Unusual effects of Be doping in the iron-based superconductor FeSe

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Abstract
Recent superconducting transition temperatures ($T_c$) over 100 K for monolayer FeSe on SrTiO₃ have renewed interest in the bulk parent compound. In KCl:AlCl₃ flux-transport-grown crystals of FeSe₀.₉₄Be₀.₀₆, FeSe₀.₉₇Be₀.₀₃ and, for comparison, FeSe, this work reports doping of FeSe using Be—among the smallest of possible dopants, corresponding to an effective ‘chemical pressure’. According to lattice parameter measurements, 6% Be doping shrank the tetragonal FeSe lattice equivalent to a physical pressure of 0.75 GPa. Using this flux–transport method of sample preparation, 6% of Be was the maximum amount of dopant achievable. At this maximal composition of FeSe₀.₉₄Be₀.₀₆, the lattice unit cell shrinks by 2.4%, $T_c$—measured in the bulk via specific heat—increases by almost 10%, the $T_c$ versus pressure behavior shifts its peak $T_c^{\text{onset}}$ downwards by ~1 GPa, the high temperature structural transition around $T_S = 89$ K increases by 1.9 K (in contrast to other dopants in FeSe which uniformly depress $T_S$), and the low temperature specific heat $\gamma$ increases by 10% compared to pure FeSe. Also, upon doping by 6% Be the residual resistivity ratio, $\rho(300 K)/\rho( T \to 0)$, increases by almost a factor of four, while $\rho(300 K)/\rho(T = T_c)$ increases by 50%.

Keywords: superconductivity, iron based, specific heat

(Some figures may appear in colour only in the online journal)

1. Introduction

FeSe has one of the lower superconducting transition temperatures ($T_c$) ~ 8 K of the iron based superconductors [1] (IBS) in its undoped, bulk form. However, superconductivity in FeSe is highly tunable. With applied pressure (7 GPa), $T_c$ can approach 37 K and, prepared as a monolayer on SrTiO₃, the $T_c$ of FeSe has reached, according to one report, 109 K, the current record for high temperature superconductivity in IBS.

S and Te are isoelectronic to Se, and are known to substitute on the Se site in FeSe. Doping FeSe with S (FeSe₁₋ₓSₓ), which shrinks the lattice size (i.e. chemical pressure), results [4] in a shallow peak in $T_c$ versus $x$ at 10.7 K for $x = 0.11$, while doping FeSe with Te (FeSe₁₋ₓTeₓ) expands the lattice and $T_c$ reaches ~14 K at FeSe₀.₅₇Te₀.₄₃. Upon doping FeSe with either S or Te, the structural transformation, $T_S$, decreases monotonically in temperature at the rate of approximately 1.2 to 1.5 K per percent of dopant for both Te [5] and S [6].

Various substitutions [7, 8] for Fe in Fe₁₋ₓMₓSe have been tried, with degradation/destruction of $T_c$ with M = Ti, V, Co, Ni, Cu and Cr. The substitution of a nominal 2% of Mn in FeSe₀.₃Te₀.₅ (i.e. Fe₀.₉₈Mn₀.₀₂Se₀.₃Te₀.₅) has been reported [9] to increase $T_c^{\text{onset}}$ in zero-field-cooled magnetic susceptibility from 13.9 to 14.4 K.

