Crystal structure, physical properties and superconductivity in $A_xFe_2Se_2$ single crystals

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Abstract. We studied the correlation among structure, transport properties and superconductivity in different $A_xFe_2Se_2$ single crystals ($A =$ K, Rb and Cs). Two sets of (00l) reflections are observed in the x-ray single-crystal diffraction patterns, and they arise from the intrinsic inhomogeneous distribution of the intercalated alkali atoms. The occurrence of superconductivity is closely related to the $c$-axis lattice constant, and the $A$ content is crucial to superconductivity. The hump observed in resistivity seems to be irrelevant to the superconductivity. There exist many deficiencies within the FeSe layers in $A_xFe_2Se_2$, although their $T_c$ does not change so much. In this sense, superconductivity is robust to the vacancies within the FeSe layers. Very high resistivity in the normal state should be ascribed to such defects in the conducting FeSe layers. $A_xFe_2Se_2$ ($A =$ K, Rb and Cs) single crystals show the same susceptibility behavior in the normal state, and no anomaly is observed in susceptibility at the hump temperature in resistivity. The clear jump in specific heat for Rb$_x$Fe$_2$Se$_2$ and K$_x$Fe$_2$Se$_2$ single crystals indicates the good bulk superconductivity of these crystals.

The newly discovered iron-based superconductors have attracted worldwide attention over the last three years [1]–[5] because of their high superconducting transition temperature ($T_c$ as high as 55 K) and the fact that superconductivity emerges in proximity to the magnetically ordered state [6, 7], and this new family was considered in comparison with superconducting cuprates to find the mechanism underlying the high-$T_c$ superconductivity. The highest

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$T_c$ of FeAs-based pnictides reaches 55 K at ambient pressure, whereas the anti-PbO-type FeSe$_x$, having an extremely simple structure composed of edge-sharing FeSe$_4$ tetrahedra formed from FeSe layers stacking along the c-axis, displays a lower $T_c$ of 8 K at ambient pressure [8]. After $T_c$ was enhanced to as high as 37 K by applying a high pressure [9], efforts to introduce structures between FeSe layers, just like in the FeAs analogues, successfully induced 30 K superconductivity by intercalating alkali (K, Rb and Cs) and Tl atoms between the FeSe layers [10]–[15]. The intercalated FeSe superconductors show some physical properties distinct from those of FeAs-based superconductors, such as superconductivity with a very high normal-state resistivity and a broad hump in resistivity. Fe content is important in controlling the magnetic and superconducting properties of iron chalcogenides. In FeSe, the additional iron would greatly affect its structural and physical properties [16], and superconductivity could be enhanced by the de-intercalation of the interstitial iron by partially replacing Se by Te [17, 18]. However, in $A_x$Fe$_2$Se$_2$, a large number of iron vacancies have been found to exist within conducting FeSe layers, [19] and the situation is much more complicated than in the case of non-intercalated FeSe compounds. Intercalated alkali atoms could be crucial to superconductivity. The normal-state resistivity should be strongly influenced by these vacancies. But the question how these vacancies affect the physical properties remains unresolved.

In this work, we systematically studied the effect of the starting materials and the heating process on the single-crystal growth of $A_x$Fe$_2$Se$_2$ ($A$ = K, Rb and Cs), measured the physical properties of these single crystals and determined their crystal structures. It is found that two sets of (00l) reflections exist in all the crystals, and superconductivity is closely related to the c-axis lattice constant, indicating that the A content is crucial to the superconductivity. The hump in resistivity arises from the defects within the conducting FeSe layers and is irrelevant to superconductivity. No anomaly is observed in magnetic susceptibility at the temperature of the hump in resistivity ($T_{hump}$). The clear jump in specific heat for superconducting K$_x$Fe$_2$Se$_2$ and Rb$_x$Fe$_2$Se$_2$ single crystals indicates the good bulk superconductivity in these crystals.

