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

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Polarized Raman scattering spectra of $K_xFe_{2-y}Se_2$ were analyzed in terms of peculiarities of both $I4/m$ and $I4/mmm$ space group symmetries. The presence of the Raman active modes from both space group symmetries (16 Raman-active modes of $I4/m$ and two Raman-active modes of $I4/mmm$ phase) confirmed the existence of two crystallographic domains with different space group symmetry in a $K_xFe_{2-y}Se_2$ sample. High resolution synchrotron powder x-ray diffraction structural refinement of the same sample confirmed the two-phase description, and determined the atomic positions and occupancies for both domains.

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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.¹⁻⁶ It was shown that the appearance of antiferromagnetism is a consequence of the Fe vacancy ordering.^{7,8} These unique properties among the superconductors opened a question whether Fe vacancies stabilize or destroy the superconductivity. Very recently, scanning tunneling microscopy (STM) measurements,⁹ conducted on $K_xFe_{2-y}Se_2$ thin films grown by molecular beam epitaxy revealed that the $K_xFe_{2-y}Se_2$ sample contains two distinct phases: an insulating phase with well-defined $\sqrt{5} \times \sqrt{5}$ order of Fe vacancies, and a superconducting KFe_2Se_2 phase containing no Fe vacancies. It was found that the presence of a single Fe vacancy locally destroys superconductivity.⁹ Recent ARPES/optical measurements combined with TEM analysis^{10,11} also show 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. Zhang *et al.*¹² performed partial assignment, 11 out of 18 Raman-active modes predicted by factor-group analysis (FGA) within the $I4/m$ symmetry group. They found that only one mode around 180 cm^{-1} exhibits a change in frequency around T_c . However, the origin of this mode remained unclear.

In this paper, RS is used to determine the influence of vacancy ordering on phonon spectra of $K_xFe_{2-y}Se_2$ single crystals. The polarized Raman spectra were analyzed in terms of peculiarities of both the $I4/m$ and $I4/mmm$ space group symmetries. 16 out of 18 Raman-active phonons of the $I4/m$ and two Raman-active phonons of the $I4/mmm$ phase, predicted by FGA for our measurement configuration, have been observed and assigned. This confirms the existence of two crystallographic do-

main in our sample. High resolution powder x-ray diffraction (PXRD) measurements on the same sample also indicate that the sample has coexisting $I4/m$ and $I4/mmm$ regions.

Single crystals of $K_xFe_{2-y}Se_2$ were grown and treated by the post-annealing and quenching technique described elsewhere in detail.^{13,14} 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 KONTI CryoVac continuous helium flow cryostat with 0.5 mm thick window.

PXRD measurements at room temperature and 400 °C were carried out at 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 results¹⁵ were Rietveld-refined with TOPAS-Academic software;¹⁶ see Fig. 1.

The sample's composition was previously measured by x-ray spectroscopy in an electron microscope to be $K_{0.64(4)}Fe_{1.44(4)}Se_2$.¹⁷ 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

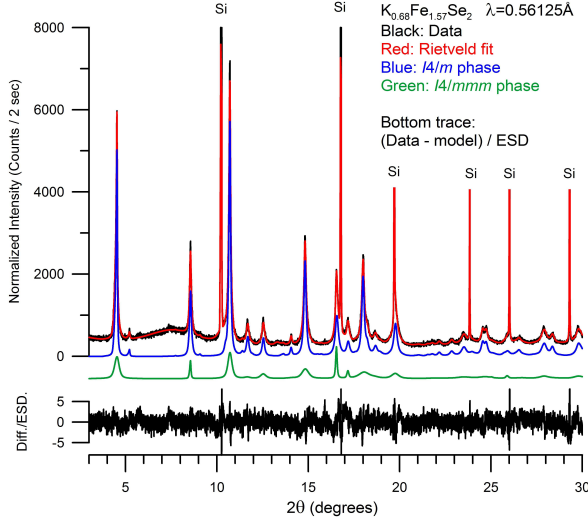


FIG. 1. (Color online) PXRd diffraction data with Rietveld fit, showing separate contributions from $I4/m$ and $I4/mmm$ phases. Peaks from Si internal standard, both main plot and scaled difference curve, are truncated. This fit has weighted R factor $R_{WP} = 5.90\%$, $\chi^2 = 2.28$.