In the present work, single crystals of nominal composition Fe₁₀.₀₅Se₀.₀₅Be₀.₁ were prepared using the flux growth method of Charveev et al [10], where the excess Fe in the nominal concentration was to insure [11] the formation of the desired room temperature tetragonal structure phase. At least with this preparation method, it was not possible to achieve further addition of Be into the lattice, and—as will
be discussed below— the actual Be concentration in the nominal Fe$_{1.063}$Se$_{0.9}$Be$_{0.1}$ sample was found to be 6%. After initial observations on these crystals, as well as on crystals of the parent compound FeSe prepared in the same manner [10], crystals of composition FeSe$_{0.97}$Be$_{0.03}$ were grown in order to check for the systematic evolution of the properties with Be content. The crystals with 6% Be as well as the parent compound were characterized using x-ray diffraction, energy dispersive spectroscopy (EDS), resistivity as a function of temperature, pressure and field, magnetic susceptibility, and specific heat. For the Fe$_{1.063}$Se$_{0.9}$Be$_{0.03}$ crystals, resistivity and magnetic susceptibility were measured. The covalent radius of Be (0.96 Å) is smaller than that of S (1.05 Å) and Se (1.2 Å) (radii for Te and Fe are 1.38 Å and 1.32 Å respectively), in agreement with the x-ray diffraction determination of the lattice parameters. The reported rapid increase [2] in $T_c$ of FeSe with applied pressure ($T_c \sim 37$ K at 7 GPa) is linked to the extreme softness of the material, which has [2] a bulk modulus of only 31 GPa. The study of another smaller substitution besides S should provide insights as to the interesting properties of FeSe as well as the properties of IBS in general.

2. Experimental

Chareev et al [10] grew Fe$_{1.06}$Se crystals in evacuated quartz tubes using a KCl–AlCl$_3$ flux, with the warm end of the tube (containing the Fe and Se starting material) at ~430 °C and the cold end of the tube (where the crystals formed) at ~375 °C. This method was also followed in the current work. Fe powder (99.998% pure) and Se powder (99.999% pure), together with Be powder (MBE grade, 99.999% pure) in the proportion 1.063:0.9:0.1 (where the excess Fe concentration is to ensure [11] the tetragonal structure), were taken into a purified atmosphere glovebox, combined with the KCl and the hydrosopic AlCl$_3$, and placed in a 10 mm ID quartz tube. Without exposure to air, this tube was then sealed under vacuum. In order to gain experience with the method (in particular the optimal ratio of flux to reactant), as well as to provide a good baseline for understanding the changes with Be-doping, pure Fe$_{1.06}$Se and Fe$_{1.06}$Se$_{0.97}$Be$_{0.03}$ crystals (nominal concentrations) were also prepared using the same technique. In order to verify reproducibility, multiple furnace runs on all three compositions were carried out with the result that the crystals from differing tubes with the same nominal concentrations gave, within error bars, the same results.

The chemical composition of both the parent compound and the nominal Fe$_{1.063}$Se$_{0.9}$Be$_{0.1}$ was measured with a Hitachi S3400 scanning electron microscope operating at 20 kV. Energy dispersive x-ray spectroscopy (EDS) was checked for each sample on three areas (each ~80 µm) and averaged. The results indicated a 1:1 stoichiometry in the parent compound (i.e. the excess Fe supplied in the growth tube does not enter into the final product crystals), and approximately Fe$_{0.94}$Be$_{0.06}$ in the nominal composition Fe$_{1.06}$Se$_{0.9}$Be$_{0.1}$ sample. On the basis of this result, crystals with an intermediate nominal Be concentration, Fe$_{1.06}$Se$_{0.97}$Be$_{0.03}$, were prepared and characterized and indeed gave resistivity and magnetic susceptibility results (as discussed below) between those of the parent compound and FeSe$_{0.94}$Be$_{0.06}$.

Our assumption in making these samples was that Be would go on the Se site, based on Be being closer in ionic radius to Se than Fe, as well as the existence of, e.g. the compound FeBe$_2$, i.e. Be is not always 2+ valent in compound formation. In order to check this assumption, single crystal x-ray diffraction was performed on crystals of FeSe and FeSe$_{0.9}$Be$_{0.06}$. And for both crystals we refined the occupancy of the Fe (2b site) and Se (2c site). The parent compound FeSe refines as 1:1, the same as the EDS result. For the crystal with 6% Be as determined by EDS, the Se site is deficient and in fact the sample composition refines as FeSe$_{0.94}$. Thus, we continued with our assumption that Be replaces Se, i.e. the Be-doped sample has the composition FeSe$_{0.94}$Be$_{0.06}$. (As will be seen below when we consider the extrapolated residual resistivity, $\rho(T \to 0)$, proportional to lattice defect scattering, this assignment is further substantiated by the lowered $\rho(T \to 0)$ and therefore lowered defect scattering in the Be doped sample, which would not obtain if the Se sublattice had 6% vacancies present.)