Single crystals of $A_x$Fe$_2$Se$_2$ ($A$ = K, Rb and Cs) were grown by the Bridgeman method as described elsewhere [12, 13]. The starting materials and the heating process are very important to obtain superconducting single crystals, and even a slight change in these conditions can significantly affect the physical properties of the obtained crystals. Three different batches of Rb$_x$Fe$_2$Se$_2$ and three different batches of K$_x$Fe$_2$Se$_2$ single crystals were grown by slightly changing the heating temperatures and starting materials. The single crystals were characterized by using x-ray single-crystal diffraction, magnetic susceptibility and electrical transport measurements. X-ray single-crystal diffraction was performed on a TTRAX3 theta/theta rotating anode x-ray diffractometer (Japan) with Cu Kα radiation and a fixed graphite monochromator. The actual compositions were determined by an x-ray energy dispersive spectrometer (EDS) mounted on a field emission scanning electronic microscope (FESEM), Sirion200. Magnetic susceptibility measurements were carried out on a Quantum Design MPMS-SQUID. Measurements of the resistivity and Hall effect were carried out on the Quantum Design PPMS-9.

Typical temperature dependence of resistivity is observed for three batches of Rb$_x$Fe$_2$Se$_2$ single crystals, as shown in figure 1. Among these crystals, Rb$_x$Fe$_2$Se$_2$-1 was obtained with the nominal composition Rb$_{0.8}$Fe$_2$Se$_{1.96}$ and through melting at 1080°C and turning off the furnace at 950°C; Rb$_x$Fe$_2$Se$_2$-2 and Rb$_x$Fe$_2$Se$_2$-3 came from the same batch with the nominal composition Rb$_{0.8}$Fe$_2$Se$_2$ and melting at 1030°C and turning off the furnace at 700°C; Rb$_x$Fe$_2$Se$_2$-4 was grown with the nominal composition Rb$_{0.8}$Fe$_2$Se$_{1.96}$ and melting conditions...
at 1030°C and switching off the furnace at 700°C. The resistivity of Rb$_x$Fe$_2$Se$_2$-1 shows a very small hump at about 290 K and then becomes metallic below this temperature with the residual resistivity ratio RRR = $R(300 \, \text{K})/R(35 \, \text{K}) \approx 37.2$. Superconductivity appears below 32.4 K and resistance reaches zero at 31.9 K. The superconducting transition width of Rb$_x$Fe$_2$Se$_2$-1 is as small as 0.5 K although the resistivity at room temperature is as large as 70 m$\Omega$ cm at 300 K. $T_{\text{hump}}$ shifts to 265 and 225 K in the case of Rb$_x$Fe$_2$Se$_2$-2 and Rb$_x$Fe$_2$Se$_2$-3, respectively. The RRR decreases to 26.1 and 17.3 for the two crystals, respectively. These results indicate that the metallicity of Rb$_x$Fe$_2$Se$_2$-2 and Rb$_x$Fe$_2$Se$_2$-3 is weaker than that of Rb$_x$Fe$_2$Se$_2$-1. However, as one can see from both the inset of figure 1 and table 1, the superconducting transition temperature seems not to vary with changes in the behavior and value of resistivity. The onset and zero resistance temperatures are 32.0 and 31.5 K for Rb$_x$Fe$_2$Se$_2$-2 and 32.4 and 31.6 K for Rb$_x$Fe$_2$Se$_2$-3. Thus one can see that the humps in resistivity seem to be irrelevant to superconductivity. Compared with those in FeAs-based pnictides [20]–[22] and FeSe [23] (usually with $\rho(300 \, \text{K})$ much less than 1 m$\Omega$ cm), the large magnitude of the normal-state resistivity reflects the existence of many deficiencies within the conducting FeSe layers in these Rb$_x$Fe$_2$Se$_2$ single crystals. As one can see from the actual compositions determined by EDS/FESEM analysis (shown in table 1), indeed, there is a large number of iron vacancies for all the crystals. The resistivity increases with increasing number of iron vacancies. A hump in resistivity should arise from such a large number of defects within the conducting FeSe layers. In this sense, superconductivity is quite robust to vacancies within the FeSe layers. For Rb$_x$Fe$_2$Se$_2$-4, although resistivity still shows a hump at around 170 K, no superconductivity can be observed, and strong semiconducting/insulator-like behavior is observed below 70 K.
Table 1. A summary of the actual compositions determined by EDS/FESEM analysis with errors within 5%, the c-axis lattice parameters \(c_1\) and \(c_2\) corresponding to the two sets of reflections with weak and strong intensities, respectively; \(T^{\text{zero}}_c\), \(T^{\text{onset}}_c\), the hump temperature in resistivity \(T^{\text{hump}}\) and RRR \((= R(300\,\text{K})/R(35\,\text{K}))\) for all the crystals of \(A_x\FeSe_2\) \((A = K, \text{Rb and Cs}).

