Vacancy-induced nanoscale phase separation in $K_xFe_{2-y}Se_2$ single crystals evidenced by Raman scattering and powder x-ray diffraction

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(Received 7 May 2012; revised manuscript received 10 July 2012; published 6 August 2012)

PACS number(s): 78.30.–j, 74.25.—q, 61.05.cp, 61.72.jd

The recent discovery of block checkerboard antiferromagnetic order of superconducting materials $A_xFe_{2-y}Se_2$ ($A = K$, Rb, Cs, and Tl) has invoked considerable debate in the scientific community. It was shown that the appearance of antiferromagnetism is a consequence of the Fe vacancy ordering. These unique properties among the superconductors opened a question whether Fe vacancies stabilize or destroy the superconductivity. Very recently, scanning tunneling microscopy (STM) measurements, conducted on $K_xFe_{2-y}Se_2$ single crystals evidenced the presence of the nanoscale phase separation between superconducting and antiferromagnetic phases in bulk crystals.

Raman scattering (RS) measurements of $K_xFe_{2-y}Se_2$ were analyzed, to the best of our knowledge, only in Ref. 12. Single crystals of $K_xFe_{2-y}Se_2$ were grown and treated by the post-annealing and quenching technique described elsewhere in detail. Before starting the RS measurements, the samples were cleaved in order to obtain a flat and shiny (001)-plane surface. The RS measurements were performed using a TriVista 557 Raman system in backscattering micro-Raman configuration. The 514.5 nm line of an Ar$^+$/Kr$^+$ mixed gas laser was used as an excitation source. The corresponding excitation power density was less than 0.2 kW/cm$^2$. All measurements were performed in the vacuum by using a KONTI CryoVac continuous helium flow cryostat with a 0.5 mm thick window.

PXRD measurements at room temperature and 400 °C were carried out at the X16C beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. The measurements were made on the same sample, several months after preparation and the Raman experiments. The sample was sealed in a 1 mm diameter glass capillary with Si as an internal standard and dilutant, and diffraction data collected at a wavelength of 0.5612 Å from a channel-cut Si(111) monochromator and Ge(111) analyzer. PXRD results were Rietveld refined with TOPAS Academic software; see Fig. 1.

The sample’s composition was previously measured by x-ray spectroscopy in an electron microscope to be $K_{0.64(4)}Fe_{1.44(4)}Se_2$. A PXRD pattern at 400 °C refined to a single phase of composition $K_{0.72(4)}Fe_{1.60(4)}Se_2$. While the results of these two measurements differ by more than the stated uncertainty, we do not believe they are in disagreement due to possible systematic errors in both measurement techniques. The room-temperature data were analyzed as a mixture of two phases: an $I4/mmm$ phase structurally identical to the high-temperature structure, and the Fe vacancy-ordered $\sqrt{3} \times \sqrt{3}$ $I4/m$ phase. This two-phase description is in agreement with the recent STM study. A fit to a single-phase model in $I4/m$ with partial vacancy ordering is significantly worse than the two-phase model ($\chi^2 = 2.88$ vs 2.28), and can therefore be excluded. The refined composition of the sample is $K_{0.68(2)}Fe_{1.57(3)}Se_2$, in satisfactory agreement with both the high-temperature PXRD and the x-ray spectroscopy results.

DOI: 10.1103/PhysRevB.86.054503

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Unit cells for both phases are built up of interspersed FeSe slabs and nets of K, stacked along the z axis; see Fig. 2. Refined atomic positions and occupancies of both phases are listed in Table I. Note that the refined occupancy of the iron sites in the superconducting 14/m/m/m phase is unity, within its standard uncertainty. On the other hand, neither Fe site in the $\sqrt{3} \times \sqrt{3}$ 14/m phase is fully occupied.

One feature of note from the PXRD refinement (Fig. 1) is that the diffraction peaks of the 14/m/m/m phase are substantially broader than those of the 14/m phase. It is difficult to quantify the effect, because 14/m/m/m peaks overlap the strongest 14/m peaks and both phases exhibit significant anisotropic microstrain broadening; an estimate from the Scherrer equation leads to an $\approx 100$ nm.

According to symmetry considerations one can expect four Raman-active phonons for the 14/m/m/m phase and 27 Raman-active phonons for the 14/m phase. The overlap of the strongest 14/m/m/m peaks and both phases exhibit an angle $\alpha$ (-$\alpha$ for the twin domain),\textsuperscript{18} to the corresponding axes (x and y) of the 14/m/m/m phase; see Fig. 2.

