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# Structural phase transition below 250 K in superconducting $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$

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Vibrational properties of iron-chalcogenide superconductor  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$  with  $T_c \sim 30$  K have been measured by Raman and optical spectroscopies over temperature range of 3-300 K. Sample undergoes  $I4/m \rightarrow I4$  structural phase transition accompanied by loss of inversion symmetry at  $T_1$ , below 250 K, observed as appearance of new fully-symmetric Raman mode at  $\sim 165 \text{ cm}^{-1}$ . Small vibration mode anomalies are also observed at  $T_2 \sim 160$  K. From first-principles vibrational analysis of antiferromagnetic  $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$  utilizing pseudopotentials all observed Raman and infrared modes have been assigned and the displacement patterns of the new Raman mode identified as involving predominantly the Se atoms.

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## I. INTRODUCTION

Discovery of high- $T_c$  superconductivity in iron-based chalcogenides  $\text{A}_y\text{Fe}_{1.6+x}\text{Se}_2$  ( $\text{A}=\text{K}, \text{Rb}, \text{Cs}, \text{ and } \text{Tl}$ ) Ref. [1] raised considerable attention since the materials exhibit unusual physical properties. Parent compound ( $y=1, x=0$ ) is an insulator,<sup>2,3</sup> crystalizes into  $\sqrt{5}x\sqrt{5}x1$   $I4/m$  Fe vacancy-ordering structure, and exhibits antiferromagnetic (AFM) order below a Neél temperature of  $\sim 560$  K Ref.[4]. Doping with alkaline metals or Tl ( $y < 1$ ) apparently preserves the Fe vacancy-ordering and give rise to superconductivity in samples with close to 2:4:5 stoichiometry<sup>5</sup>. Early transport<sup>2</sup> and neutron diffraction<sup>4</sup> studies suggested that the superconductivity coexists with AFM order. Alternatively, the doping is discussed in terms of microscopic phase separation<sup>6-10</sup>: a mixture of vacancy-ordered AFM insulating phase and superconducting phase (SC). Due to recent experimental evidences<sup>11-14</sup> the consensus seems emerge: the AFM and SC phases are specially separated, the AFM phase occupies from  $\sim 80$  Ref. [11] to 95 % Ref. [12] of the sample volume, and SC phase is homogeneous and does not contains Fe-vacancies nor magnetic moments.<sup>12-14</sup>

Raman scattering study of superconducting  $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$  observed at least 13 phonon modes<sup>15</sup>. The crystal symmetry of sample was determined as  $C_{4h}$  or lower. Zhang *et al.* performed LDA vibration analysis of nonmagnetic  $I4/m$   $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$  phase and assigned majority of observed Raman modes. The vibrational properties  $\text{K}_{0.88}\text{Fe}_{1.63}\text{S}_2$  isostructural to  $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$  confirmed Fe-vacancy ordering: 14 Raman active modes predicted by factor-group analysis were observed and assigned. The authors concluded that the phonon energies in the range of 80-300 K are driven by anharmonicity effects without any signatures of electron-phonon interaction<sup>16</sup>. Impact of iron and potassium composition on Raman vibration spectra of  $\text{A}_{0.8}\text{Fe}_{1.6}\text{Se}_2$  ( $\text{A}=\text{K}, \text{Rb}, \text{ and } \text{Tl}$ ) was presented in Ref. [17].

The optical studies to date showed at least ten IR-active modes at low temperatures.<sup>18,19</sup> The in-plane optical conductivity of ( $T_c = 31$  K) is incoherent at 300 K, dominated by IR-active modes and high-frequency excitations<sup>19</sup>, but become coherent just above the  $T_c$ . Small carrier concentration

prompted authors<sup>10,19</sup> to suggest that the global superconductivity is due to Josephson coupling of nanoscale-sized superconducting phase in the AFM ordered insulating phase.

In this paper we report on Raman scattering and *ab*-plain optical conductivity studies of superconducting  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$  ( $T_c \sim 30$  K) in the  $T$ -range from 3 to 300 K. At least 19 Raman-active and 12 IR-active modes are observed at 3 K. The  $\sim 136, 143, 242, \text{ and } 277 \text{ cm}^{-1}$  Raman and  $\sim 208 \text{ cm}^{-1}$  IR mode exhibit Fano-like shape. The Raman Fano modes are due the vibration coupling to AFM spin fluctuations, while the IR- mode is coupled to charge carriers in low-frequency part of optical conductivity. Raman phonon linewidth contains approximately equal contributions of two-phonon lattice anharmonicity on one hand and bare self-energy and broadening due to intrinsic defects on the other hand, except for the  $\sim 100 \text{ cm}^{-1}$  mode dominated by inhomogeneous broadening. We show that  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$  undergoes  $I4/m \rightarrow I4$  structural phase transition at  $T_1$  below 250 K. Several modes which are not Raman- and IR-active in the measured geometry in  $I4/m$  become clearly visible in  $I4$  phase. Symmetry of the Se-Fe slab is broken at  $T_1$ . At  $T_2 \sim 160$  K Raman vibration modes exhibit weak anomalies seen as small discontinuity of vibration frequencies and change in vibration intensity vs temperature dependencies. Raman vibration intensities of a few modes increases between  $T_1$  and  $T_2$ , saturating above the  $T_2$ , except for three modes dominated by *c*-axis atomic displacements: *c*-axis structural distortions within the slab appear to build up on cooling down to 3 K. The low-frequency optical conductivity displays weak temperature dependence above  $T_1$  followed by faster increase below the  $T_2$ .

## II. EXPERIMENTAL

The crystal of iron-chalcogenide superconductors were grown by a self-melting method with nominal concentration of 0.8:2.1:2.0 (K:Fe:Se). The actual chemical composition was determined by EDXS as  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$  (KFS). Two-step transitions were seen in resistivity curve<sup>10</sup>, a sharp drop at 42 K is followed by a major superconducting transition with

$T_c \sim 30$  K. Further details of sample characterization can be found elsewhere.<sup>10</sup>

KFS crystals were never exposed to air. Sealed vial was open under 99.999%  $N_2$ , crystal removed and glued on replaceable copper sample holder of a helium Oxford Instruments cryostat, dried and cleaved along the  $ab$ -plane, transferred to the He-flow cryostat, and quickly cooled below water freezing temperature. Raman data were obtained on two single crystals. Data presented in this paper refer to the sample with more detail temperature dependence records. It is worth mentioning that results obtained on the second sample are consistent with findings reported here.