| Sample name  | \(A: \text{Fe: Se}\) | \(c_1\) (Å) | \(c_2\) (Å) | \(T^{\text{zero}}_c\) (K) | \(T^{\text{onset}}_c\) (K) | \(T^{\text{hump}}\) (K) | RRR    |
|--------------|----------------------|-------------|-------------|----------------|----------------|----------------|--------|
| \(\text{Rb}_x\FeSe_2-1\) | 0.75: 1.77: 2 | 14.873 | 14.569 | 31.9 | 32.4 | 290 | 37.2 |
| \(\text{Rb}_x\FeSe_2-2\) | 0.82: 1.67: 2 | 14.873 | 14.582 | 31.5 | 32.0 | 265 | 26.1 |
| \(\text{Rb}_x\FeSe_2-3\) | 0.79: 1.64: 2 | 14.874 | 14.574 | 31.6 | 32.4 | 225 | 17.3 |
| \(\text{Rb}_x\FeSe_2-4\) | 0.88: 1.54: 2 | 14.792 | 14.604 |            |            | 170 |        |
| \(\text{K}_x\FeSe_2-1\)   | 0.76: 1.72: 2 | 14.292 | 14.086 | 31.2 | 31.7 | 220 | 21.2 |
| \(\text{K}_x\FeSe_2-2\)   | 0.75: 1.66: 2 | 14.282 | 14.062 | 29.2 | 30.8 | 120 | 0.65 |
| \(\text{K}_x\FeSe_2-3\)   | 0.94: 1.50: 2 | 14.201 | 14.107 |            |            | 160 |        |
| \(\text{Cs}_x\FeSe_2\)    | 0.81: 1.61: 2 | 15.556 | 15.285 | 28.3 | 30.3 | No hump < 300 K | 16.3 |

Figure 2. The Hall coefficient as a function of temperature for single crystals: \(\text{Rb}_x\FeSe_2-2\), \(\text{Rb}_x\FeSe_2-3\) and \(\text{Rb}_x\FeSe_2-4\). The inset shows the field-linear dependence of \(\rho_{xy}\) in the normal state for the crystal \(\text{Rb}_x\FeSe_2-3\).

For comparison, we measured the temperature dependence of the Hall coefficient on exactly the same pieces of \(\text{Rb}_x\FeSe_2-2\), \(\text{Rb}_x\FeSe_2-3\) and \(\text{Rb}_x\FeSe_2-4\) as shown in figure 2. First we confirmed the linearity of the Hall resistivity \(\rho_{xy}\) to magnetic field in the normal state, for example on the crystal \(\text{Rb}_x\FeSe_2-3\), as shown in the inset of figure 2. Then the temperature-dependent curves of the Hall coefficient were obtained by the subtraction of the temperature-dependent curves of the voltages measured at 6 T and –6 T \((R_H = |V_{xy}(6\,\text{T}) - V_{xy}(-6\,\text{T})| \times (S/w)/2I\), where \(S\) is the area of the cross section of the crystal, \(w\) is the distance between
Figure 3. X-ray single-crystal diffraction patterns for different batches of Rb$_x$Fe$_2$Se$_2$ single crystals.

the two Hall bars and $I$ is the electrical current). The Hall coefficients of the superconducting crystals Rb$_x$Fe$_2$Se$_2$-2 and Rb$_x$Fe$_2$Se$_2$-3 are positive at high temperature, gradually decrease with decreasing temperature and then become negative at low temperature. The sign change of the Hall coefficient was observed previously in superconducting Tl$_0.58$Rb$_{0.42}$Fe$_{1.72}$Se$_2$ samples [24]. Actually, from the angle-resolved photoemission spectroscopy (ARPES) results for $A_x$Fe$_2$Se$_2$ ($A = K$ and Cs) [25, 26], the $A_x$Fe$_2$Se$_2$ are electron-overdoped and only electron pockets can be observed. However, hole pockets could exist in superconducting samples according to the sign change of the Hall coefficient, suggesting possibly multi-band nature of superconductivity. For a sample without superconductivity, the Hall coefficient is negative in the entire temperature range. This indicates that the dominant carrier is the electron for non-superconducting crystals. This suggests that the hole pocket might be quite important for superconductivity. Therefore, further investigations are required. Furthermore, no anomaly in the Hall coefficient is observed at $T_{hump}$. This suggests that the humps in resistivity for $A_x$Fe$_2$Se$_2$ crystals are irrelevant to a structural or magnetic transition, whereas the anomaly of resistivity in an underdoped FeAs-based superconductor is always relevant to a structural/magnetic transition.

