Sustained phase separation and spin glass in Co-doped K\textsubscript{x}Fe\textsubscript{2−y}Se\textsubscript{2} single crystals

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We present Co substitution effects in K\textsubscript{x}Fe\textsubscript{2−y}Co\textsubscript{z}Se\textsubscript{2} (0.06 ≤ z ≤ 1.73) single-crystal alloys. By 3.5% of Co doping superconductivity is suppressed, whereas phase separation of semiconducting K\textsubscript{2}Fe\textsubscript{2}Se\textsubscript{2} and superconducting/metallic K\textsubscript{1}Fe\textsubscript{2}Se\textsubscript{2} is still present. We show that the arrangement and distribution of the superconducting phase (stripe phase) are connected with the arrangement of K, Fe, and Co atoms. Semiconducting spin glass is found in proximity to the superconducting state, persisting for large Co concentrations. At high Co concentrations a ferromagnetic metallic state emerges above the spin glass. This is coincident with changes of the unit cell and arrangement and connectivity of the stripe conducting phase.

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I. INTRODUCTION

Since the discovery of high-temperature Fe-based superconductivity [1], many types of Fe-based superconductors have been reported, including K\textsubscript{x}Fe\textsubscript{2−y}Se\textsubscript{2} [2,3]. Various novel phenomena were observed by chemical substitution on the Fe site. For example, Co and Ni doping in FeAs tetrahedra of LaFeAsO and BaFe\textsubscript{2}As\textsubscript{2}-based pnictides gives rise to superconductivity [4–7], whereas Co doping in FeSe suppresses superconductivity [8,9]. In particular, A\textsubscript{1}Fe\textsubscript{2−y}Se\textsubscript{2} (A = K, Cs, Rb, Tl) materials are strongly sensitive to chemical substitutions [10–12].

Among several different types of Fe-based superconductors, A\textsubscript{x}Fe\textsubscript{2−y}Se\textsubscript{2} (A = K, Cs, Rb, Tl) materials generate significant attention due to unique characteristics such as the absence of the peak in the Brillouin zone center and phase separation with the Fe-vacancy order where the crystal separates into (super)conducting stripes (block) and magnetic semiconducting matrix regions on the 0.01–100-μm scale [13–18]. The mechanism of the conducting and nonconducting states in proximity to K\textsubscript{1}Fe\textsubscript{2}Se\textsubscript{2} is of great importance for understanding superconductivity [19,20]. Consequently, the details of phase separation, phase stoichiometry, compositions, and their magnetic and electric ground states are currently being debated and are of high interest.

In this study we have investigated K\textsubscript{x}Fe\textsubscript{2−y}Co\textsubscript{z}Se\textsubscript{2} (0.06 ≤ z ≤ 1.73) single-crystal alloys, where y is a Fe/Co vacancy. A rich phase diagram is discovered, where phase-separated superconducting state of K\textsubscript{2}Fe\textsubscript{2}Se\textsubscript{2} turns into a spin glass and then into a KCo\textsubscript{0.73}Se\textsubscript{2} ferromagnetic metal with no phase separation. We show that the microstructure arrangement and connectivity are rather important for ground-state changes, in addition to changes induced by Co substitution for Fe.

II. EXPERIMENT

Single crystals of K\textsubscript{x}Fe\textsubscript{2−y}Co\textsubscript{z}Se\textsubscript{2} (0.06 ≤ z ≤ 1.73) were synthesized as described previously [21]. Plate-like crystals with size up to 10 × 10 × 3 mm\textsuperscript{3} were obtained. A high-energy medium-resolution synchrotron x-ray experiment at 300 K was conducted on the X7B beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. The setup utilized an x-ray beam 0.5 × 0.5 mm in size with a wavelength of 0.3196 Å (E = 38.7936 keV) configured with a focusing double-crystal bent Laue monochromator and a Perkin-Elmer amorphous silicon image plate detector mounted perpendicular to the primary beam path. Finely pulverized samples were packed in cylindrical polyimide capillaries 1 mm in diameter and placed 377.81 mm away from the detector. Multiple scans were performed to a total exposure time of 240 s. The two-dimensional (2D) diffraction data were integrated and converted to intensity versus θ using the software FIT2D [22]. Structural refinements were carried out using the GSAS modeling program [23] operated by the EXPGUI platform [24]. The backscattered images and energy dispersive x-ray spectroscopy (EDX) mappings were performed in a JEOL-6500 scanning electron microscope (SEM). Electrical transport, thermal transport, heat capacity, and magnetization measurements were carried out in Quantum Design PPMS-9 and MPMS-XL5. Raman scattering measurements were performed on freshly cleaved (001)-oriented samples using TriVista 557 and Jobin Yvon T64000 Raman systems in backscattering micro-Raman configuration. The 514.5-nm laser line of a mixed Ar+/Kr+ gas laser was used as an excitation source. All measurements were carried out at room temperature in the vacuum.

