Evidence of superconductivity-induced phonon spectra renormalization in alkali-doped iron selenides

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Abstract
Polarized Raman scattering spectra of superconducting KₓFe₂₋ₓSe₂ and non-superconducting K₀.₈Fe₁.₈Co₀.₂Se₂ single crystals were measured in the temperature range from 10 K up to 300 K. Two Raman active modes from the I₄/m/mm phase and seven from the I₄/m phase are observed in the frequency range from 150 to 325 cm⁻¹ in both compounds, suggesting that the K₀.₈Fe₁.₈Co₀.₂Se₂ single crystal also has a two-phase nature. The temperature dependence of the Raman mode energy is analyzed in terms of lattice thermal expansion and phonon–phonon interaction. The temperature dependence of the Raman mode linewidth is dominated by temperature-induced anharmonic effects. It is shown that the change in Raman mode energy with temperature is dominantly driven by thermal expansion of the crystal lattice. An abrupt change of the A₁g mode energy near Tc was observed in KₓFe₂₋ₓSe₂, whereas it is absent in non-superconducting K₀.₈Fe₁.₈Co₀.₂Se₂. Phonon energy hardening at low temperatures in the superconducting sample is a consequence of superconductivity-induced redistribution of the electronic states below the critical temperature.

Keywords: iron selenides, Raman scattering, superconductivity

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the discovery of superconductivity in the FeSe layered compound KₓFe₂₋ₓSe₂ [1], considerable attention has been focused on iron selenide materials due to their relatively high superconducting transition temperatures (Tc) [2–5]. Recent investigations of single-layer FeSe films grown on SrTiO₃ revealed superconductivity with Tc above 100 K, which is the highest critical temperature among all iron-based materials discovered so far [6]. Alkali metal-doped iron chalcogenides have some interesting features that distinguish them from other iron-based superconductors [7, 8]. Angle-resolved photoemission measurements showed that there are no hole pockets at the Fermi level in KₓFe₂₋ₓSe₂, which opens the possibility for a different type of pairing mechanism than in the iron pnictides [9]. This is consistent with observed negative values of the Hall constant RH in the temperature range 0–150 K [10], which implies that conduction is predominantly governed by electron-like carriers.

The most striking feature of KₓFe₂₋ₓSe₂ single crystals is the presence of two distinct phases: insulating and metallic/superconducting [8, 11, 12]. The insulating phase has antiferromagnetically, \( \sqrt{5} \times \sqrt{5} \), ordered Fe vacancies with large iron magnetic moments, whereas the superconducting...
phase is free of vacancies [11]. Resistivity measurements on a sample with nominal composition K$_{0.8}$Fe$_2$Se$_2$ revealed that superconductivity occurs below $T_C \sim 30$ K [1]. However, it was later established that superconductivity appears only in Fe-deficient samples. A broad hump in the in-plane resistivity $\rho_{xy}(T)$, whose position varies between 105 K and 240 K (depending on the sample preparation), presumably occurs due to the type of connection between the two phases [10, 13]. Below the hump, K$_x$Fe$_{2-x}$Se$_2$ is metallic due to an intrinsic property of the metallic/superconducting state, since insulating regions do not contribute to the spectral weight close to the Fermi energy, as observed by angle-resolved photoemission spectroscopy [14, 15]. It was also shown that M-doping on the Fe site (M = Cr, Co, Ni, Zn) strongly suppresses superconductivity [16, 17]. However, the correlation between antiferromagnetically ordered iron vacancies and superconductivity remains unclear.

Raman scattering studies of K$_x$Fe$_{2-x}$Se$_2$ single crystals have been performed by several groups [18–20]. Zhang et al [18] considered phonon properties of this compound in terms of the I4/m space group. They observed and assigned 11 out of 18 Raman active modes. Their analysis revealed that a phonon of unknown origin, at about 180 cm$^{-1}$ (which was assigned as the $A_g$ symmetry mode) exhibits abrupt hardening of $\sim 1$ cm$^{-1}$ at the superconducting critical temperature $T_C$. Lazarević et al [19] analyzed lattice dynamics of K$_{x}$Fe$_{2-x}$Se$_{2}$ in terms of I4/m and I4/mmm phases. They observed and assigned two (of two possible) modes from the high-symmetry phase and 16 out of 18 phonon modes from the low-symmetry phase. They also observed a Raman mode at about 180 cm$^{-1}$ and assigned it as of $A_{1g}$ symmetry originating from the superconducting I4/mmm phase. In [20], the authors argued that new Raman modes, at about 165, 201 and 211 cm$^{-1}$, appear on cooling the sample below 250 K. Based on this, it is concluded that K$_x$Fe$_{2-x}$Se$_2$ single crystal exhibits a structural phase transition from I4/m to I4 space group. They assumed a Fano-like shape for some phonons and analyzed the temperature dependence of the Raman mode energy and linewidth in terms of lattice anharmonicity. To the best of our knowledge, the Raman spectrum of K$_x$Fe$_{2-x}$Se$_2$ single crystals doped with Co is unknown.