As shown in figure 1, one can observe almost the same $T_c$ for single crystals with different $T_{hump}$. X-ray single-crystal diffraction was carried out for the same four pieces of Rb$_x$Fe$_2$Se$_2$ single crystals, as shown in figure 1, to determine the relationship between superconductivity and the structure. The x-ray diffraction (XRD) patterns are shown in figure 3. Surprisingly, two sets of (00$l$) reflections are observed in all four samples. The two $c$-axis lattice parameters $c_1$ and $c_2$ are obtained (listed in table 1). The $c$-axis lattice parameters $c_1$ and $c_2$ correspond to two sets of reflections with weak and strong intensities, respectively. Neutron diffraction experiments performed by Bao et al [27] in K$_x$Fe$_{2-y}$Se$_2$ crystals indicated that there could exist both a denser Fe vacancy pattern with $I/4m$ symmetry and a looser Fe vacancy pattern with $Pmna$ symmetry around room temperature. The difference between $c_1$ and $c_2$ is larger than 1% here, so the appearance of these two sets of (00$l$) reflections cannot be simply attributed to the different Fe vacancy patterns. Nonetheless, these different Fe vacancy patterns would lead to different local
Figure 4. (a) X-ray single-crystal diffraction patterns for different batches K$_x$Fe$_2$Se$_2$ of single crystals: K$_x$Fe$_2$Se$_2$-1 (blue line), K$_x$Fe$_2$Se$_2$-2 (red line) and K$_x$Fe$_2$Se$_2$-3 (black line). (b) The temperature dependence of resistivity of the three different K$_x$Fe$_2$Se$_2$ single crystals. The inset is a zoomed plot of panel (b) at about $T_c$.

alkali contents due to the charge balance and consequently one can ascribe these two distinct sets of reflections to the inhomogeneous distribution of the intercalated Rb atoms. Alternatively, another picture including the phase separation may be used to interpret the two sets of (00l) reflections. By using a tunneling electronic microscope, Wang et al [28] observed in KFe$_{1.8}$Se$_2$ single crystals the phase separation, with the intergrowth of the Fe vacancy order state and disorder state along the $c$-axis. This phase separation could also lead to a different distribution of alkali atoms and consequently quite different $c$ values. From the fact that superconducting crystals show nearly fully shielding fraction, reflections with $c$2 should be responsible for the superconductivity. From the superconducting crystal to the non-superconducting one, $c$1 is reduced by 0.55%, while $c$2 is enhanced by more than 0.14%. It was found that insulator-like behavior is enhanced with the loss of superconductivity. This indicates that superconductivity may exist within a limited range of the $c$-axis lattice parameter. In other words, the Rb content is crucial for the occurrence of superconductivity because the $c$-axis lattice parameter strongly depends on Rb content.

We then carefully measured the resistivity and XRD patterns for three pieces of K$_x$Fe$_2$Se$_2$ crystals, as shown in figure 4. These K$_x$Fe$_2$Se$_2$ crystals exhibited resistivity behavior that differed clearly from each other. K$_x$Fe$_2$Se$_2$-1 was grown by using K$_{0.8}$(FeSe)$_2$ as the starting
Figure 5. (a) The x-ray single-crystal diffraction pattern for the Cs$_x$Fe$_2$Se$_2$ single crystal; (b) the temperature dependence of resistivity for the Cs$_x$Fe$_2$Se$_2$ single crystal. The inset is a zoomed plot of panel (b) at about $T_c$.

