Vacancy defect control of colossal thermopower in FeSb$_2$

Qianheng Du$^{1,2,5}$, Lijun Wu$^3$, Huibo Cao$^3$, Chang-Jong Kang$^4$, Christie Nelson$^5$, Gheorghe Lucian Pascut$^{4,6}$, Tiglet Besara$^{7,9}$, Theo Siegistic$^{7,8}$, Kristjan Haule$^6$, Gabriel Kotliar$^{1,4}$, Igor Zaliznyak$^6$, Yimei Zhu$^1$ and Cedomir Petrovic$^{1,2,5}$

Iron diantimonide is a material with the highest known thermoelectric power. By combining scanning transmission electron microscopic study with electronic transport neutron, X-ray scattering, and first principle calculation, we identify atomic defects that control colossal thermopower magnitude and nanoprecipitate clusters with Sb vacancy ordering, which induce additional phonon scattering and substantially reduce thermal conductivity. Defects are found to cause rather weak but important monoclinic distortion of the unit cell $Pnmm \rightarrow Pm$. The absence of Sb along [010] for high defect concentration forms conducting path due to Fe $d$ orbital overlap. The connection between atomic defect anisotropy and colossal thermopower in FeSb$_2$ paves the way for the understanding and tailoring of giant thermopower in related materials.

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INTRODUCTION

Thermoelectric materials exploit thermoelectric effect where temperature difference is converted into electric power and vice versa$^{1,2}$. High operating temperatures are favorable for significant contribution, whereas in cryogenic environment electronic correlations could also be significant$^{3-8}$. The iron diantimonide is a correlated narrow-gap semiconductor$^{9,10}$. It also features colossal thermopower $S$ and highest known thermoelectric power factor at cryogenic temperatures; whereas both electronic diffusion and phonon-drag mechanism have been proposed, reported maximum $S$ values vary between 0.1 and 50 mV K$^{-1}$ and in some crystals quasi-one-dimensional (quasi-1D) conductivity has been observed$^{11-15}$. Interstitial Fe atoms in the unit cell that create impurity states connected with phonon drag have been postulated but never observed$^{16}$. The connection with fine details of crystal structure is not understood since, for example, FeAs$_2$ features an order of magnitude higher thermal conductivity and should have higher thermopower within the phonon drag mechanism when compared to FeSb$_2$, but experiments show $S$ maxima about six times smaller in iron diarsenide$^{14}$.

Atomic defects have been used to enhance high-temperature thermoelectric performance by lowering phonon thermal conductivity in the figure of merit $ZT = S^2\sigma T/\kappa$, where $T$ is temperature, $S$ is thermopower, and $\sigma$ ($\kappa$) are electrical (thermal) conductivities. When operating temperatures are not high, material must maximize its thermoelectric power factor ($S^2\sigma$) where $S$ provides considerable contribution, whereas in cryogenic environment electronic correlations could also be significant$^{9,10}$. The absence of Sb along [010] for high defect concentration forms conducting path due to Fe $d$ orbital overlap. The connection between atomic defect anisotropy and colossal thermopower in FeSb$_2$ paves the way for the understanding and tailoring of giant thermopower in related materials.