Raman spectra were excited with  $Kr^+$  laser line of  $\lambda = 647.1$  nm ( $E = 1.92$  eV) with less than 10 mW of incident laser power focused into a spot of  $\sim 50 \times 100 \mu m^2$  on the freshly cleaved  $ab$ -plane crystal surface. The scattered light collected close to the backscattered geometry was focused to a  $100 \times 240 \mu m^2$  entrance slits of a custom triple-stage spectrometer equipped with 1800 lines/mm gratings. The instrumental resolution was  $\sim 1.4$   $cm^{-1}$ . To record symmetry resolved Raman spectra we employed circularly polarized light with the optical configurations selecting either the same or opposite chirality for incident and scattered light. The former is referred to as right-right (RR) and the latter as to right-left (RL) configurations. For the  $C_{4h}$  point group the  $B_g$  ( $A_g$ ) symmetry is probed in the RL (RR) scattering geometry. Temperature dependent Raman spectra were collected at 3, 45, 100, 150, 160, 180, 200, 260, and 300 K with  $T$ -stability better than 0.1 K. An estimated local heating in the laser spot did not exceed 4 K.

Optical measurements were done by Bruker Vertex 80v spectrometer in the frequency range from 25 to 10000  $cm^{-1}$ . The sample was under vacuum of  $2 \times 10^{-5}$  Pa. An in-situ gold and aluminum over-coating technique was used to get the reflectance  $R(\omega)$  for light polarized in the KFS ( $ab$ )-planes. The real part of conductivity  $\sigma_1(\omega)$  was obtained by the Kramers-Kronig transformation of the  $R(\omega)$ . Optical spectra were collected at 8, 35, 170, and 300 K.

### III. RESULTS

$K_{0.8}Fe_{1.6}Se_2$  crystallizes into tetragonal structure  $I4/m$  (space group #87) Ref. [4], resulting in the irreducible vibrational representation:

$$\Gamma_{vib} = 9A_g \oplus 8B_g \oplus 8E_g \oplus 9A_u \oplus 7B_u \oplus 10E_u \quad (1)$$

All  $g$ -modes are Raman active, but only the  $A_g$  and  $B_g$  are selected with RR and RL polarizations under the measured geometry. The  $A_u$  and  $E_u$  vibrations are infrared active along the  $c$ -axis and in the  $ab$ -plane. The  $B_u$  modes are silent. The Fe(1)-vacancy related vibration modes are excluded. Throughout this paper we adopted commonly used site designation: K(1), K(2), Fe(1), Fe(2), Se(1) and Se(2) stand, respectively, for Wyckoff positions of  $2a$ ,  $8h$ ,  $4d$ ,  $16i$ ,  $4e$ , and  $16i$ , refer to a legend of Fig.1.

Raman spectra of  $K_{0.75}Fe_{1.75}Se_2$  are shown in Fig 1(a) and 1(b) for RL and RR polarizations, respectively. At 300 K,

at least 7(9) modes are observed in RL (RR) in good agreement with  $9A_g + 8B_g$  expected in the  $I4/m \sqrt{5} \times \sqrt{5}$  cell of  $K_{0.8}Fe_{1.6}Se_2$ <sup>15</sup>. The  $A_g$  modes at  $\sim 112$  and  $267$   $cm^{-1}$  are dominated by both chiral and breathing displacements of K(2) and Fe(2) atoms, respectively, Fig. 1(d,e). Below 200 K new modes appear (marked with red arrows): at  $\sim 201$   $cm^{-1}$  in RL and at  $\sim 165$  and  $\sim 211$   $cm^{-1}$  in the RR. The  $\sim 136$  and  $\sim 277$   $cm^{-1}$  phonons in the RL and  $\sim 144$  and  $\sim 242$   $cm^{-1}$  phonons in RR exhibit Fano shapes in whole temperature range of this study. The Fano modes become more symmetric with temperature decrease. Phonon modes parameters are derived from least square fit to experimental data and are summarized in Table I.

Low-frequency region of optical conductivity adopted from Fig. 2 in Ref. [10] is shown in Fig 1(c). In agreement with previous studies<sup>10,19</sup>,  $\sigma_1(\omega)$  is small (characteristic of a poor metal) and it is dominated by the infrared-active vibrations and interband features at higher energies. At 170 and 300 K 9 IR-active modes are observed. The  $\sim 208$   $cm^{-1}$  mode exhibits a Fano-like shape, becoming more asymmetric on cooling. At 170 K and below, at least three new modes (red arrows) are formed, Fig. 1(c). An inspection of the Table I revealed that Raman and IR modes reported in this work do not overlap. It's therefore tempting to conclude that inversion symmetry is preserved. In Section IV we argue that inversion symmetry is actually broken below  $T_1 \sim 250$  K. The conductivity displays relatively weak temperature dependence above 170 K followed by about two-fold increase of the continuum as temperature drops from 170 to 35 K. In agreement with previous studies<sup>18,19</sup>, a Drude-like peak is seen in 35 K data, shortly before sample becomes superconducting.

#### A. First-principles phonon modes analysis

We performed first-principles density functional theory (DFT) calculations using local density approximation (LDA) with Perdew Zunger (PZ) parameterization for the exchange-correlation energy functional as implemented in *Quantum Espresso* simulation package<sup>20</sup>. We used ultrasoft pseudopotentials<sup>21</sup> for K, Fe and norm-conserving pseudopotential<sup>22</sup> for Se to describe the interaction between the ionic cores and the valence electrons. The pseudopotentials include 9 valence electrons for K ( $3s^2, 3p^6, 4s^2$ ), 16 for Fe ( $3s^2, 3p^6, 3d^6, 4s^2$ ), and 6 for Se ( $4s^2, 4p^4$ ) atoms. We used a plane wave basis with energy cutoff of 40 Ry for wave function and 360 Ry for the charge density and a  $6 \times 6 \times 4$  Monkhorst Pack<sup>23</sup>  $k$ -point mesh for the Brillouin zone (BZ) integration.