The single crystal x-ray diffraction gave a- and c-lattice parameters for the crystals of the parent FeSe compound equal to 3.7731 and 5.533 Å respectively, consistent with literature values. For the 6% Be-doped sample, the measured values of a and c were 3.7456 and 5.480 Å respectively. This indicated a shrinkage in the size of the lattice, as expected from the smaller Be radius, and guaranteed that the smaller Be did in fact replace either Fe or Se in the FeSe lattice and was not segregated as some second phase, leaving the lattice parameter unchanged, or enter the lattice interstitially, which would expand the lattice. Using the known bulk modulus of 31 GPa, this shrinkage corresponds to a physical pressure of ~0.75 GPa.

The high-pressure resistivity measurements were carried out in an OmniDAC gas membrane-driven diamond anvil cell from Almax-EasyLab. The cell was placed inside a custom, continuous flow cryostat built by Oxford Instruments. Optical access to the cell was provided through windows at the bottom of the cryostat and an optical fiber entering through a feedthrough at the top, allowing pressure to be measured at low temperature. The pressure was calibrated using the fluorescence of the $R_1$ peak of small ruby spheres placed next to the sample [12]. One of the diamonds used was a designer diamond anvil [13] containing eight symmetrically arranged, deposited tungsten microprobes encapsulated in high-quality homoepitaxial diamond. This diamond had a tip diameter of ~180 µm, and the opposing anvil had a culet diameter of ~500 µm. Resistance was measured in the crystalline ab-plane using the four-probe Van der Pauw method with currents of ≤1 mA. Gaskets were preindented from 250 µm to ~30 µm thickness and were made of 316 stainless steel. Quasihydrostatic soft, solid steatite was used as the pressure-transmitting medium. The samples were cleaved from single crystals and had dimensions of ~70 µm × 70 µm × 10 µm.

The magnetic susceptibility was measured in a SQUID magnetometer from Quantum Design, while the resistivity and specific heat were measured in cryostats designed and
and for pure FeSe is significantly higher than our value of 24.7.

The superconducting onset transition temperature of the two crystals are 8.45 and 8.25 K, and RRR = 27 respectively, while the Be-doped sample has \( T_{c(\rho \to 0)} \) of 9.21 K, 9.06 K, and 102 respectively. (For a single crystal of FeSe0.97Be0.03, the resistivity data—not shown—give \( T_c(\rho \to 0) = 8.79 \) K, i.e. between the values for the parent compound and the 6% Be doped compound. The extrapolated normal state residual resistivity, \( \rho(\rho \to 0) \), of the FeSe0.97Be0.03 is also between that of FeSe and the 6% Be doped compound.)

The resistivities of the as-prepared single crystals of FeSe and FeSe0.94Be0.06 versus temperature showing the shift of \( T_{c(\rho \to 0)} \), \( T_{c(mid)} \) and \( T_{c(onset)} \) caused by the addition of Be. The midpoint, \( \rho = 0 \) \( T_c \), and RRR values of FeSe as determined by resistivity measurements of our single crystals are 8.45 and 8.25 K, and RRR = 27 respectively, while the Be-doped sample has \( T_{c(mid)} \) of 8.45 K and \( T_{c(onset)} \) of 9.06 K. The midpoint, \( \rho = 0 \) \( T_c \), and RRR values of FeSe as determined by resistivity measurements of our parent compound as shown. (Data for FeSe and FeSe 0.94Be0.06 are shown up to higher temperatures, with values for the FeSe0.95Be0.05 ~6% higher at room temperature. Although the extrapolated normal state resistivities down to \( T = 0 \) for the Be doped samples, 3% (not shown) and 6%, are lower than that for the parent FeSe compound—indicating less scattering from lattice defects—the behavior at high temperatures shows increased temperature dependent scattering (possibly from magnetic defects).

built in the Department of Physics, University of Florida. The low temperature specific heat measurements were carried out using established techniques [14].