material and melting at 1030°C for 3 h. The K$_x$Fe$_2$Se$_2$-2 and K$_x$Fe$_2$Se$_2$-3 were grown by using K$_{0.8}$(FeSe)$_2$ as the starting material and melting at 1030°C for 2 h and 950°C for 20 h, respectively. Two sets of (00l) reflections can be observed in figure 4(a), suggesting an inhomogeneous distribution of intercalated K atoms in the K$_x$Fe$_2$Se$_2$ crystals just like in the case of Rb$_x$Fe$_2$Se$_2$ crystals. Such an inhomogeneous distribution of the intercalated K atoms could arise from the existence of two types of Fe vacancy order observed in neutron experiments [27] or from the phase separation along the c-axis, [28] similar to what was mentioned above for Rb$_x$Fe$_2$Se$_2$. For the non-superconducting sample, the c-axis lattice constant $c_1$ is smaller by more than 0.64%, and $c_2$ is larger by 0.15% than those in the superconducting samples. These results are consistent with the results observed for the Rb$_x$Fe$_2$Se$_2$ samples, indicating that the content of alkali atoms plays a crucial role in the occurrence of superconductivity. K$_x$Fe$_2$Se$_2$-1 shows a broad resistivity hump at about 220 K and superconductivity at 31.7 K. For K$_x$Fe$_2$Se$_2$-2, $T_{hump}$ shifts to 120 K and superconductivity shows up at 30.3 K. Although superconductivity disappears in K$_x$Fe$_2$Se$_2$-3, the $T_{hump}$ for K$_x$Fe$_2$Se$_2$-3 is higher than that for the superconducting K$_x$Fe$_2$Se$_2$-2, strongly demonstrating that the superconductivity is not correlated to the hump in resistivity. $T_{hump}$ could reflect the vacancy level within the conducting FeSe layers. This suggests that the vacancies within the FeSe layers have much weaker correlation to superconductivity than does the content of intercalated alkali atoms.

Figure 5 shows the x-ray single-crystal diffraction pattern and the temperature dependence of resistivity for Cs$_x$Fe$_2$Se$_2$ single crystals. Totally metallic resistivity can be observed below
300 K. Superconductivity was observed at $T_{\text{onset}} = 30.3$ K and $T_{\text{zero}} = 28.3$ K. In the XRD patterns of figure 5(a), very small reflections corresponding to $c1$ can still be found except for the main reflections with $c2$. This suggests that the inhomogeneous distribution of alkali atoms is common in all the $A_xFe_2Se_2$ single crystals. It is worthy of note that the superconductivity always shows up around 30 K for the $A_xFe_2Se_2$ crystals on changing the intercalated alkali atom $A$ from K, Rb to Cs. The $T_c$ seems not to depend on the ionic radii of the intercalated alkali atoms although the superconductivity strongly depends on the $A$ content. As shown in figures 1 and 4(b), the hump in resistivity changes in a pronounced manner for the same alkali atom case, while the $T_c$ is nearly the same (about 30 K). Very large normal-state resistivity is observed in all the $A_xFe_2Se_2$ single crystals mentioned above, suggesting a large number of deficiencies within the conducting FeSe layers for all these crystals. Based on these observations, $T_c$ seems to be robust to the vacancies within the FeSe layers.

Magnetic susceptibility was measured on the $A_xFe_2Se_2$ single crystals to investigate the correlation between the normal-state resistivity and magnetism. Figure 6 shows the anisotropic

**Figure 6.** The temperature dependence of the susceptibility at a magnetic field of 5 T applied parallel and perpendicular to the $c$-axis for (a) $Rb_xFe_2Se_2$-1, (b) $Rb_xFe_2Se_2$-2 and (c) $Rb_xFe_2Se_2$-4.
The temperature dependence of the susceptibility at a magnetic field of 5 T applied parallel and perpendicular to the c-axis in the case of (a) K$_x$Fe$_2$Se$_2$-2 and (b) Cs$_x$Fe$_2$Se$_2$.

magnetic susceptibility at a magnetic field of 5 T applied within the $ab$-plane and along the c-axis for Rb$_x$Fe$_2$Se$_2$-1, Rb$_x$Fe$_2$Se$_2$-2 and Rb$_x$Fe$_2$Se$_2$-4, respectively. Although the samples show very different resistivity behavior, such as different $T_{hump}$, magnitude of resistivity and $T_c$ values, the normal-state susceptibility shows quite similar behavior. When the field is applied within the $ab$-plane, the magnitude of susceptibility varies within 20% in the normal state and the susceptibility itself shows a broad minimum. No anomaly can be found at $T_{hump}$, suggesting that the hump in resistivity cannot be ascribed to a magnetic transition. Figure 7 shows the susceptibility at a magnetic field of 5 T applied parallel and perpendicular to the c-axis in the case of K$_x$Fe$_2$Se$_2$-2 and Cs$_x$Fe$_2$Se$_2$, respectively. Similar behavior to that of Rb$_x$Fe$_2$Se$_2$ crystals shown in figure 6 is observed. These results indicate that although the electronic properties change dramatically from system to system and from crystal to crystal, the magnetic property does not change considerably.