We optimized structure of  $K_{0.8}Fe_{1.6}Se_2$  with a four spin cluster AFM ordering as discussed by Bao *et al.*<sup>4</sup> using experimental lattice constants obtained at 11 K. The calculation was done using a primitive unit cell of 22 atoms with K(1) and Fe(1) vacancies at  $2a$  and  $4b$  Wyckoff sites of space group  $I4/m$  respectively. Structural optimization is carried through minimization of energy using Hellman-Feynman forces at each atoms in Broyden-Fletcher-Goldfarb-Shanno scheme. The optimized structure shows a very good agree-

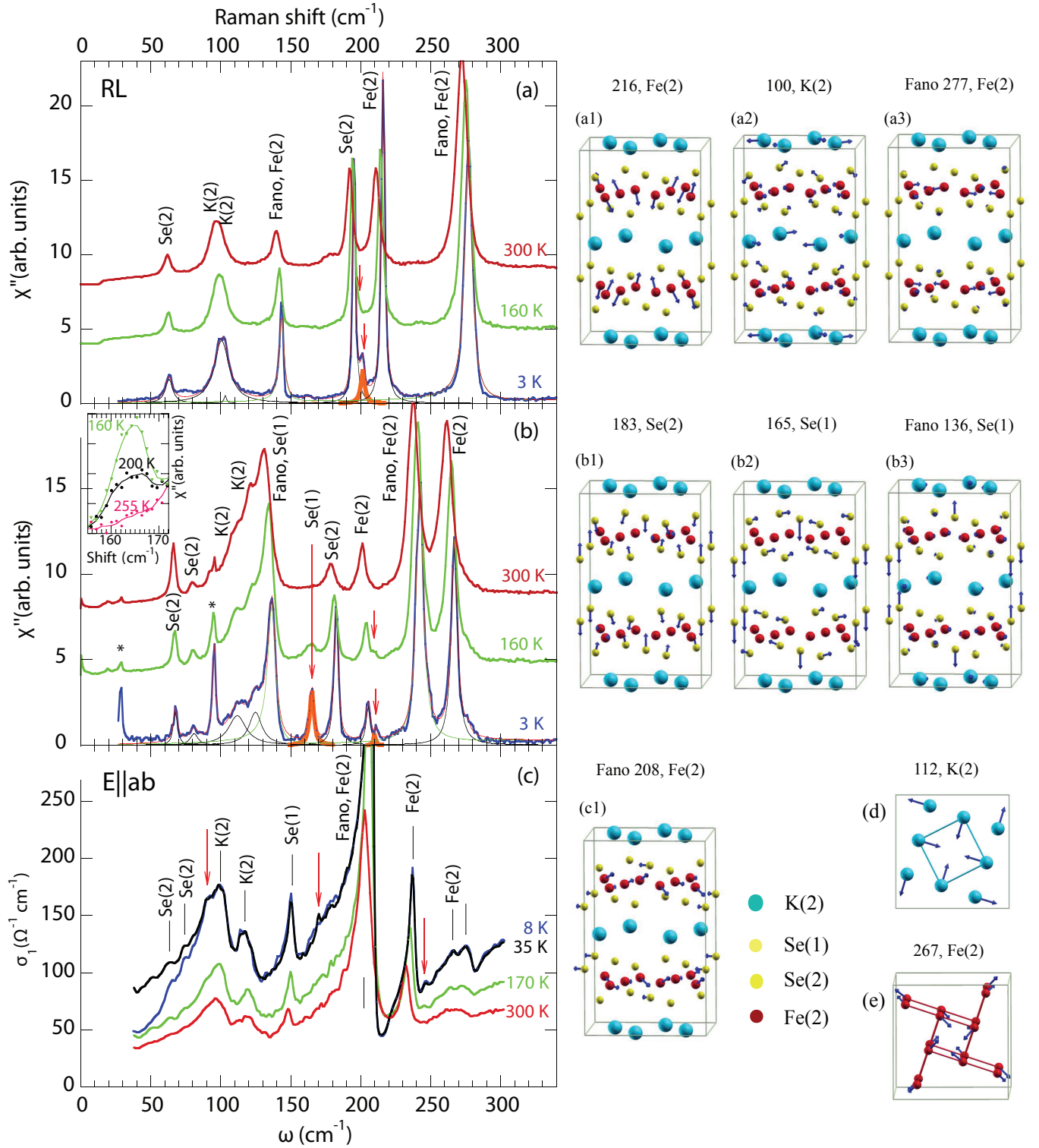


FIG. 1: (Color online) Raman response function of  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$  in (a) RL and (b) RR channels at 3 (blue), 160 (green), and 300 K (red). (c)  $ab$ -plane optical conductivity of  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$  from the same batch of samples at 8, 35, 170, and 300 K, adopted from Fig. 2 in Ref. [10]. Fits are illustrated on the 3 K spectra. Modes belonging to  $I4/m$  Ref. [4] are shown in black (Lorentz) and green (Fano). New phonons appearing at  $T_1$  in the range of 200 to 255 K [insert in (b)], usually referred as seen below  $\sim 250$  K, are shown in orange and marked with arrows. Predominant atomic contribution is labeled for each vibration mode. Computed displacement patterns of selected Raman modes in AFM  $I4/m$ ,  $\sqrt{5} \times \sqrt{5}$  unit cells of  $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$  are shown to the right from the vibration spectra: The  $B_g$  modes at  $\sim 216$  and  $100$  cm<sup>-1</sup> and Fano mode at  $277$  cm<sup>-1</sup> are visualized in (a1)-(a3). The displacement patterns of  $A_g$  mode at  $\sim 183$ ,  $A_u$  mode at  $\sim 165$  (becomes Raman active  $A$  mode below  $T_1$ ), and Fano  $A_g$  mode at  $\sim 136$  cm<sup>-1</sup> are shown in (b1), (b2), and (b3). Nine IR-active modes observed throughout the  $T$ -range of this study are marked with black bars in (c). At least three new modes (red arrows) seen at 170 K. The displacement patterns for IR Fano mode at  $\sim 208$  cm<sup>-1</sup> is shown in (c1). 2D atomic displacement patterns of  $A_g$  modes involving both chiral and breathing displacements: (d) K(2)-based  $\sim 112$  cm<sup>-1</sup> and (e) Fe(2)  $267$  cm<sup>-1</sup>. All displacements are not up to scale. Two peaks at  $\sim 29$  and  $95$  cm<sup>-1</sup> marked by \* in (b) are due to plasma lines of Kr- laser.