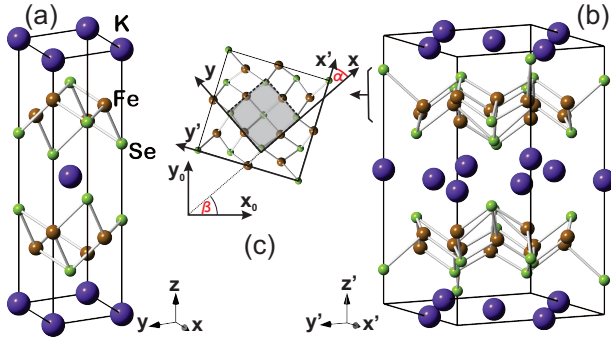


FIG. 2. (Color online) Crystal structure of $K_xFe_{2-y}Se_2$ in (a) $I4/mmm$ and (b) $I4/m$ unit cell (black lines). (c) FeSe slab in (001) plane. The solid line illustrates $I4/m$ unit cell and the shaded square illustrates $I4/mmm$ unit cell.

$I4/mmm$ phase structurally identical to the high temperature structure, and the Fe vacancy-ordered $\sqrt{5} \times \sqrt{5}$ $I4/m$ phase. This two-phase description is in agreement with the recent STM study.⁹ 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.

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 $I4/mmm$ phase is unity, within its standard uncertainty. On the

TABLE I. Structural parameters for $K_xFe_{2-y}Se_2$ two-phase powder sample at room temperature. Standard uncertainties given in parentheses are derived from counting statistics, and are generally smaller than plausible estimates of accuracy.

Phase I					
Space Group $I4/mmm$					
Lattice $a=3.898(1)$ Å, $c=14.091(4)$ Å					
MoleFraction 19(1)%					
Atom	site	x	y	z	Occ
K	2a	0	0	0	0.82(4)
Fe	4d	0	0.5	0.25	0.99(3)
Se	4e	0	0	0.354(1)	1
Phase II					
Space Group $I4/m$					
Lattice $a=8.703(3)$ Å, $c=14.160(1)$ Å					
Mole Fraction 81(1)%					
Atom	site	x	y	z	Occ
K1	2b	0	0	0.5	1.00(6)
K2	8h	0.583(4)	0.242(2)	0.5	0.56(2)
Fe1	16i	0.296(1)	0.596(1)	0.247(1)	0.84(1)
Fe2	4d	0	0.5	0.25	0.33(2)
Se1	4e	0	0	0.139(1)	1
Se2	16i	-0.089(1)	0.302(1)	0.353(1)	1

other hand, neither Fe site in the $\sqrt{5} \times \sqrt{5}$ $I4/m$ phase is fully occupied.

One feature of note from the PXRd refinement (Fig. 1) is that the diffraction peaks of the $I4/mmm$ phase are substantially broader than those of the $I4/m$ phase. It is difficult to quantify the effect, because $I4/mmm$ peaks overlap the strongest $I4/m$ peaks and both phases exhibit significant anisotropic microstrain broadening; an estimate from the Scherrer equation leads to an $I4/mmm$ domain size on the order of 100 nm.

According to symmetry considerations one can expect four Raman-active phonons for $I4/mmm$ and 27 Raman-active phonons for $I4/m$ phase (Table II). When Raman scattering is measured at the (001) plane of the $K_xFe_{2-y}Se_2$ sample, two Raman-active phonons ($A_{1g}+B_{1g}$) of the $I4/mmm$ phase and 18 Raman-active phonons ($9A_g+9B_g$) of the $I4/m$ phase, can be observed. Here, one must have in mind that the x' and y' axes of the $I4/m$ phase are rotated by an angle α ($-\alpha$ for the twin domain),¹⁸ to the corresponding axes (x and y) of the $I4/mmm$ phase, see Fig. 2.

In general, the intensity of a given Raman-active phonon can be expressed as $I \sim |\mathbf{e}_s \hat{R} \mathbf{e}_i|^2$, where \mathbf{e}_i and \mathbf{e}_s are incident and scattered light polarization vectors.¹⁹ \hat{R} is Raman scattering tensor, a 3×3 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 $I4/mmm$ and $I4/m$ domains for the arbitrary crystal orientation (see Fig 2), we have to transform the corresponding Raman tensors in terms of laboratory coordinate system $\mathbf{x}_0\mathbf{y}_0\mathbf{z}_0$, $\hat{R}^{x_0y_0z_0} = \Phi \hat{R}^{xyz} \Phi$. When measuring the Raman intensity of a phonon with polarization vectors \mathbf{e}_s and \mathbf{e}_i along the main axes of the Raman

TABLE II. Top panel gives the type of atoms together with their site symmetries, each site contributions to the Γ point phonons as well as Raman tensors, phonon activities and selection rules for both $I4/mmm$ and $I4/m$ phases.