Figure 8(a) shows the temperature dependence of the specific heat ($C/T$) around $T_c$ at a magnetic field of 0 T and 9 T for Rb$_x$Fe$_2$Se$_2$-2 and K$_x$Fe$_2$Se$_2$-1, respectively. At 0 T, one can see a clear specific heat anomaly at $T_c$. Although 9 T is far less than the upper critical field, which is estimated to be higher than 100 T [12, 13], the anomaly in specific heat is completely suppressed. The specific heat jump ($C(0 T) - C(9 T))/T$ against $T$ is plotted in figure 8(b) for the two crystals. The heat capacity jumps for Rb$_x$Fe$_2$Se$_2$-2 and K$_x$Fe$_2$Se$_2$-1 crystals show almost the same behavior. The clear heat capacity jump in the superconducting samples definitely indicates good bulk superconductivity in these crystals.
Figure 8. (a) The heat capacity as a function of temperature for Rb$_x$Fe$_2$Se$_2$-2 and K$_x$Fe$_2$Se$_2$-1 at a magnetic field of 0 T and 9 T applied along the c-axis. (b) The heat capacity difference between 0 T and 9 T for Rb$_x$Fe$_2$Se$_2$-2 and K$_x$Fe$_2$Se$_2$-1. A clear heat peak was observed, indicating the good bulk superconductivity.

The x-ray single-crystal diffraction patterns reveal two sets of (00$l$) reflections existing in all the crystals of A$_x$Fe$_2$Se$_2$. These two sets of reflections strongly depend on the starting composition and heating process. Although the superconducting phase is dominant, the trace of the second phase is still observed as shown in figures 3, 4(a) and 5(a). These results suggest the existence of an inhomogeneous distribution of the A atoms in all the crystals. It is found that superconductivity is closely related to the $c$-axis lattice constant, indicating that the A content is crucial to the superconductivity because the $c$-axis lattice parameter strongly depends on the A content. The A content in single crystals is quite sensitive to the nominal composition and the condition of crystal growth. Therefore, it is not easy to grow single crystals with superconductivity. The very large normal-state resistivity relative to other iron pnictide superconductors suggests a large number of deficiencies within the conducting FeSe layers for all the A$_x$Fe$_2$Se$_2$ single crystals. Indeed, from table 1, the elemental analysis shows large Fe deficiencies for all the crystals. The hump in resistivity should arise from such defects and seems to be irrelevant to superconductivity. Despite the existence of many deficiencies within the conducting FeSe layers in A$_x$Fe$_2$Se$_2$, $T_c$ does not change much on varying A from K to Rb.
and Cs. Therefore, superconductivity seems robust to such vacancies. No anomaly in magnetic susceptibility is observed at \( T_{\text{hump}} \). This suggests that the humps in resistivity in \( \text{A}_x\text{Fe}_2\text{Se}_2 \) are not related to a structural or magnetic transition, whereas the anomaly of resistivity in the underdoped FeAs-based superconductor is always relevant to a structural/magnetic transition.

In conclusion, we systematically studied the structure by using the x-ray single-crystal diffraction and measured the transport properties in \( \text{A}_x\text{Fe}_2\text{Se}_2 \) single crystals. All the samples show two sets of (00\( l \)) reflections in x-ray single-crystal diffraction patterns, indicating the intrinsically inhomogeneous distribution of intercalated A atoms. The occurrence of superconductivity is closely related to the c-axis lattice parameter, suggesting that the A content is crucial to superconductivity in \( \text{A}_x\text{Fe}_2\text{Se}_2 \). The very large magnitude of normal-state resistivity reflects a large number of deficiencies within the conducting FeSe layers, consistent with the elemental analysis results. The hump in resistivity should originate from these defects and is found to be irrelevant to superconductivity. In this sense, superconductivity is robust to vacancies within the FeSe layers. No anomaly in susceptibility is observed to be associated with the hump in resistivity. The clear jump in specific heat for \( \text{Rb}_x\text{Fe}_2\text{Se}_2 \) and \( \text{K}_x\text{Fe}_2\text{Se}_2 \) superconducting single crystals indicates good bulk superconductivity in these crystals.

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