TABLE I: Assignment of observed Raman and IR vibration modes in  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$  based on comparison with first-principle calculations utilizing pseudopotentials. Raman and IR modes which appear below  $T_1 \sim 250$  K are marked by  $^+$  and  $^\#$ . The Lorentz parameters for Raman and  $ab$ -plane IR modes, respectively, at 3 and 35 K were obtained from fit to the experimental data shown in Fig. 1. Here  $\omega_i$  and  $\Gamma_i$  (in  $\text{cm}^{-1}$ ) are the frequency and FWHM, of the  $i$ -th mode. Error bars estimated from covariance are 0.2-0.4 and 0.4-2.0  $\text{cm}^{-1}$  for  $\omega_i$  and  $\Gamma_i$ . Raman data from Ref. [15] and IR data from Ref. [19] are shown for comparison. Computed vibration frequencies are shown for  $I4/m$  structure. Total number of modes is less than in Eq(1) because K(1) and acoustic modes are not computed/omitted. Vibration frequencies in  $I4$  are less than 10  $\text{cm}^{-1}$  apart are not shown in this Table.  $A_g$ ,  $B_g$ , and  $E_u$  modes in  $I4/m$  becomes, respectively  $A$ ,  $B$ , and  $E$  modes in  $I4$ , refer to Sect IV.

AFM, $I4/m$	Raman ( $\omega, \Gamma$ )	Ref.[15]	IR ( $\omega, \Gamma$ )	Ref.[19]
63.6 $A_g$	67.6, 3.5	66.3		
79.9 $A_g$	81.0, 6.1			
89.0 $A_g$	111.8, 15.0			
108.2 $A_g$	124.8, 11.1	123.8		
126.0 $A_g$	Fano 135.9	134.6		
173.5 $A_g$	182.5, 3.4			
211.1 $A_g$	205.3, 3.6	202.9		
236.0 $A_g$	Fano 242.3	239.4		
265.9 $A_g$	267.0, 5.3	264.6		
57.9 $B_g$	63.1, 6.2	61.4		
66.4 $B_g$	- -			
98.2 $B_g$	100.6, 12.8	100.6		
117.3 $B_g$	103.3, 2.1			
134.9 $B_g$	Fano 143.6	141.7		
206.0 $B_g$	195.3, 2.6			
224.0 $B_g$	216.1, 3.0	214.3		
262.7 $B_g$	Fano 277.1	274.9		
59.0 $E_g$				
79.9 $E_g$				
95.1 $E_g^\#$			98.9, 8.2	102.3
104.5 $E_g$				
156.9 $E_g^\#$			171.2, 4.9	
206.5 $E_g$				
224.0 $E_g$				
251.3 $E_g^\#$			246.3, 5.	
61.1 $A_u$				
92.7 $A_u$				
96.3 $A_u$				
172.4 $A_u^+$	165.2, 3.6			
212.4 $A_u^+$	211.0, 1.4			
249.7 $A_u$				
271.0 $A_u$				
67.7 $B_u$				
76.0 $B_u$				
89.3 $B_u$				
116.2 $B_u$				
181.9 $B_u^+$	200.5, 3.4			
240.5 $B_u$				
273.0 $B_u$				
62.5 $E_u$			63.8, 7.1	65.2
73.9 $E_u$			74.2, 6.1	73.6
85.9 $E_u$			91.3, 16.	93.7
96.5 $E_u$			118.5, 10.	121.9
140.7 $E_u$			150.1, 4.0	151.7
219.3 $E_u$			Fano 207.6	208.3
233.3 $E_u$			236.6, 4.4	238.3
268.3 $E_u$			267.2, 6.1	267.1
			276.1, 4.9	278.6

ment with the experiment. We also allowed inversion symmetry breaking displacement and found that  $I4$  structure has slightly lower energy ( 3.5 meV) compared to  $I4/m$ , however the splitting of atomic coordinates was very small. We find that both the structures exhibit a band gap of  $\sim 0.4$  eV.

Frequencies of the zone center phonons are determined using linear response method<sup>24</sup> for the relaxed structures are listed in the first column of Table I for the AFM  $I4/m$   $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$ . Since all nine  $A_g$  modes anticipated in the parent AFM  $I4/m$   $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$  are observed at room temperature, there is a unique correspondence between computed and measured vibration frequencies summarized in Table I. Computed  $B_g$  mode at 66.4  $\text{cm}^{-1}$  is not observed. The  $B_g$  vibration at  $\sim 117.3$   $\text{cm}^{-1}$  submerges to the broad  $B_g$  mode at  $\sim 100$   $\text{cm}^{-1}$ , Fig. 1(a) and is revealed in the fit. Importantly, two  $A_g$  modes at 79.9 and 89.0  $\text{cm}^{-1}$  cannot be reproduced in non-magnetic (NM)  $I4/m$   $\sqrt{5} \times \sqrt{5}$  structure either undoped  $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$  or vacancy-free  $\text{KFe}_2\text{Se}_2$  also computed in this work but not listed in the Table I. Therefore, accounting for the spin degree of freedom is essential for accurate mapping of the observed Raman modes. The 8 out of 9 observed IR active modes at 300 K are assigned, Table I and Fig. 1(c). The remaining  $E_u$  mode at  $\sim 278$   $\text{cm}^{-1}$  is likely due to finite Fe(1) population in the superconducting sample: an extra  $E_u$  mode appears in NM vacancy-free  $I4/m$  at 294  $\text{cm}^{-1}$ . In summary, the observed Raman and IR- vibration frequencies above  $\sim 200$  - 250 K are in good agreement with computed frequencies. Below 200 - 250 K, new Raman modes at  $\sim 165$ , 201, and 211  $\text{cm}^{-1}$  and IR-active modes at  $\sim 99$ , 171, and 246  $\text{cm}^{-1}$  show up. Their vibration frequencies corresponds well to the computed frequencies of Raman active A, B and IR active E in the  $I4$  structure, Table I.