$I4/mmm$ (D_{4h}^{17} and $Z^B=1$)		$I4/m$ (C_{4h}^5 and $Z^B=5$)	
Atoms (Site symmetry)	Irreducible representations	Atoms (Site symmetry)	Irreducible representations
K (D_{4h})	$A_{2u}+E_u$	K1 (C_{4h})	A_u+E_u
Fe (D_{2d})	$A_{2u}+B_{1g}+E_g+E_u$	K2 (C_s)	$2A_g+A_u+2B_g+B_u+E_g+2E_u$
Se (C_{4v})	$A_{1g}+A_{2u}+E_g+E_u$	Fe1 (C_1)	$3A_g+3A_u+3B_g+3B_u+3E_g+3E_u$
		Fe2 (S_4)	$A_u+B_g+E_g+E_u$
		Se1 (C_4)	$A_g+A_u+E_g+E_u$
		Se2 (C_1)	$3A_g+3A_u+3B_g+3B_u+3E_g+3E_u$
Raman tensors			
$\hat{R}_{A_{1g}}^{xyz} = \begin{pmatrix} a e^{i\varphi_a} & 0 & 0 \\ 0 & a e^{i\varphi_a} & 0 \\ 0 & 0 & b e^{i\varphi_b} \end{pmatrix}$	$\hat{R}_{B_{1g}}^{xyz} = \begin{pmatrix} c e^{i\varphi_c} & 0 & 0 \\ 0 & - c e^{i\varphi_c} & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\hat{R}_{A_g}^{x'y'z} = \begin{pmatrix} a' e^{i\varphi'_a} & 0 & 0 \\ 0 & a' e^{i\varphi'_a} & 0 \\ 0 & 0 & b' e^{i\varphi'_b} \end{pmatrix}$	$\hat{R}_{B_g}^{x'y'z} = \begin{pmatrix} c' e^{i\varphi'_c} & d' e^{i\varphi'_d} & 0 \\ d' e^{i\varphi'_d} & - c' e^{i\varphi'_c} & 0 \\ 0 & 0 & 0 \end{pmatrix}$
Activity and selection rules			
$\Gamma_{Raman} = A_{1g}(\alpha_{xx}+\alpha_{yy}, \alpha_{zz}) + B_{1g}(\alpha_{xx}-\alpha_{yy}) + 2E_g(\alpha_{xz}, \alpha_{yz})$		$\Gamma_{Raman} = 9A_g(\alpha_{x'x'}+\alpha_{y'y'}, \alpha_{zz}) + 9B_g(\alpha_{x'x'}-\alpha_{y'y'}, \alpha_{x'y'}) + 9E_g(\alpha_{x'z}, \alpha_{y'z})$	
$\Gamma_{infrared} = 2A_{2u}(\mathbf{E} \mathbf{z}) + 2E_u(\mathbf{E} \mathbf{x}, \mathbf{E} \mathbf{y})$		$\Gamma_{infrared} = 9A_u(\mathbf{E} \mathbf{z}) + 7B_u(\text{silent}) + 10E_u(\mathbf{E} \mathbf{x}, \mathbf{E} \mathbf{y})$	
$\Gamma_{acoustic} = A_u + E_u$		$\Gamma_{acoustic} = A_u + E_u$	

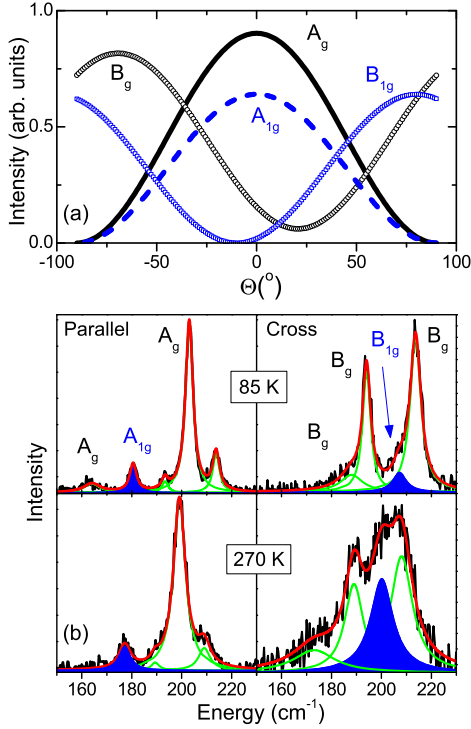


FIG. 3. (Color online) (a) Raman intensity angular dependencies of A_g , B_g , A_{1g} and B_{1g} modes for arbitrary parameters in the single domain case. (b) Raman scattering spectra of $K_xFe_{2-y}Se_2$ single crystals measured in parallel and crossed polarization configurations. Sample was orientated so that $\mathbf{e}_s \parallel 1/\sqrt{2}[1, 1, 0]$ of the $I4/mmm$.