3. Results and discussion

3.1. Resistivity and magnetic susceptibility

The resistivities of the as-prepared single crystals of FeSe and FeSe0.94Be0.06 are shown in figure 1, with increases in \( T_{c(midpoint)} \) (≈0.76 K) and \( T_c \) (\( \rho \to 0 \)) of 0.81 K in the Be-doped over the parent compound as shown. (Data for FeSe0.97Be0.03, not shown for clarity, give an increase of \( T_c \) (\( \rho \to 0 \)) of 0.54 K.)

The superconducting onset transition temperature of the two Be-doped (FeSe0.97Be0.03 and FeSe0.96Be0.04) samples as measured by magnetic susceptibility, more of a bulk measurement, (shown in figure 3) increase by ~0.3 and ~0.6 K versus

\[ T_c(\rho \to 0) \] for FeSe0.97Be0.03 crystals was 9.21 K, 9.06 K, and 102 respectively. (For a single crystal of FeSe0.97Be0.03, the resistivity data—not shown—give \( T_c(\rho \to 0) = 8.79 \) K, i.e. between the values for the parent compound and the 6% Be doped compound. The extrapolated normal state residual resistivity, \( \rho(\rho \to 0) \), of the FeSe0.97Be0.03 is also between that of FeSe and the 6% Be doped compound.)

The values for FeSe are comparable to literature values [17] for good quality single crystal samples, indicating the high quality of the undoped FeSe samples in the present work. However, it is not hard to find in the literature rather broadened resistive transitions where \( T_{c(onset)} \) for pure FeSe is significantly higher than our value of 9.04 K, see e.g. the ~13.5 K value in polycrystalline material of [18] (where \( T_c(\rho \to 0) \) was only 7.5 K). Note the apparent \( \rho \) linear-with-\( T \) behavior for \( T > T_c \) to 20 K for both samples, and the larger linear-with-\( T \) slope for the Be-doped sample—see figure 2 for the extent of this linear behavior.

\[ \rho \] for FeSe and FeSe 0.94Be0.06 are shown up to higher temperatures, with values for the FeSe0.95Be0.05 ~6% higher at room temperature. Although the extrapolated normal state resistivities down to \( T = 0 \) for the Be doped samples, 3% (not shown) and 6%, are lower than that for the parent FeSe compound—indicating less scattering from lattice defects—the behavior at high temperatures shows increased temperature dependent scattering (possibly from magnetic defects).

the undoped parent compound respectively. (Specific heat of the parent compound compared to FeSe0.94Be0.06 is discussed below in the next section.)

The samples measured for magnetic susceptibility had masses in the range of 4.4 mg for the FeSe0.97Be0.03 up to 10 mg for the other two compositions. Thus, 50 G was chosen as the measurement field in order to achieve good signal to noise ratio in our MPMS system from Quantum Design. Both the FeSe and the FeSe0.94Be0.06 Samples showed no signs (neither a large finite susceptibility above \( T_c \) nor a saturation in the magnetization, \( M \), measured versus field) of an Fe second phase. The FeSe0.97Be0.03 sample however (see figure 3) showed a slight elevation in \( \chi \) above \( T_c \), as well as a small moment (0.02 \( \mu_B \)/mole) that saturates at 0.3 to 0.4 T (\( M \) versus \( H \) data not shown.) Another collage of FeSe0.97Be0.03 crystals showed ~0.1 \( \mu_B \)/mole and a much more visible finite \( \chi \) for temperatures above \( T_c \). Thus, despite their good RRR value and the increase in \( T_c \) versus the parent compound, the 3% Be-doped samples did, in some crystals, show a magnetic impurity phase. This may account for the larger resistivity at finite temperatures in the FeSe0.95Be0.05 [17].