Displacement patterns of selected vibration modes are illustrated in Fig. 1. Raman modes shown in (a1) and (b1) correspond to Fe  $B_{1g}$  and As  $A_{1g}$  vibrations in the 122 iron-arsenides<sup>25</sup>. In AFM  $I4/m$  both modes got finite ( $x, y$ ) displacements. The  $B_g \sim 100$   $\text{cm}^{-1}$  mode is dominated by in-plane K displacements with some admixture of Se and Fe displacements. Its large  $T$ -independent linewidth is related to static disorder associated with K(2) sites. The  $A_u \sim 172.4$   $\text{cm}^{-1}$  patterns are shown in (b2). Being non-Raman active in the AFM  $I4/m$  phase it becomes new Raman mode  $A$  in the low- $T$  phase AFM  $I4$ , Fig. 1(b2). Fig. 1 visualizes atomic displacement of one IR-active (c1) and two out of four observed Raman active Fano modes (a3 and b3) discussed in this paper. The striking feature of all but Se-based  $A_g \sim 136$   $\text{cm}^{-1}$  is essential involvement of Fe(2) atomic displacements. In  $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$  Fe atoms carry magnetic moment as large as  $3.3\mu_B$  Ref. [4], while electronic structure near  $E_f$  is dominated by Fe  $d$ -states<sup>3</sup>. The Fano modes coupling to electronic and magnetic degrees of freedom are explored in the following section.

## B. Origin of Fano vibration modes

Asymmetric line shapes are characteristic of Fano resonances arising from coupling between the phonons and an

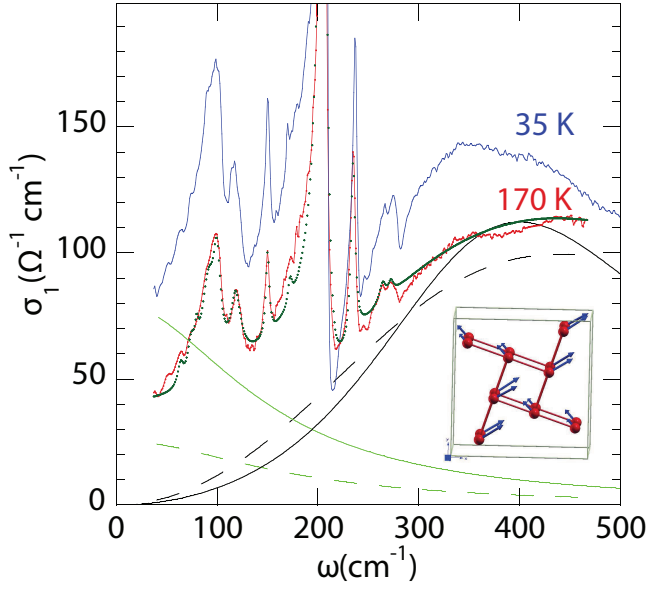


FIG. 2: (Color online) Optical conductivity at 35 K (blue) and 170 K (red) along with a fitting curve (dark green dots). Drude components (green) and MIR Lorentz terms (black) are shown with solid(dashed) curves for 35(170) K. Insert: c-axis view of  $ab$ - plane displacement patterns (not up to scale) of the Fe(2) atoms.

electronic continuum, electronic or magnetic in origin. Dipole transition in the IR- absorption does not directly couple the AFM excitations, but couples charge carriers. Raman scattering probes both electronic and magnetic excitations. The  $208 \text{ cm}^{-1}$  IR- and  $\sim 144, 242$ , and  $277 \text{ cm}^{-1}$  Raman Fano modes are dominated by Fe(2) atomic displacements. Interestingly, the IR mode gets more asymmetric [Fig. 2] while four Raman modes [Fig. 3(a-d)] become more symmetric on cooling.

The optical conductivity at 35 and 170 K is shown in Fig. 2. Taking 170 K spectrum as an example, the experimental conductivity is fitted as sum of Drude peak (dashed green), broad Lorentz component (dashed black) describing interband transition at  $\sim 400 \text{ cm}^{-1}$ , the beginning of mid-infrared (MIR) peak, and eleven Lorentz and one Fano phonon modes. Both Drude and MIR become slightly more coherent and better pronounced as temperature decreases to 35 K. At frequency of Fano mode, the Drude contribution increases, while the MIR contribution slightly decreases. Therefore, enhancement in the IR Fano peak asymmetry is due to the vibration coupling to charge carriers in the Drude tail.

Four Fano Raman modes are presented in Fig. 3(a)-(d) at 3 and 160 K. They were obtained by removal of fitted in phonons from data shown in Fig 1(a,b). Clearly, all Raman modes exhibit similar  $T$  dependence: (a) they are less symmetric, and (b) they characterized by larger background at 160 K than at 3 K. The observed behavior is reminiscent of  $T$ -dependence of a new mode observed in AFM 122 systems. The mode appears at  $T_N$  as a Fano-shaped one and it becomes progressively more symmetric with temperature decrease. The Fano peak derives from vibration coupling to