III. RESULTS AND DISCUSSION

The obtained high-energy synchrotron x-ray-diffraction data of the K\textsubscript{x}Fe\textsubscript{2−y}Co\textsubscript{z}Se\textsubscript{2} series [Fig. 1(a)] can be fitted very well with 14/m and 14/mmm space groups for z ≤ 0.92(4), while they are fitted by the 14/mmm space group only for z > 0.92(4). This implies coexistence of
14/m and 14/mm/m phases when $z \leq 0.92(4)$. The typical fit for a phase-separated sample with $z = 0.92(4)$ is shown in Fig. 1(b). Notably, for $0.27 \leq z \leq 0.92$ intensities of reflections characteristic of the 14/m phase become appreciably weaker and rather broad, indicative of disorder and loss of structural coherence of this structural component, as well as its presumably diminishing contribution. However, quantitative phase analysis was not feasible due to the limited resolution of the measurement and due to the diffuse nature of the signal with broad and overlapping reflections. The evolution of extracted lattice parameters with Co content is shown in Figs. 1(c) and 1(d). Lattice parameters for the a axis of the 14/mm/m space group are converted into comparable numbers for the 14/m space group using the formula $14/m = \sqrt{5} 14/mm/m$. Nonmonotonic evolution of the lattice parameters highlights the complex crystal structure and bonding in K$_{x}$Fe$_{2-y-z}$Co$_{z}$Se$_{2}$.

The surface morphologies (Fig. 2) show that the Co-doped crystals separate into two regions, a stripe- (domain-) like brighter area that is 1–2 μm thick and a darker matrix area, similar to pure K$_{x}$Fe$_{2-y}$Se$_{2}$ [17], implying that the phase separation is preserved with Co doping. Distributions of the elements of K$_{x}$Fe$_{2-y-z}$Co$_{z}$Se$_{2}$ in the samples investigated by EDX mapping are shown in Figs. 2(a)–2(c). The brighter colored area is the area covered by each element. Se is uniformly distributed for all three samples, while K, Fe, and Co display a pattern similar to the backscattered electron image. This suggests that only K, Fe, and Co elements are responsible for phase separation. It is clear that the K and Fe concentrations are lower in the stripes (domains) than in the matrix, while Co concentration is higher in the stripes than in the matrix. Hence, Co atoms prefer to enter into the stripe (domain) phase, which is consistent with the report that Co substitution strongly suppresses superconductivity [12]. The stripe- (domain-) like brighter area maintain its shape across the terraces created by the cleaving, as shown by the marked ellipses in Fig. 2. This may suggest that the stripe- (domain-) like brighter areas form a three-dimensional spider-web-like network [17].

The average stoichiometry was measured by EDX for several single crystals in the same batch with multiple measuring points. The results indicate that the crystals are homogeneous within the scale of around $1 \times 1 \times 0.5$ mm$^3$. The determined stoichiometries when fixing Se stoichiometry to 2 are shown in Table I. Defects and vacancies of Fe and Co