The magnitudes of the reported values for \( \rho \) depend on the geometry (\( \rho = R * A/L \)), where \( R \) is the measured resistance in ohms, \( A \) is the cross sectional area, and \( L \) is the distance between the contacts. Errors in this geometrical factor of 10% are inherent in the procedure.
If instead of S, Te is used, this ratio results in RRR values that either stay approximately the same as seen in the resistance data, although the transitions are shifted downwards in temperature as is typical when comparing resistive (corresponding to a 1D pathway) and magnetic susceptibility (corresponding to 2D shielding) results.

Figure 3. dc magnetic susceptibility versus temperature (cooled in zero field, i.e. these are diamagnetic shielding, not flux expulsion, measurements) for FeSe, FeSe$_{0.97}$Be$_{0.03}$ and FeSe$_{0.94}$Be$_{0.06}$ single crystals. The increase in $T_c$ upon Be-doping is approximately the same as seen in the resistance data, although the transitions are shifted downwards in temperature as is typical when comparing resistive (corresponding to a 1D pathway) and magnetic susceptibility (corresponding to 2D shielding) results.

Figure 4. Resistivity of Fe$_{1.063}$Se$_{0.94}$Be$_{0.06}$ and Fe$_{1.063}$Se$_{0.94}$Be$_{0.06}$ single crystals at the tetragonal to orthorhombic phase transition at $T_S$. As seen, the scattering at finite temperatures in the Be doped samples (perhaps from magnetic impurities—see figure 3) causes a higher resistivity than in the parent compound at the structural ordering transition.

It is interesting to note the large increase in the residual resistivity ratio, $\text{RRR}_s (\equiv \rho(300\,\text{K})/\rho(T \to 0))$ (see figure 1) from RRR = 27 for FeSe to RRR = 52 in the crystals doped with 3% Be and RRR = 102 for the crystals doped with 6% Be. (A second batch of FeSe$_{0.94}$Be$_{0.06}$ had RRR = 105 and a second batch of FeSe$_{0.97}$Be$_{0.03}$ had RRR = 84). If instead of $\rho(300\,\text{K})/\rho(T \to 0)$, $\rho(300\,\text{K})/\rho(T = T_c^+)$ is used, this ratio increases from 16.0 for pure FeSe to 24.7 for crystals doped with 6% Be. Doping FeSe with either S or Te on the Se site results in RRR values that either stay approximately the same [8, 15] ($S, x = 0.1$ and $0.18$) relative to the parent FeSe compound, or decrease [8] ($Te, x = 0.25, 0.5$). Similarly, doping FeSe on the Fe site also causes a decrease in RRR (Co [8], $x = 0.05, 0.1, 0.2$; Mn [16], $x = 0.02$).

It is worth stressing that the RRR ($\equiv \rho(300\,\text{K})/\rho(T \to 0)$) value for the FeSe$_{0.9}$Be$_{0.06}$ sample being almost four times that of the FeSe primarily comes from the lower residual resistivity extrapolated to $T = 0$, $\rho(T \to 0)$, in the Be-doped versus that in the parent compound (0.0067 m$\Omega$ cm versus 0.017 m$\Omega$ cm, a factor of 2.5) rather than the higher $\rho(300\,\text{K})$ (0.70 m$\Omega$ cm in Fe$_{1.063}$Se$_{0.94}$Be$_{0.06}$ versus 0.43 m$\Omega$ cm, a factor of 1.6, for the parent compound.) One possibility to explain the lower residual resistivity in FeSe$_{0.9}$Be$_{0.06}$ would be from the addition of carriers to the Fermi sea. However, as discussed in the next section, the specific heat results show only a 10% increase in the electronic specific heat coefficient $\gamma$, proportional to the dressed density of electronic states at the Fermi energy. Another possible source for the lower $\rho(T \to 0)$ values in the Be-doped compounds could be that the addition of Be caused improved sublattice order. Improved lattice order is in fact consistent with the high angle x-ray reflections from a collage of crystals oriented aligned with the x-ray beam in the c-axis direction, e.g. the [005] line in the 6% Be-doped sample is 20% narrower than seen for pure FeSe.