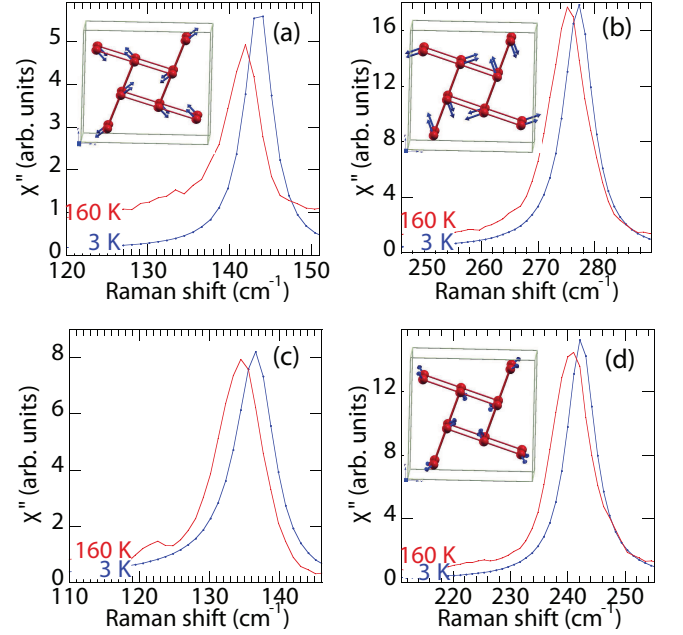


FIG. 3: (Color online) Raman Fano modes for (a)  $\sim 142$  and (b)  $\sim 277 \text{ cm}^{-1}$  in RL and (c)  $\sim 137$  and (d)  $\sim 242 \text{ cm}^{-1}$  in RR. Inserts: c-axis view of  $ab$ - plane displacement patterns (not up to scale) of the Fe(2) atoms. The 3D displacement patterns are shown in Fig. 1.

magnetic continuum, the AFM spin fluctuations.

### C. Temperature dependence of Raman mode linewidth and phonon frequencies

Selected linewidth and phonon frequencies as function of temperature are shown in Fig. 4. The  $T$ -dependent phonon frequencies qualitatively agree with those reported by Zhang *et al* in  $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$  (Fig 5 in Ref. [15]) and by Lazarević *et al* in isostructural  $\text{K}_{0.88}\text{Fe}_{1.63}\text{S}_2$  (Fig. 3(b-j) in Ref. [16]). In the latter work, the authors concluded that the Raman active phonon energies in the range of 80-300 K are fully driven by anharmonicity effects<sup>16</sup>. Interpretation offered in the present work is different: the residual linewidth is compatible [Fig. 4(a,c)] or larger [Fig. 4(e)] than the temperature dependent increment between 3 and 300 K. Therefore, self-energy of non-Fano phonons (i.e. at  $\sim 195$  and  $216 \text{ cm}^{-1}$  in  $B_g$  and at  $\sim 68, 205$ , and  $267 \text{ cm}^{-1}$  in  $A_g$  channels) consist of approximately equal contributions of two-phonon lattice anharmonicity on one hand and bare self-energy and broadening due to intrinsic defects on the other. Self-energy of  $\sim 100 \text{ cm}^{-1}$  mode involving the K(2) atomic displacements is dominated by inhomogeneous broadening. The new  $\sim 165 \text{ cm}^{-1}$  mode appearing at  $T_1$  in the range of 200 to 250 K becomes fully coherent below  $\sim 40$ -60 K: the linewidth presented in Fig. 4(g) quickly reduces by  $\sim 5$  times as temperature decreases from 200 to 60 K, followed by saturation below  $\sim 40$  K. The mode hardens on cooling by  $\sim 1.0 \text{ cm}^{-1}$  [Fig. 4(h)] in the traceable  $T$ -range.



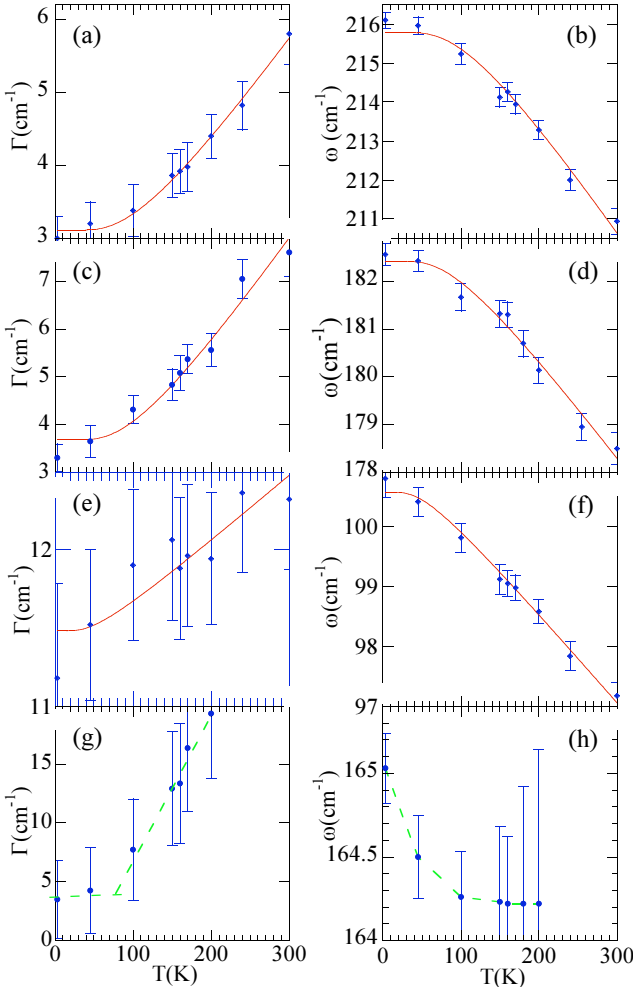


FIG. 4: (Color online) Linewidth (first row) and subsequent phonon frequencies (second row) of Fe(2)  $B_g \sim 216$ , Se(2)  $A_g \sim 182$ , K(2)  $B_g \sim 100$ , and Se(1)  $A_g \sim 165 \text{ cm}^{-1}$  modes. Solid red lines describe two-phonon anharmonic decay<sup>26</sup>. Dashed green lines are guided to the eye. The atomic displacement patterns of the modes are visualized in Fig 1 (a1, b1, a2, and b2).