<table>
<thead>
<tr>
<th>Nominal composition K:Fe:Co:Se</th>
<th>Measured composition</th>
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<tbody>
<tr>
<td>K:Fe:Co:Se</td>
<td>K</td>
</tr>
<tr>
<td>1:1:8:0.2:2</td>
<td>0.79(5)</td>
</tr>
<tr>
<td>1:1:4:0:6:2</td>
<td>0.76(1)</td>
</tr>
<tr>
<td>1:1:1:2</td>
<td>0.77(2)</td>
</tr>
<tr>
<td>1:0:6:1:4:2</td>
<td>0.81(2)</td>
</tr>
<tr>
<td>1:0:2:1:8:2</td>
<td>0.78(2)</td>
</tr>
<tr>
<td>1:0:2:2</td>
<td>0.60(6)</td>
</tr>
</tbody>
</table>
increases, while the K ratio remains almost constant, similar to the ratio of Co increases, the sum of Fe and the Co ratio slightly increases, consistent with resistivity [Fig. 3(b)]. The obtained ρ values and Debye temperatures θD in KFe2−x−yCo2Se2 are listed in Table III. The Debye temperature for the KFe2−x−yCo2Se2 series are similar, suggesting that there are no considerable changes in atomic weight, structure, and bonding. A small γ value for z = 0.27(0) implies a low density of states at the Fermi level, similar to typical semiconductors, while large γ values for z > 0.92(4) suggest accumulation of the density of states, as expected in metals.

Thermoelectric power S(T) of the KFe2−y−zCo2Se2 series shows negative values for all different Co concentrations, which reveals that dominant carriers are electrons [Fig. 3(c)]. The magnitude of S(z) decreases as the Co ratio increases to around 50% [z = 0.92(4)] and saturates [inset in Fig. 3(c)]. There are no obvious peaks in the thermoelectric power for the KFe2−y−zCo2Se2 series between 2 and 350 K, suggesting that there are no dramatic Fermi surface changes.

The temperature-dependent dc magnetic susceptibilities of the KFe2−y−zCo2Se2 series show irreversible behaviors between zero-field cooling (ZFC) and field cooling (FC) at low temperature [Fig. 4(a)]. This is a typical behavior of a spin glass in magnetic field caused by the frozen magnetic spins in random directions below the characteristic temperature Tf. Insets in Figs. 4(a) and 4(b) also suggest a spin glass due to the linear field dependence of the magnetic susceptibility in random directions below the characteristic temperature Tf. Insets in Figs. 4(a) and 4(b) also suggest a spin glass due to the linear field dependence of the magnetic susceptibility in random directions below the characteristic temperature Tf.

TABLE III. Summary of ρ0 values and activation energy Ea in KFe2−y−zCo2Se2.

<table>
<thead>
<tr>
<th>z</th>
<th>ρ0 (mΩ cm)</th>
<th>Ea (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06(0)</td>
<td>24.3(4)</td>
<td>67.7(4)</td>
</tr>
<tr>
<td>0.27(0)</td>
<td>4.20(9)</td>
<td>47.1(5)</td>
</tr>
<tr>
<td>0.61(6)</td>
<td>3.07(1)</td>
<td>26.6(1)</td>
</tr>
<tr>
<td>0.92(4)</td>
<td>2.15(3)</td>
<td>21.4(3)</td>
</tr>
<tr>
<td>1.50(3)</td>
<td>0.597(7)</td>
<td>12.4(2)</td>
</tr>
</tbody>
</table>

As shown in Fig. 3(a), 3.5% of Co doping in KFe2−y−zCo2Se2 completely suppresses the superconductivity and results in a semiconducting ρ(T), consistent with previous research [12]. As Co composition increases, there is a crossover from a semiconductor to metallic state. Besides K2Co1.73(4)Se2, all other crystals are metallic below a resistivity maximum ρmax and semiconducting above ρmax, similar to KFe2−y−zCo2−zS2 [21]. The high-temperature part (above 200 K) of ρ(T) can be fitted by the thermal activation model ρ = ρ0 exp(Ea/kB T), where ρ0 is a prefactor, Ea is an activation energy, and kB is Boltzmann’s constant [Fig. 3(a)]. The obtained ρ0 and Ea are listed in Table II and are mostly smaller than values for KFe2−y−zS2 and KFe0.85Ag1.15Te2 [25,28].