In any case, the lower residual resistivity $\rho(T \to 0)$ measured for the Be-doped crystals argues strongly (as discussed above) that there are not 6% vacant sites on the Se sublattice as would be one possible conclusion from the refinement of the x-ray diffraction results, but that in fact the doped Be resides on the Se sublattice.

At present there is no explanation for why Be might improve sublattice order, leaving this as an interesting puzzle for further investigation.

The resistivities of FeSe, FeSe$_{0.97}$Be$_{0.03}$ and FeSe$_{0.94}$Be$_{0.06}$ in the vicinity of where the tetragonal—orthorhombic structural transition takes place at $T_S \approx 89$ K are shown in figure 4. The structural transition shifts upwards in temperature approximately 1.9 K with the addition of 6% Be. This increase in $T_S$ tracking an increase in $T_c$ in Be-doped FeSe is contrary [1] to the great majority of results in IBS, where an increase of doping drives $T_c$ upwards on a superconducting ‘dome’, while at the same time the structural transition temperature $T_S$ is depressed. Also, as discussed above in the Introduction, doping FeSe with either S [6] or Te [5] reduces $T_S$. If we consider the addition of Be simply as equivalent to chemical pressure, based on the shrinkage of the c- and a-axis lattice parameters, this increase in $T_S$ is contrary to measurements of $T_S$ under pressure where $T_S$ decreases quite rapidly [19] with pressure, at about 25 K GPa$^{-1}$.4

One possible way to understand this behavior is to note the fact that the RRR is significantly increased in the Be-doped samples, i.e. consistent with an improvement in the sublattice order. This would improve local chemical and electronic uniformity [20], resulting in a higher structural ordering temperature. Such an improvement of $T_S$ with increasing RRR was seen in [17]$^4$ study of vapor grown FeSe crystals. As we will see below when comparing the specific heat of Be-doped

4 See footnote 3.
Figure 5. $T_{\text{onset}}$ versus pressure in a diamond anvil cell for FeSe$_{0.94}$Be$_{0.06}$ and FeSe. $T_{\text{onset}}$ exceeds 40 K at about 7 GPa for FeSe$_{0.94}$Be$_{0.06}$, while this peak $T_c$ is shifted higher by ~1 GPa for the undoped FeSe. The data shown here for pure FeSe are similar to those taken by Sun et al [21], except peak $T_{\text{onset}}$ in their data is ~2–3 K lower, and their data extended only to 10 GPa. Suppression of $T_c$ with field applied in the $c$-axis direction up to 9 T was also studied (not shown) at ambient pressure. $H_c^2(0)$ shifts upward by 1 T in the 6% Be-doped compound versus the undoped parent compound.

One of the important characterizations of FeSe$_{0.94}$Be$_{0.06}$, with its lattice already ‘pre-compressed’ via the addition of the smaller Be, is how its superconducting transition temperature responds to pressure. $T_{\text{onset}}$ as a function of pressure is shown in figure 5 for both FeSe$_{0.94}$Be$_{0.06}$ and for the undoped FeSe prepared using the same [10] method in this work. Figure 6 shows a sample determination of how $T_{\text{onset}}$ is determined at 5.3 GPa.

Figure 5 shows that the increase in $T_c$ in the Be-doped FeSe does not lead to a higher eventual peak $T_c$ achieved with pressure, but rather just shifts the $T_c$ versus $P$ curve to slightly lower pressure, i.e. the peak $T_{\text{onset}}$ is reached approximately 1 GPa earlier. Thus, numerically the addition of 6% Be to FeSe is approximately equivalent to a 1 GPa pressure shift in the $T_c$ versus $P$ curve. The ‘chemical pressure’ of Be substitution, determined from the shrinkage in the lattice parameter together with the known bulk modulus, as discussed above is approximately equivalent to 0.75 GPa, roughly equivalent to this high pressure result.