tensor only the absolute value of one tensor component contributes to the Raman intensity. However, in other scattering geometries, where \mathbf{e}_s and \mathbf{e}_i 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 $\mathbf{x}_0 \parallel \mathbf{e}_s$ and $\Theta = \angle(\mathbf{e}_s, \mathbf{e}_i)$, the Raman intensities

for the Raman tensors represented in Table II are given by:

$$\begin{aligned}
 I_{A_g}(\theta) &\sim |a'|^2 \cos^2 \theta & I_{A_{1g}}(\theta) &\sim |a|^2 \cos^2 \theta \\
 I_{B_g}(\theta) &\sim (c' \cos(\theta + 2(\beta \pm \alpha)) + d' \sin(\theta + 2(\beta \pm \alpha)))^2 \\
 I_{B_{1g}}(\theta) &\sim |c|^2 \cos^2(\theta + 2\beta).
 \end{aligned}
 \tag{1}$$

Fig. 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_g symmetry can be observed for every value of Θ , whereas the ones of the A_g and A_{1g} symmetry vanish for crossed polarization configuration, independently of the crystal orientation. The B_{1g} reaches maximum intensity for $\Theta = -2\beta$ and vanishes for $\Theta = 90^\circ - 2\beta$.

Fig. 3 (b) shows RS spectra of $K_xFe_{2-y}Se_2$ single crystals measured at 85 K and 270 K in parallel and crossed polarization configuration. First we will discuss the Raman modes of the high symmetry phase $I4/mmm$. RS study of $(Sr,K)Fe_2As_2$,²⁰ isostructural to our high symmetry phase, revealed that the A_{1g} and B_{1g} 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_{1g} and B_{1g} symmetry vibrations of the As and Fe atoms of the high symmetry phase, respectively. Appearance of the B_{1g} mode at similar energies in both $(Sr,K)Fe_2As_2$ (210 cm^{-1}) and $K_xFe_{2-y}Se_2$ (207 cm^{-1}) is expected since the lattice parameter a for both crystal structures ($(Sr,K)Fe_2As_2$ and $I4/mmm$ phase of $K_xFe_{2-y}Se_2$) 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 atoms vibrations. Replacement of lighter As atom with heavier Se atom at the C_{4v} site results only in a shift of the A_{1g} mode in $K_xFe_{2-y}Se_2$ towards the lower energies (180 cm^{-1}), in comparison to the same mode in $(Sr,K)Fe_2As_2$ (185 cm^{-1}). Remarkable decrease of the B_{1g} mode relative intensity with lowering temperature, can be Fe va-

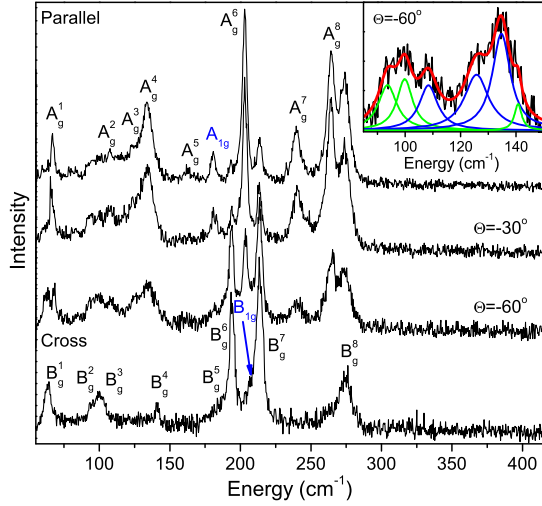


FIG. 4. (Color online) Raman scattering spectra of $K_xFe_{2-y}Se_2$ single crystals measured at 85 K in parallel ($\theta = 0^\circ$), $\theta = 30^\circ$, $\theta = 60^\circ$ and cross ($\theta = 90^\circ$) polarization configuration. Inset: Analysis of the $\theta = 60^\circ$ spectra low energy region using Lorentz lineshapes.

cancy order/disorder related.

Raman modes of the lower symmetry phase ($I4/m$), Fig. 3 (b), at 163 and 203 cm^{-1} that are observed in parallel but not in crossed polarization configuration, are assigned as A_g symmetry modes. Three modes at about 194, 188 and 214 cm^{-1} , which appear for crossed polarization configuration, are assigned as B_g modes.