The heat capacity of the KFe2−y−zCo2Se2 series also exhibits the crossover from semiconducting to metal as Co increases, consistent with resistivity [Fig. 3(b)]. C/T−T2 relations between 5 and 10 K can be fitted by the formula C/T = γ + βsT2 + βT4. The Debye temperatures are obtained from θD = (12π2N R/5β)1/3, where N is the atomic number in the chemical formula and R is the gas constant. The obtained γ values and Debye temperatures θD for different Co ratios are listed in Table III. The Debye temperature for the KFe2−y−zCo2Se2 series are similar, suggesting that there are no considerable changes in atomic weight, structure, and bonding. A small γ value for z = 0.27(0) implies a low density of states at the Fermi level, similar to typical semiconductors, while large γ values for z > 0.92(4) suggest accumulation of the density of states, as expected in metals.
ac susceptibility $\chi_{300}$ K (red open inverse triangle). (c) Temperature dependence of $M$ and $H$ (solid lines). (e) $\chi$ dependence of the real part of ac susceptibility and thermoremanent magnetization. The frequency-dependent susceptibility $\chi'(T)$ at $H = 1$ kOe in ZFC and FC below 350 K. Insets in (a) and (b) are $M-H$ curves of $K_{Fe_{2-y}Co_{y}Se_2}$ with $z = 0.61(6)$ for $H \perp c$ and $H \parallel c$, respectively, at 1.8 K (black solid inverse triangle) and 300 K (red open inverse triangle). (c) Temperature dependence of ac susceptibility $\chi'(T)$ measured at five different frequencies for $z = 0.27(0)$ of $K_{Fe_{2-y}Co_{y}Se_2}$. The inset shows the frequency dependence of $T_f$ with the linear fitting (solid line). (d) TRM vs time for $z = 0.27(0)$ of $K_{Fe_{2-y}Co_{y}Se_2}$ at 10 K and $t_w = 100$ s with different dc fields with fittings using stretched exponential function (solid lines). (e) $M_{TRM}$ vs $t$ at 10 and 150 K with $H = 1$ kOe and $t_w = 100$ s. (f) $H$-field dependence $\tau(s)$ (black solid square) and $1-n$ (red solid circle).

Confirmation of the spin glass comes from the frequency dependence of the real part of ac susceptibility and thermoremanent magnetization. The frequency-dependent susceptibility $\chi'(T)$ is shown in Fig. 4(c). As frequency increases, the characteristic temperature $T_f$ peak position increases, whereas its magnitude decreases [30]. The frequency dependence of the peak shift is fitted by $K = \Delta T_f/(T_f \Delta \log f)$ (Fig. 4), and the obtained $K$ value is 0.036(1), in agreement with the canonical spin-glass values ($0.0045 \leq K \leq 0.08$) [30]. Thermoremanent magnetization (TRM) is shown in Fig. 4(d).

The sample was cooled down from 200 K (above $T_f$) to 10 K (below $T_f$) in four different magnetic fields, then kept at 10 K for $t_w = 100$ s. After that, the magnetic field was removed, and $M_{TRM}(t)$ was measured. As observed in Fig. 4(d), $M_{TRM}(t)$ decays very slowly for all three different magnetic fields towards its nonzero equilibrium value [30]. On the other hand, $M_{TRM}(t)$ measured at 150 K (above $T_f$) relaxes quickly in a short time [less than $\sim 100$ s; Fig. 4(e)]. Slow relaxation behavior is fitted well by the stretched exponential function, $M_{TRM}(t) \sim M_0 \exp[-(t/\tau)^\alpha]$, where $M_0$, $\tau$, and $\alpha$ are the glassy component, the relaxation characteristic time, and the critical exponent, respectively. As shown in Fig. 4(f), the obtained $\tau$ increases as the $H$ field increases, whereas $1-n$ stays close to 1/3, consistent with theoretical and experimental results for a spin-glass system [31,32].

Unpolarized Raman scattering spectra of a $K_{0.6Co_{0.73}Se_2}$ single crystal measured from the (001) plane for the two sample orientations at 100 K using the Jobin Yvon T64000 Raman system. According to selection rules for the $I4/mmm$ space group, peaks at about 174 and 184 cm$^{-1}$ (at 100 K) are assigned as $B_1g$ and $A_1g$ Raman modes, respectively [33,34].