In general, the intensity of a given Raman-active phonon can be expressed as $I \sim |e_i R e_i|^2$, where $e_i$ and $e_j$ are incident and scattered light polarization vectors.\textsuperscript{19} $\hat{R}$ is a Raman scattering tensor, a $3 \times 3$ complex matrix which describes the properties of the phonon with the respect to Raman scattering, expressed in the crystal principal axes basis. In order to obtain proper selection rules for 14/m/m/m and 14/m domains for the arbitrary crystal orientation (see Fig. 2), we have to transform the corresponding Raman tensors in terms of laboratory coordinate system $x_0 y_0 z_0$, $\hat{R}_{x_0 y_0 z_0} = \Phi \hat{R}^{x_0 y_0 z_0} \Phi$. When measuring the Raman intensity of a phonon with polarization vectors $e_i$ and $e_j$ along the main axes of the Raman tensor, only the absolute value of one tensor component contributes to the Raman intensity. However, in other scattering geometries, where $e_i$ and $e_j$ are not parallel to the main axes of $\hat{R}$, the relative phase difference between Raman tensor elements influences the strength of the scattering process. For our scattering configuration in which $x_0 || e_i$ and $\Theta = \angle(e_x, e_y)$, the Raman intensities for the Raman tensors represented in Table II are given by

$$
I_{A_x}(\Theta) \sim |a|^2 \cos^2 \Theta,
I_{A_y}(\Theta) \sim |a|^2 \cos^2 \Theta,
I_{B_x}(\Theta) \sim (c' \cos[\Theta + 2(\beta \pm \alpha)])^2,
I_{B_y}(\Theta) \sim |c|^2 \cos^2 (2\Theta + 2\beta).
$$

(1)

Figure 3(a) displays $I(\Theta)$ according to Eqs. (1) for one arbitrary choice of parameters with $\alpha = 27^\circ$ and $\beta = 50^\circ$. As can be
seen, modes of the $B_\gamma$ symmetry can be observed for every value of $\Theta$, whereas the ones of the $A_\gamma$ and $A_{1\gamma}$ symmetry vanish for crossed polarization configuration, independently of the crystal orientation. The $B_{1\gamma}$ reaches maximum intensity for $\Theta = -2\beta$ and vanishes for $\Theta = 90^\circ - 2\beta$. Figure 3(b) shows RS spectra of K$_x$Fe$_{2-y}$Se$_2$ single crystals measured at 85 and 270 K in parallel and crossed polarization configurations. First we will discuss the Raman modes of the high-symmetry phase 14/mmm. RS study of (Sr,K)Fe$_2$As$_2$,20 isostructural to our high symmetry phase, revealed that the $A_{1\gamma}$ and $B_{1\gamma}$ symmetry modes appear at 185 and 210 cm$^{-1}$ (at 20 K). According to this assignment the peaks at about 180 and 207 cm$^{-1}$ (at 85 K, see Fig. 3) can be identified as the $A_{1\gamma}$ and $B_{1\gamma}$ symmetry vibrations of the As and Fe atoms of the high-symmetry phase, respectively. Appearance of the $B_{1\gamma}$ mode at similar energies in both (Sr,K)Fe$_2$As$_2$ (210 cm$^{-1}$) and K$_x$Fe$_{2-y}$Se$_2$ (207 cm$^{-1}$) is expected since the lattice parameter $a$ for both crystal structures [(Sr,K)Fe$_2$As$_2$ and the 14/mmm phase of K$_x$Fe$_{2-y}$Se$_2$] are nearly the same and, as shown,20 the substitution of K for Sr does not significantly change the frequencies of Raman modes involving As and Fe atom vibrations. Replacement of the lighter As atom with the heavier Se atom at the C$_{4\alpha}$ site results only in a shift of the $A_{1\gamma}$ mode in K$_x$Fe$_{2-y}$Se$_2$ toward the lower energies (180 cm$^{-1}$), in comparison to the same mode in (Sr,K)Fe$_2$As$_2$ (185 cm$^{-1}$). The remarkable decrease of the $B_{1\gamma}$ mode relative intensity with lowering temperature can be Fe vacancy order/disorder related.

Raman modes of the lower-symmetry phase (14/m), Fig. 3(b), at 163 and 203 cm$^{-1}$ that are observed in parallel but not in crossed polarization configuration, are assigned as $A_\gamma$ symmetry modes. Three modes at about 194, 188, and 214 cm$^{-1}$, which appear for the crossed polarization configuration, are assigned as $B_\gamma$ modes.