Fig. 4 shows Raman scattering spectra of $K_xFe_{2-y}Se_2$ 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 out of six Raman active modes, three of which (at about 107, 123 and 134 cm^{-1}) are of the A_g symmetry (blue lines at the inset Fig. 4) and the remaining (at about 94, 100 and 140 cm^{-1}) are of the B_g symmetry (green lines at 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 $K_xFe_{2-y}Se_2$ single crystals (above 230 cm^{-1}) showed three peaks, which we assigned as A_g symmetry modes (at about 240 cm^{-1} and 264 cm^{-1}) and the B_g symmetry one (274 cm^{-1}).

Fig. 5 (a) shows Raman scattering spectra of $K_xFe_{2-y}Se_2$ single crystals in the 160-225 cm^{-1} spectral range measured at 85 K as a function of Θ . The relative intensities change of the analyzed modes as a function of Θ are presented in Fig. 5 (b). Solid line represent calculated spectra by using Eqs. (1) with one consistent set of parameters with the angle $\beta = 47(5)^\circ$, which confirms supposed orientation of the sample (see Caption Fig. 3). When analyzing the B_g mode relative intensity angular dependence, one must have in mind that $I4/m$

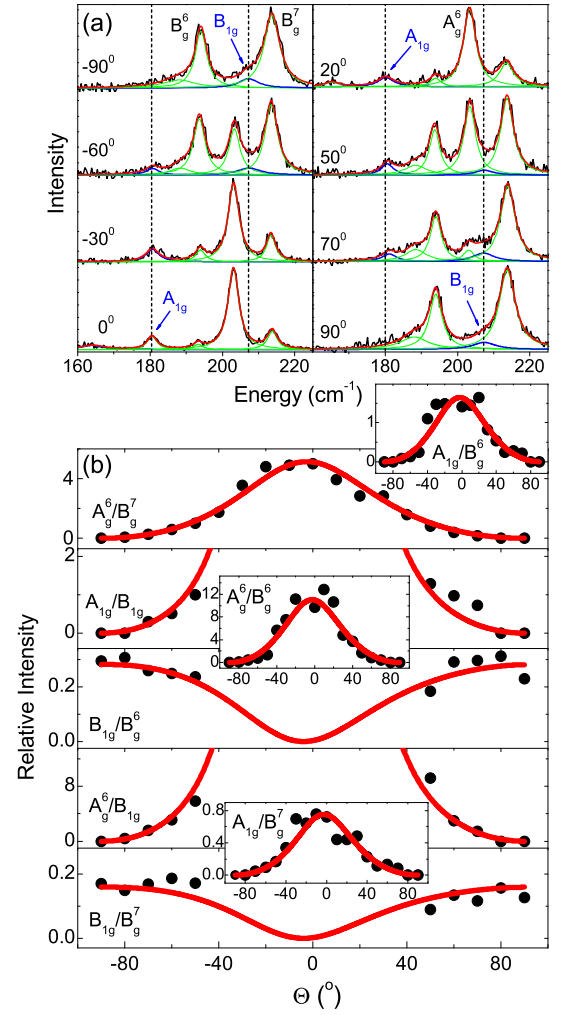


FIG. 5. (Color online)(a) Raman scattering spectra of $K_xFe_{2-y}Se_2$ single crystals measured at 85 K as a function of Θ . (b) Relative intensities of the Raman active modes as a function of Θ .

domains with the orientation α 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} mode relative intensity angular dependence (Fig. 5 (b)) also confirmed our previous assignment, about the two phase nature of the $K_xFe_{2-y}Se_2$ sample. Analysis of the 194 and 214 cm^{-1} modes relative intensity (denoted as B_g^6 and B_g^7) confirmed the B_g nature of these modes. Additionally, we found that the angle between principal axes of the $I4/mmm$ and $I4/m$ phase domains 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 $K_xFe_{2-y}Se_2$ single crystals. Polarized Raman spectra were analyzed in terms of peculiarities of both $I4/m$ and $I4/mmm$ symmetries. We have observed (at 85 K) $8A_g$ (67, 107, 123, 134, 163, 203, 240 and 264 cm^{-1}) and $8B_g$

(63, 94, 100, 140, 188, 194, 214 and 274 cm^{-1}) modes originating from the vibrations of the $I4/m$ phase and A_{1g} (180 cm^{-1}) and B_{1g} (207 cm^{-1}) modes originating from the vibrations of the $I4/mmm$ phase. This confirmed the two-phase nature of $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$ sample. The structural refinement of the PXRD data of $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$ crystals confirmed the two-phase nature of the sample, as well as the fact that the Fe sites in the high symmetry superconducting $I4/mmm$ phase are fully occupied,

whereas there is a substantial density of Fe vacancies in the $\sqrt{5} \times \sqrt{5}$ $I4/m$ phase.

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