RESULTS AND DISCUSSION

Sample characterization

We first fabricated several crystals from Sb melt using different decanting methods, purity of raw elements, and crucibles (see Supplementary Note 4 and Table 7). Then we picked two crystals: one with expected high purity (S8) and the other with expected low purity (S3). To shed light on the atomic-scale structure, we performed high-resolution scanning transmission electron microscopy (STEM) with a high-angle annular dark field (HAADF) detector as its contrast is proportional to $Z^2$ along the atom column, where $Z$ is the atomic number. Figure 1a, b show the STEM-HAADF images taken from S3 and S8 crystals, respectively. The strong and weak dots in the images correspond to Sb and Fe atoms, respectively. The atomic arrangement in the images is consistent with the FeSb$_2$ structure with $Pnmm$ symmetry, as shown in the insets where the atomic projections are embedded in the magnified image. Due to the $Z$-contrast nature of the STEM-HAADF image, the peak intensity of each dot can be used to count the atoms along the column$^{12}$. Higher peak intensity indicates more atoms along the column, while weaker peak intensity indicates less atoms, thus more vacancies along the column. It is seen that the peak intensity of Fe is quite uniform in crystal S8 (Fig. 1b), indicating the relative uniform distribution of Fe. However, the peak intensity of Fe varies in crystal S3, e.g., there are less Fe in area I than that in area II, as shown in the magnified image in the insets of Fig. 1. a We also observe Sb intensity variation, indicating the variation of Sb occupations. The Sb occupations or vacancies can be better resolved by refining each Sb column peak with the second-order polynomial function. Figure 1c, d shows the peak intensity maps of Sb for crystals S3 and S8, respectively. There are four Sb atoms in a FeSb$_2$ unit cell. In crystal S3, the Sb peak intensity is the same in some area (inset III in Fig. 1c), consistent with the $Pnmm$ symmetry.
In the other area, however, the Sb peak intensity changes periodically and orders along Pnmm [010] direction, as shown in the inset II in Fig. 1c, where two Sb peaks (orange squares) are stronger than the other two Sb (green squares) within the unit cell. This indicates the ordering of Sb vacancies and reduction of the Pnmm symmetry in this area. In [100] projection, orange and red spheres represent high and low Sb occupancy, respectively, embedded in the inset II. The size of the phase separation clusters with Sb vacancy ordering is about a few nanometers. These clusters are similar to the nanoprecipitates observed in PbTe-AgSbTe$_2$ system$^{23,24}$. They induce additional phonon scattering, thus reduce the thermal conductivity and phonon mean free path (MFP) of crystal S3. For crystal S8, the Sb vacancy ordering is observed in nearly all locations and also along [010] direction. In area IV (Fig. 1d), two Sb peaks (orange) are stronger than the other two Sb (red). While in the area V, one Sb peak (yellow square) is stronger than the other three Sb (orange squares).

Sb vacancy ordering results in a Pnmm-forbidden peak observed in single-crystal synchrotron X-ray diffraction (Fig. 1e–g) of crystal S8, consistent with weak structural distortion observed in neutron diffraction measurements (Fig. 1h–k). Neutron diffraction shows the presence of weak (h,0,l), $h+l = \text{odd}$ and (0,k,j), $k+l = \text{odd}$ type Bragg reflections, which are forbidden in Pnmm crystal structure previously refined for the stoichiometric FeSb$_2$.$^{9,10,25}$ The presence of these forbidden reflections hints that the symmetry of the crystal lattice is lower. Comprehensive structural refinement (Fig. 1h–k) and also Supplementary Note 1 and Tables 1–4 indicate that one of the two Sb sites, which are equivalent in Pnmm space group, shows displacive monoclinic distortions and site deficiency. This induces change in the structural symmetry (Pnmm → Pm), making two Sb sites inequivalent, i.e., Sb1 site is fully occupied while Sb11 site contains substantial number of vacancies that do not change with temperature (Fig. 1i). We find that the Sb11 site is 0.82(2) occupied while both Fe sites are 0.94(2) occupied; the chemical vacancies do not change with temperature, whereas intensity of Pnmm-forbidden peaks at 300 K is 2/3 of that at 5 K (see Supplementary Note 1 and Tables 1–4).

**Electrical and thermal transport properties**

Having established the presence of atomic vacancies, next we focus on electrical and thermal transport properties of crystals S3 and S8 as well as of six additional crystals engineered to have different defect content. Figure 2a–c presents electronic and thermal transport difference among all eight iron diantimonide crystals. Crystals S7 and S8 have about 1–2 order of magnitude higher electrical resistivity when compared to crystals S1, S2, and S3 in the temperature region 10–20 K (Fig. 2a). Moreover, crystals S1, S2, and S3 have clear weak (semi)metallic resistivity in 60–300 K temperature region. Low-temperature thermopower $S$ shows large variation (Fig. 2b); $|S|$ maxima change by several orders of magnitude from S1 (14 μV K$^{-1}$) to S8 (20 mV K$^{-1}$). Figure 2c shows thermal conductivity $\kappa$ vs temperature for all crystals. The small $\kappa(7)$ maxima are coincident with small thermopower, consistent with phonon-drag mechanism$^{15–17}$.
In what follows, we focus on the deviation from the ideal stoichiometry. The contribution of different relaxation processes to $\tau$ and their difference among investigated crystals in the simplest form can be assessed from:

$$\tau^{-1} = \tau_0^{-1} + \tau_1^{-1} + \tau_{U}^{-1}$$

$$= \frac{v}{\xi} + A\omega^{4} + B\omega^{3}T e^{-\frac{\omega}{\theta}}$$

(1)

where $\tau_0$, $\tau_1$, and $\tau_U$ are the relaxation times for boundary scattering, impurities or defect scattering, and Umklapp processes, respectively. The $L$, $A$, and $B$ are fitting parameters in the fit of the experimental lattice thermal conductivity using Callaway model (Fig. 2d):

$$K_L = \frac{k_b}{2m^*v_s} \left( \frac{k_b}{h} \right)^3 \int_0^{\frac{\pi}{2}} \frac{\tau x^4 e^x}{(e^x - 1)^2} dx$$

(2)

In this model, $x = \frac{\omega}{\theta}$ is dimensionless, $\omega$ is the phonon frequency, $k_b$ is the Boltzmann constant, $h$ is the Plank constant, $\theta$ is the Debye temperature, and $v_s$ is the velocity of sound. Fit parameters are listed in Table 1. Since Umklapp scattering processes are of importance at high temperature, we mainly focus on parameters $A$ and $L$. In crystals S5, S6, S7, and S8 with large phonon MFP, surface scattering is more important when compared to S1, S2, S3, and S4 where the impurity scattering processes are much stronger as inferred from $A$ (Table 1), which features inverse scaling with $\tau$. The decrease of MFP in the investigated crystals is clearly related to the defect scattering of phonons.

We note that, in the Callaway model, the parameter $\tau_B = L/v$ represents the relaxation time determined by boundary scattering. The $L$ is the phonon MFP at low temperature in the boundary scattering regime, which is different from grain size. For the rod-like sample with the square cross-section and infinite length, it depends on the side dimension only. For the finite length and rectangular cross-section, there are correction factors, i.e., it not only depends on two side dimensions but also on their ratio and sample length.

From the data collected on crystal S3 (Fig. 1h–k) and Supplementary Table 3, the refined crystal stoichiometry is Fe$_{0.93}$Sb$_{1.83}$. STEM-HAADF image simulations (Fig. 2e–n) show Fe$_{0.93}$Sb$_{1.83}$ for crystal S3 (in good agreement with neutron refinement) and Fe$_{0.95}$Sb$_{1.85}$ for crystal S8.
Next, from the thermal conductivity fits (Table 1), we note differences among crystals due to defect scattering, given by parameter $A$ in the Callaway model. From the changes in parameter $A$, we estimate the defects content, i.e., the stoichiometry of all investigated crystals by assuming linear relation between defect scattering and defect concentration. The results are shown in Fig. 2a, p and in Table 1. The relative stoichiometry ratio of Sb:Fe differs from the ideal stoichiometric 2:1 in all crystals in linear manner, albeit with differences that are <2.3 atomic %.

Thermally activated resistivity $>50$ K (Fig. 2a) stems from the intrinsic energy gap; however, the resistivity shoulder in the region of $S_{\text{max}}$ around 10 K is a fingerprint of the in-gap impurity states that couple to phonon drag. Magnetoresistance (MR) is strong in the temperature range where such states are dominant in electronic transport; a single in-gap band gives only one peak in MR. High-thermopower crystals S6 and S8 show one MR peak in electronic transport; a single in-gap band gives only one peak in 1D conductivity in optics. Occupancy of Fe

d/or orbital overlap due to the absence of Sb along [010], weak metallicity, and metal–insulator transition on cooling.