Unpolarized Raman scattering spectra of $K_{Fe_{2-y}Co_{y}Se_2}$ single crystals are presented in Fig. 5(b). For $z = 1.73(4)$ samples, only two peaks, which were assigned as $A_{1g}$ ($\sim 180$ cm$^{-1}$) and $B_{1g}$ ($\sim 169$ cm$^{-1}$) modes, can be observed in the Raman spectrum. These modes are also observed for $z = 1.50(3)$ and $z = 0.92(4)$ samples. In fact, the $A_{1g}$ mode can be observed in Raman spectra for all concentrations of cobalt, suggesting that superconducting/metalllic $K_{Fe_{2}Se_2}$ phase is present in all investigated samples. The energy of this mode does not change significantly by varying concentrations of Co or for different transition-metal ions [33,34]. For the intermediate concentration $0.61(6) \leq z \leq 1.5$ the broad structure around 250 cm$^{-1}$ has been observed, which probably originates from the crystalline disorder in the semiconducting $K_{2}Fe_{2}Se_{3}$ phase. In general, high disorder may cause relaxation of the selection rules, resulting in the appearance of broad asymmetric structures. With further decreasing the Co concentration [$z \leq 0.27(0)$], a large number of Raman modes can be clearly observed in the spectra in addition to the $A_{1g}$ mode of the superconducting/metalllic $K_{Fe_{2}Se_2}$ phase. These
FIG. 5. (Color online) (a) Raman scattering spectra of K_{0.6}Co_{1.73}Se_{2} single crystals in various scattering configurations (x = [100], y = [010], x′ = 1/\sqrt{2}[110], y′ = 1/\sqrt{2}[1\bar{1}0]). (b) Raman scattering spectra of K_{x}Fe_{2−}\_zCo_{z}Se_{2}, [0 \leq z \leq 1.73(4)] single crystals measured at room temperature from the (001) plane of the samples.

modes originate from the lattice vibrations within the ordered low-symmetry semiconducting K_{2}Fe_{4}Se_{5} phase [33,35].

The magnetic and transport phase diagram of K_{x}Fe_{2−}\_zCo_{z}Se_{2} series is presented in Fig. 6. When z ∼ 0 there is superconductivity below T_{c} ∼ 30 K and metallic resistivity below and semiconducting above about 125 K [3]. By 3.5% Co doping, not only is superconductivity completely suppressed, but so is conductivity with emerging spin-glass magnetic order below T_{f} ∼ 70 K in 1 kOe. A semiconducting/bad-metal spin glass is found in proximity to the superconducting state, similar to copper oxides. As Co concentration increases, the spin-glass state is maintained, while the semiconductor to metal crossover is present at low temperatures up to z ∼ 0.6. After that, the spin glass and metallicity decrease up to z ∼ 0.9. With a further increase in Co concentration, metallic conductivity spreads to higher temperatures, while the spin glass is suppressed to the lower-temperature region (below ∼20 K), and the ferromagnetic ground state emerges above the spin glass. K_{x}Co_{z}Se_{2} with z = 1.73(4) is a metal, consistent with previous reports [29]. We also note that ground-state changes (Fig. 6) are concurrent with lattice parameter variations. Lattice parameters a and c for 14/m show a general drop as z is increased, in contrast to lattice parameters of 14/mmm. When the ferromagnetism emerges, lattice parameter c in 14/mmm rapidly increases and is saturated, similar to the temperature dependence of the Curie temperature.

It should be noted that both metallic conductivity and the total area of brighter stripe (block) regions increase with z. This could imply that the brighter stripe (block) area is metallic, whereas the matrix is semiconducting, both with and without Co doping [36,37]. The z = 0.06(0) crystal shows semiconducting behavior through the entire temperature region we measured (1.8 K ≤ T ≤ 300 K), even though the metallic brighter stripe (block) areas are present (Fig. 2). This is most likely because the connectivity of the three-dimensional metallic stripe (block) area is insufficient to create metallic percolation in the crystal.

The composite nature of our crystals and nano- to mesoscale mix of (super)conducting and semiconducting magnetic regions may also create states at interfaces [38,39]. This somewhat complicates the physical interpretation of bulk measurements. However, since in K_{x}Fe_{2−}\_zSe_{2} nanoscale phase
IV. CONCLUSION

We have demonstrated how the structure, phase separation, transport, and magnetic property evolve with Co doping concentration in K$_2$Fe$_{2-x}$Co$_x$Se$_2$ single crystals. A rich ground-state phase diagram was discovered. By 3.5% Co doping superconductivity is suppressed, while phase separation is still present, which asserts the significance of the arrangement and connectivity of phases for superconductivity. A semiconducting spin glass was discovered in close proximity to the superconducting state in the phase diagram, similar to copper oxides. A ferromagnetic metal state emerged above ~50% Co concentration, in agreement with the structural changes. The metallicity becomes dominant as the area of stripe (block) phases increases; however, the connectivity of stripe phases may also be important for metallic conductivity.

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