#### IV. DISCUSSION

The new  $165 \text{ cm}^{-1}$  mode appearing at  $T_1$  in the range of 200-250 K, [insert of Fig. 1(b)], usually referred as seen at  $T_1$  below  $\sim 250 \text{ K}$  throughout this paper, is not Raman active in the  $I4/m$  phase (Table I), fully symmetric in character, and it quickly becomes coherent with  $T$ -decrease [Fig. 3(g)]. The question arises whether this mode signifies crystal symmetry lowering on a structural phase transition. If it is associated with symmetry lowering, it would become allowed phonon mode in one of subgroups of  $C_{4h}$ . The  $C_{4h}$  encompass the  $C_4$  (loss of inversion and rotation-reflection),  $C_{2h}$  (loss of  $4^{th}$  order rotation axis),  $S_4$  (loss of inversion and  $4^{th}$  order rotation axis),  $C_2$  (loss of inversion,  $4^{th}$  order rotation axis, and rotation-reflection), and  $C_1$  (primitive) subgroups. We did not observe leaking of four-fold axis symmetry that would results in the cross-polarization intensity leakages beyond small leak-

ages of polarization optics which don't correlate with temperature dependence of the  $165 \text{ cm}^{-1}$  mode. Thus,  $C_{2h}$ ,  $C_2$ , and  $C_1$  subgroups are excluded. The  $S_4$  (space group #82) is excluded because there is no new  $A$ -type Se(1) mode associated with the transition. Therefore,  $I4/m$  ( $C_{4h}$ , space group #87) becomes  $I4$  ( $C_4$ , space group #79). From the factor-group analysis  $A_g$ ,  $B_g$ , and  $E_u$  modes in  $C_{4h}$  becomes, respectively  $A$ ,  $B$ , and  $E$  modes in  $C_4$ . Instead of  $9A_g + 8B_g$  Raman active and  $8E_u$  infrared active modes in high- $T$   $I4m$  phase one would expect to encounter  $17A + 15B$  Raman and  $17E$  IR-active modes in low- $T$  phase under the measured geometry. Here we excluded acoustic and Fe(1)-related modes, since the Fe(1)-site is mostly empty site in  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$ . The Raman active modes do not overlap with  $ab$ -plane IR active modes, not only in high- but in low- $T$  phases. This explains seemingly puzzling absence of IR mode leakages into the Raman spectra noted in Section 3. Since new Raman modes (at  $\sim 165$ ,  $201$ , and  $211 \text{ cm}^{-1}$  and IR-active modes (at  $\sim 99$ ,  $171$ , and  $246 \text{ cm}^{-1}$ ) appears below  $T_1$  and those modes are non-Raman(non-IR) active  $A_u(E_g)$  or silent  $B_u$  in  $I4m$  (Table I) we suggest that  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$  undergoes  $I4/m \rightarrow I4$  structural phase transition accompanied by loss of inversion symmetry at  $T_1$  below  $\sim 250 \text{ K}$ . Our first-principles calculations utilizing pseudopotentials also narrowly favor  $I4$  over the  $I4/m$  structure. The small total energy difference is likely because computations do not include all correlations and/or the calculations are performed for the undoped  $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$ .

Temperature dependence of selected phonon frequencies and intensities are shown in Fig. 5(a,b) and 5(c,d), respectively. Apart from the structural phase transition at  $T_1 \sim 250 \text{ K}$ , clearly there is a second characteristic temperature,  $T_2 \sim 160 \text{ K}$ . At  $T_2$  majority of phonon vibration frequencies exhibit consistent discontinuity up to  $\sim 0.3 \text{ cm}^{-1}$  [Fig. 5(a, b)], while quite a few modes display slop changes in their intensity vs temperature dependencies [Fig. 5(c, d)]. Since no new vibration modes (Raman or IR) are observed below the  $T_2$  the  $T_2$  is not constituent a structural phase transition, but rather referred as phonon anomaly temperature. Anomaly of a single  $A_g$  mode at  $66 \text{ cm}^{-1}$  at  $160 \text{ K}$  was mentioned by Zhang *et al.*<sup>15</sup>. We would like to point out that the phonon anomalies seen at the  $T_2 \sim 160 \text{ K}$  involve majority of measured Raman modes.

From experimental data at hand we could point out two implications of the observed structural phase transition on low- $T$  properties of  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$ . First, symmetry of the Se(1,2)-Fe(2) slab is broken at  $T_1$ , sample becomes ferroelectric, and  $c$ -axis structural distortions within the stab appears to build up on cooling. This is seen in Raman phonon peak intensities, Fig. 5(c,d), which are directly proportional to polarizability tensor. As sample enters the low- $T$  phase ( $T < T_1$ ), polarizability of quite a few Raman-active modes build-up till  $\sim T_2$ , followed by saturation at  $T < T_2$  ( $B$ -symmetry at  $63$ ,  $100.6$ , and  $277$ ;  $A$ -symmetry at  $81$  and  $267$ , Fano-shape  $136$  and  $242 \text{ cm}^{-1}$ ) or reduction ( $A$ -symmetry at  $68$ ,  $112$ , and  $125 \text{ cm}^{-1}$ ). However, polarizabilities of Fe(2)-based  $B$  mode at  $\sim 216$ , As(2)-based  $A$  mode at  $\sim 183$ , and As(1)-based  $A$  mode at  $\sim 165 \text{ cm}^{-1}$  continue to build up till  $\sim 45$ ,  $3$ , and  $3 \text{ K}$ , respectively. The scaling relationships among the three