3.2. Specific heat

The specific heat of single crystals of FeSe$_{0.94}$Be$_{0.06}$ and FeSe is shown in figure 7. We wish to stress that the comparison between the specific heat of these two samples is fairly precise: the relative precision should be better than ±3% since the same mass sample with the same addenda on the same platform in the same apparatus was measured. Plus, we have intentionally—rather than taking literature data [4, 23, 24] for the specific heat of FeSe (where reported $\gamma$ values vary by at least 10% even when restricting the samples to only single crystals grown by the same Chareev et al [10] flux growth technique)—grown FeSe single crystals with the same method as for our FeSe$_{0.94}$Be$_{0.06}$ crystals to provide the best intercomparability. Since the bulk $T_{\text{onset}}$ determined by specific heat of our FeSe$_{0.94}$Be$_{0.06}$ single crystals (as well as $T_c^{\text{midpoint}}$ determined by resistivity, RRR, and $T_{\text{onset}}$ determined from dc susceptibility) are higher than the literature values [4, 23, 24], as well as our values, for undoped FeSe, there is no doubt that the doped Be has an effect.

As can be seen in the specific heat data (fit to $C/T = \gamma + \beta T^2$) of figure 7, doping Be into FeSe—in addition to raising the bulk $T_{\text{onset}}$ by ~0.8 K versus our comparison crystals of FeSe—also increases the specific heat $\gamma$ value by about 10%. The slight (~3%) change in $\beta(\propto 1/\Theta_D^2)$ gives a minor change in the respective Debye temperatures, $\Theta_D$ (215 K for the Be-doped and 218 K for the pure FeSe) which can be seen in the slightly faster rise in $C/T$ for $T > T_c$ in figure 7. However, this slight change in the Debye temperature is within the respective error bars of the two sets of data. Literature values [4, 23, 24] for the Debye temperature of FeSe single crystals are ~210 K. On the other hand, the increase in the specific heat $\gamma$ in the Be-doped compound, although only 10% in size, relative to the undoped FeSe is—with the effort spent in this work to achieve internal precision—significant.
4. Summary and conclusions

Introducing Be into FeSe produces a slight increase in \( T_c \) comparable to that seen for S [4] with the introduction of a few percent of S. While \( T_c \) shifts upwards by 10% in FeSe\(_{0.93}\)Be\(_{0.06}\), the structural transition around 89 K shifts upwards by 1.9 K (1 K for 3% Be) and the \( T_c \) versus pressure curve shifts to lower pressures by \( \sim 1 \) GPa. X-ray determination of the room temperature tetragonal lattice parameters, coupled with the known bulk modulus of 31 GPa for FeSe, indicates a shrinkage of the lattice corresponding to \( \sim 0.75 \) GPa. The residual resistivity ratio, possibly indicative of the perfection of sublattice ordering, increases by \( \sim \) factor of four (two) with the addition of 6% (3%) Be. This large increase in RRR is surprising since doping with a foreign atom in a lattice typically enhances scattering. The low temperature specific heat indicates, within a rather small error bar, that the introduction of 6% Be does not significantly change the lattice stiffness (Debye temperature) in FeSe, while the electronic specific heat coefficient increases from 5.2 to 5.8 mJ mol K\(^{-2}\). This contrasts with literature results [4] for FeSe\(_{0.93}\)S\(_{0.09}\), \( T_c \) = 10.1 K, where the \( \gamma \) value reported was a decrease to 4.9 mJ mol K\(^{-2}\), versus the value reported [4] in the same work for pure FeSe of \( \gamma = 5.3 \) mJ mol K\(^{-2}\). Thus, it would be reasonable to conclude that the differences between S and Be doping (both smaller than Se) relate to the different electronic properties of the dopants. Work is underway to introduce Be into both FeSe\(_{1-x}\)S\(_x\) and FeSe\(_{1-x}\)Te\(_x\) to further investigate the utility of Be doping for understanding the superconductivity in FeSe and its derivatives.

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