) could enhance the correlation effects in RuSe$_2$ even further via geometric frustration. This has been theoretically considered and experimentally verified in pyrite NiS$_2$. Since geometrical frustration coupled with strong Coulomb interaction may enhance thermoelectric power, putative antiferromagnetic states in RuSe$_2$ materials of interest. The $ZT=S^2/\rho k$ value at 300 K (730 K) is only about 0.003 (0.005 assuming about 100 W/Km). Thermal conductivity is rather high and very far away from the amorphous limit. Nanoengineering of RuSe$_2$ objects may reduce thermal conductivity and could lead to much larger values of $ZT$.

In conclusion, we report enhanced thermoelectric power and electronic correlations in RuSe$_2$. RuSe$_2$ shows a semiconducting behavior with a thermally activated gap. The band structure calculation confirmed the semiconducting characteristic, albeit with significantly underestimated gap implying the importance of the electron correlation effect. The Seebeck coefficient of RuSe$_2$ approaches - 250 $\mu$V/K near 730 K, showing the electron-type carriers. Small Ir doping results in the significant suppression of the resistivity and the Seebeck coefficient. The sample with 20% Ir doping shows a semiconductor-metal transition at about 20 K, while the magnetic field restores the semiconducting behavior at low temperature. Our results shows the large Seebeck coefficient of RuSe$_2$ and implies the important role of electron and magnetic correlations.

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| Nominal Composition | Lattice(Å) | $x_{Se}$ | Uiso-Ru (Å) | Uiso-Se (Å) | Refined Composition | R(%) |
|---------------------|------------|----------|-------------|-------------|---------------------|------|
| RuSe$_2$            | 5.94164(3) | 0.3807(2)| 0.0039(3)   | 0.0051(3)   | Ru$_{0.99(1)}$Se$_2$ | 7.3  |
| Ru$_{0.9}$Ir$_{0.1}$Se$_2$ | 5.94319(7) | 0.3794(2)| 0.0042(3)   | 0.0058(3)   | Ru$_{0.92(1)}$Ir$_{0.08(1)}$Se$_2$ | 5.6  |
| Ru$_{0.8}$Ir$_{0.2}$Se$_2$ | 5.94740(7) | 0.3784(2)| 0.0045(3)   | 0.0061(3)   | Ru$_{0.84(1)}$Ir$_{0.16(1)}$Se$_2$ | 4.5  |

| Nominal Composition | Se-Ru (Å) | Se-Ru-Se (°) | Se-Ru-Se (°) |
|---------------------|--------|-------------|-------------|
| RuSe$_2$            | 2.4742(3) | 94.71(2)   | 85.29(2) |
| Ru$_{0.9}$Ir$_{0.1}$Se$_2$ | 2.4722(3) | 94.82(2) | 85.18(2) |
| Ru$_{0.8}$Ir$_{0.2}$Se$_2$ | 2.4720(3) | 94.91(2) | 85.09(2) |