**Band structure calculations**

GW+i-DMFT calculations (see Supplementary Note 5) show that bands associated with quasi-1D dispersion along 6.536 Å are Fe derived: bottom of the conduction band is dominated by Fe $xy$ orbital, whereas top of the valence bands is dominated by Fe $xz/yz$ bands. First-principle calculation results (Fig. 4b–h) confirm that structure distortion to the $Pm$ space group is energetically favorable in Sb-deficient $Pnma$ FeSb$_2$ unit cell. However, the Sb vacancies also induce Fe dangling bonds that might influence electronic structure through conducting impurity band at the Fermi level for high Sb defect concentration.

To explore how Sb atom vacancy and its ratio affect the electronic structure of FeSb$_2$, we studied two cases of Sb vacancy ratios: one and two Sb vacancies in a $2 \times 2 \times 3$ super-cell of FeSb$_2$. To simulate the experimental situation, we only consider Sb vacancies at the Sb11 site. Hence, Sb vacancies for both cases
FeSb₂. In the experiment, the maximum value of thermoelectric conducting path. Anisotropy in the electronic structure and triggers the quasi-1D conductivity. Our study demonstrates the potential of low-level atomic defects to control thermopower magnitude and quasi-1D electronic conduction. This paves the way toward computational predictions of colossal thermopower induced by atomic point defect engineering.

**METHODS**

**Crystal synthesis**

Single crystals of FeSb₂ were grown as described before, albeit with different starting purity of Fe and Sb and with variable methods of crystal decanting from Sb liquid. Whereas within one single batch thermopower values \( S_{\text{max}} \) exhibit variations, especially for low-purity starting materials such as Fe 99.5% and Sb 99.99% and lower, the use of high-purity starting materials, such as Fe 99.999% and Sb 99.99999%, elimination of quartz wool in excess Sb decanting and use of filter screw-top crucibles developed for flux crystal growth above the quartz melting point reduces the variation. This produces FeSb₂ crystals with about 5–20 mV K⁻¹ thermopower peak within single batch. On the other hand, we note that, among different batches with variable starting materials purity and decanting method, \( S(T) \) and \( \rho(T) \) measured on same crystal exhibit close correspondence to values presented in Fig. 2 in the main text.
Transport, thermal, and magnetic measurements

Crystals were oriented using a Laue camera and cut along the b-axis for magnetization, resistivity, and thermopower measurement in a Quantum Design MPMS-5 and PPMS-9.

Scanning tunneling microscopy

STEM-HAADF imaging and electron diffraction were performed using the double aberration-corrected JEO-LAR-AM200CF microscope with a cold-field emission gun and operated at 200 keV. The images are filtered in frequency space by applying periodic mask to remove noise.

X-ray and neutron diffraction

Synchrotron single-crystal X-ray diffraction was performed at NSLS-II beamline 4-ID, using a photon energy of 11.44 keV with an incident beam intensity of $3 \times 10^{10}$ photons s$^{-1}$. Single-crystal neutron diffraction was performed at the HB3A four-circle diffractometer (FCD) equipped with a two-dimensional Anger camera detector at the High Flux Isotope Reactor at the Oak Ridge National Laboratory. Neutron wavelength of 1.005 Å was used from the bent perfect Si-331 monochromator$^{30}$. Room temperature single-crystal X-ray diffraction was performed at NHMFL Tallahassee using an Oxford Diffraction Xcalibur 2 charge-coupled device FCD with graphite-monochromated Mo Kα radiation.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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AUTHOR CONTRIBUTIONS

C.P. designed research. Q.D. and C.P. made crystals. Q.D. carried out transport, magnetization, and thermal measurements and analysis with C.P. TEM measurement and analysis was done by L.W. and Y.Z. C.N. performed synchrotron X-ray diffraction measurement. H.C. and I.Z. carried out neutron diffraction measurements and solved

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new structure with input from L.W. and Y.Z. T.B. and T.S. carried out laboratory single-crystal measurements. C.-J.K., G.L.P., K.H., and G.K. carried out first-principle calculations. C.P. supervised the project and wrote the paper with Q.D. and with input from L.W., I.Z., C.-J.K., and G.K. The manuscript reflects contribution and ideas of all authors.

COMPETING INTERESTS
The authors declare no competing interests.

ADDITIONAL INFORMATION
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Correspondence and requests for materials should be addressed to Q.D. or C.P.

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