Figure 4 shows Raman scattering spectra of K$_x$Fe$_{2-y}$Se$_2$ single crystals measured at 85 K in four different polarization configurations. A multiple peak structure has been observed for parallel polarization configuration in the low-energy region between 80 and 150 cm$^{-1}$. By comparison of this spectral region with other polarization configurations (Fig. 4) we found that this structure consists of six Raman active modes, three of which (at about 107, 123, and 134 cm$^{-1}$) are of $A_\gamma$ symmetry (blue lines in the inset of Fig. 4) and the remaining (at about

\[ \Gamma_{\text{Raman}} = A_{1\gamma}(\alpha_{\gamma},\gamma) + B_{1\gamma}(\alpha_{\gamma},\gamma) + 2E_{\gamma}(\alpha_{\gamma},\gamma) \]

\[ \Gamma_{\text{infrared}} = 2A_{\gamma}(E \parallel z) + 2E_{\gamma}(E \parallel x, E \parallel y) \]

\[ \Gamma_{\text{acoustic}} = A_\gamma + E_\gamma \]

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FIG. 4. (Color online) Raman scattering spectra of K$_x$Fe$_{2−y}$Se$_2$ single crystals measured at 85 K in parallel ($\theta = 0^\circ$), $\theta = 30^\circ$, $\theta = 60^\circ$, and cross ($\theta = 90^\circ$) polarization configuration. Inset: Analysis of the $\theta = 60^\circ$ spectra low-energy region using Lorentz lineshapes.

94, 100, and 140 cm$^{-1}$) are of $B_g$ symmetry (green lines in the inset of Fig. 4). The lowest-energy modes appear at 63 cm$^{-1}$ ($B_g$) and 67 cm$^{-1}$ ($A_g$). Analysis of the high-energy spectral region of the Raman spectra of K$_x$Fe$_{2−y}$Se$_2$ single crystals (above 230 cm$^{-1}$) showed three peaks, which we assigned as $A_g$ symmetry modes (at about 240 and 264 cm$^{-1}$) and a $B_g$ symmetry one (274 cm$^{-1}$).

Figure 5(a) shows Raman scattering spectra of K$_x$Fe$_{2−y}$Se$_2$ single crystals in the 160–225 cm$^{-1}$ spectral range measured at 85 K as a function of $\Theta_1$. The relative intensities change of the analyzed modes as a function of $\Theta_1$ are presented in Fig. 5(b). The solid lines represent calculated spectra by using Eqs. (1) with one consistent set of parameters with the angle $\beta = 47(5)^\circ$, which confirms the supposed orientation of the sample (see the caption of Fig. 3). When analyzing the $B_g$ mode relative intensity angular dependence, one must have in mind that $A_{4g}$ domains with the orientation $\alpha$ and $−\alpha$ appear with the same probability in the sample and both contribution must be taken into account. Analysis of the $A_{1g}$ and $B_{1g}$ modes’ relative intensity angular dependences [Fig. 5(b)] also confirmed our previous assignment about the two-phase nature of the K$_x$Fe$_{2−y}$Se$_2$ sample. Analysis of the 194 and 214 cm$^{-1}$ modes’ relative intensities (denoted as $B_6^g$ and $B_7^g$) confirmed the $B_g$ nature of these modes. Additionally, we found that the angle between principal axes of the $I_{4}^{m}$ and $I_{4}^{m}$ phases, in the (001) plane is about $\alpha = 29(6)^\circ$, which is in agreement with the expected value of $\sim 26.6^\circ$ for the $\sqrt{5} \times \sqrt{5}$ modulation.

In conclusion, Raman scattering was used to determine the influence of vacancy ordering on phonon spectra of K$_x$Fe$_{2−y}$Se$_2$ single crystals. Polarized Raman spectra were analyzed in terms of peculiarities of both $I_{4}^{m}$ and $I_{4}^{mmm}$ symmetries. We have observed (at 85 K) 8$A_g$ (67, 107, 123, 134, 163, 203, 240, and 264 cm$^{-1}$) and 8$B_g$ (63, 94, 100, 140, 188, 194, 214, and 274 cm$^{-1}$) modes originating from the vibrations of the $I_{4}^{m}$ phase and $A_{1g}$ (180 cm$^{-1}$) and $B_{1g}$ (207 cm$^{-1}$) modes originating from the vibrations of the $I_{4}^{mmm}$ phase. This confirmed the two-phase nature of K$_x$Fe$_{2−y}$Se$_2$ sample. The structural refinement of the PXRD data of K$_x$Fe$_{2−y}$Se$_2$ crystals confirmed the two-phase nature of the sample, as well as the fact that the Fe sites in the high-symmetry superconducting $I_{4}^{mmm}$ phase are fully occupied, whereas there is a substantial density of Fe vacancies in the $\sqrt{5} \times \sqrt{5}$ $I_{4}^{m}$ phase.

This work was supported by the Serbian Ministry of Education and Science under Projects No. ON171032 and 054503-4.
No. III45018. Work at Brookhaven is supported by the US Department of Energy (DOE) under Contract No. DE-AC02-98CH10886 (M.A. and E.S.B.) and in part by the Center for Emergent Superconductivity, an Energy Frontier Research Center funded by the DOE Office for Basic Energy Science (H.L. and C.P.).