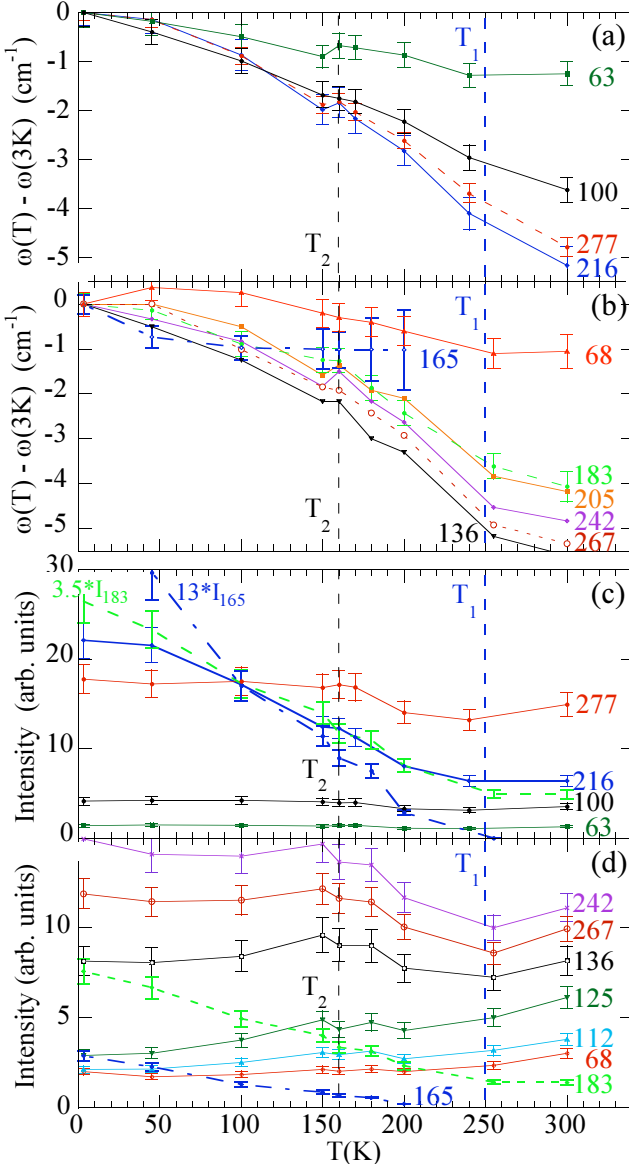


FIG. 5: (Color online) Temperature dependence of selected phonon frequencies (a,b) and intensities (c,d). Some error bars are omitted in (b) for clarity.  $T_1$  and  $T_2$  mark temperatures of structural phase transition at  $\sim 250$  K and phonon anomalies at  $\sim 160$  K. In (c) intensity of the Fe(2)-based  $B(B_g) \sim 216$   $\text{cm}^{-1}$  (solid blue line) scales almost perfectly to  $3.5 \pm 0.2$  times intensity of Se(2)-based  $A(A_g) \sim 183$   $\text{cm}^{-1}$  (dashed green line) in the range of 45 to 250 K. It also satisfactory scales to  $13 \pm 1$  times intensity of the Se(1)-based  $A \sim 165$   $\text{cm}^{-1}$  (dot-dashed blue line) in the range of  $\sim 100$  to 200 K. Note there are four Se(2) per one Se(1) atom.

are shown in Fig. 5(c). The scaling is not surprising, giving to similar displacements patterns of the modes along the  $c$ -axis [Fig.1(a1), (b1), and (b2)], so that their Raman activities are driven by polarizability of the electronic orbitals forming the Fe-Se slabs. In iron-arsenides (122-systems) the Fe-As slab is perfectly symmetric and the Raman-active As-based  $A_{1g}$  mode has extremely low intensity (polarizability) if measured in the same geometry<sup>25</sup>. It becomes visible upon doping de-

stroying the symmetry of the slab. In  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$ , intrinsic population of Fe- and K- vacancies makes the Se(2)-based  $A_g \sim 183$   $\text{cm}^{-1}$  mode effortlessly visible at room temperature. The atomic displacements associated with the  $I4/m \rightarrow I4$  phase transition which have sizable  $ab$ -plane components are likely quenched below  $T_2$ , while  $c$ -axis displacements continue to build up on cooling. Second implication concerns the temperature dependence of low-frequency optical conductivity shown in Fig. 1(c). The conductivity displays weak temperature dependence above  $T_1$  followed by faster increase below the  $T_2$ , in agreement with similar temperature dependence reported by Homes *et al.*<sup>19</sup>

Onset of superconductivity at  $\sim 30$  K has little effect on phonons. Using 3 and 45 K data points, the upper estimated phonon energy shifts are  $-0.3 \pm 0.4$   $\text{cm}^{-1}$  ( $|\Delta\omega|/\omega \sim 0.44\%$ ) for 67.6  $\text{cm}^{-1}$  and  $+0.6 \pm 0.4$   $\text{cm}^{-1}$  ( $|\Delta\omega|/\omega \sim 0.36\%$ ) for 165.0  $\text{cm}^{-1}$  modes. Small frequencies renormalization implies either weak  $e$ - $ph$  interaction or that the phonons used in our analysis belongs to the AFM phase in the phase separated models<sup>6,7,10,12,13</sup>: spectator AFM phonons would not feel onset of the superconductivity, unless via the proximity effect.

## V. CONCLUSIONS

Raman scattering and optical conductivity were used to determine lattice vibration frequencies of superconducting crystal  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$  in temperature range from 3 to 300 K. 19 Raman-active and 12 IR-active modes are observed at 3 K. The  $\sim 136$ , 143, 242, and 277  $\text{cm}^{-1}$  Raman and  $\sim 208$   $\text{cm}^{-1}$  IR mode exhibit Fano-like shape. The Raman Fano modes are due to the vibration coupling to AFM spin fluctuations, while the IR- mode is coupled to charge carriers in low-frequency part of optical conductivity. Raman phonon linewidths contain approximately equal contributions of two-phonon lattice anharmonicity on one hand and bare self-energy and broadening due to intrinsic defects on the other hand. The  $\text{K}_{0.75}\text{Fe}_{1.75}\text{Se}_2$  undergoes  $I4/m$  (space group #87)  $\rightarrow I4$  (space group #79) structural phase transition at  $T_1$  below  $\sim 250$  K. Several modes which are not Raman- and IR-active in the measured geometry in  $I4/m$  become visible in  $I4$  phase including Raman modes at  $\sim 165$ , 201, and 211  $\text{cm}^{-1}$  and IR-active modes at  $\sim 99$ , 171, and 246  $\text{cm}^{-1}$ . Weak phonon anomalies are also observed at  $T_2 \sim 160$  K. Symmetry of the Se(1,2)-Fe(2) slab is broken at  $T_1$ .  $ab$ -plane structural distortions are likely quenched below  $T_2$ , while  $c$ -axis structural distortions within the slab continues to build up on cooling down to 3 K.

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