In order to determine the impact of superconductivity on the phonon properties of alkali-doped iron selenides, we have performed a Raman scattering study of superconducting K$_x$Fe$_{2-x}$Se$_2$ and non-superconducting K$_{0.8}$Fe$_{1.2}$Co$_{0.2}$Se$_2$ single crystals. Raman spectra were measured in the temperature range from 10 to 300 K. All phonons expected to appear in the investigated energy range, according to [19], are observed in both single crystals. A detailed analysis of the temperature dependence of energy and linewidth for seven observed Raman active modes is performed.

2. Experiment

K$_{0.8}$Fe$_{1.2}$Co$_{0.2}$Se$_2$ and K$_{0.8}$Fe$_{1.2}$Co$_{0.2}$Se$_2$ single crystals were grown and characterized as described in detail elsewhere [21]. Raman scattering measurements were performed on (0 0 1)-oriented samples, 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 Raman scattering measurements were carried out at low laser power, in order to minimize local heating of the sample. All measurements were performed in vacuum, using a KONTI CryoVac continuous flow cryostat with 0.5 mm thick window. The samples were cleaved just before their placement in the cryostat in order to obtain a flat shiny surface. For the data extraction from the Raman spectra, a Voigt profile has been used, where a Gaussian width of 2 cm$^{-1}$ represents the spectral resolution of the instrument.

The FeSe layer is the basic building block for all iron selenide superconductors. An FeSe single crystal (see figure 1(a)) crystallizes in the tetragonal crystal lattice (P4/nmm space group), with two formula units per unit cell [22]. The site symmetries of individual atoms in this space group are $D_{2d}$ (Fe) and $C_4v$ (Se). Factor group analysis gives the normal mode distribution in the Brillouin zone center:

\[
(D_{2d}) : \Gamma = A_{2g} + B_{2g} + E_g + E_u,
\]

\[
(C_4v) : \Gamma = A_{1g} + A_{2u} + E_g + E_u.
\]

In total, $A_{1g}$($\alpha_{x+y}, \alpha_{z}$), $B_{1g}$($\alpha_{x-y}, \alpha_{z}$) and $2E_g$($\alpha_{x}, \alpha_{z}$) phonons are Raman active. $A_{1g}$($B_{1g}$) modes represent vibrations of Se (Fe) ions along the $z$-axis, whereas $E_g$ modes originate from vibrations of Fe and Se ions within the $ab$ plane [23].

A K$_{x}$Fe$_{2-x}$Se$_2$ single crystal consists of K ions intercalated between the FeSe slabs, which dominantly determines its physical properties [1]. At high temperature it crystallizes in the I4/mmm space group. On cooling below 532 K partial symmetry breaking occurs, as a consequence of Fe vacancy ordering [8]. Recent studies revealed that, at low temperatures, K$_{x}$Fe$_{2-x}$Se$_2$ single crystals consist of two phases separated at the nanometer scale: a superconducting phase (I4/mmm) and an insulating phase (I4/m) [11, 12, 19]. By comparing the crystallographic data for FeSe [22] and K$_{x}$Fe$_{2-x}$Se$_2$ [1], it can be seen that the intralayer Fe–Fe distances and Fe–Se bond lengths increase in K$_{x}$Fe$_{2-x}$Se$_2$ by only a few per cent.

![Figure 1](image-url)
Site symmetries of atoms in the I4/mmm group (see figure 1(b)) are D_{4h} (K), C_{4v} (Se) and D_{2h} (Fe). By applying symmetry analysis, it follows that

\[(D_{4h}) : \Gamma = A_{2u} + E_{1u},\]

\[(D_{2h}) : \Gamma = A_{2u} + B_{1g} + E_{g} + E_{u},\]

\[(C_{4v}) : \Gamma = A_{1g} + A_{2u} + E_{g} + E_{u},\]

\[(C_{ub}) : \Gamma = A_{u} + E_{u} + E_{u} + E_{1u},\]

\[(C_{a}) : \Gamma = 2A_{g} + A_{u} + 2B_{g} + B_{u} + E_{g} + 2E_{u},\]

\[(S_{4}) : \Gamma = A_{u} + B_{u} + E_{g} + E_{u},\]

\[(C_{4}) : \Gamma = A_{g} + A_{u} + E_{g} + E_{u},\]

\[(C_{1}) : \Gamma = 3A_{g} + 3A_{u} + 3B_{g} + 3B_{u} + 3E_{g} + 3E_{u}.\]

One can expect 27 Raman active phonons originating from the I4/m phase: 9A_g(\alpha_x\gamma, \alpha_y\alpha), 9B_g(\alpha_x\gamma, \alpha_y\alpha) and 9E_g(\alpha_x\gamma) modes. Due to the (0 0 1) orientation of our samples, only A_g and B_g modes can be observed in the Raman spectra [26]. According to the analysis of Raman mode intensities, A_g phonons vanish in the crossed polarization configuration, whereas B_g modes are observable in both crossed and parallel polarization configurations [19].

3. Results and discussion

Figure 2(a) shows polarized Raman scattering spectra of K_{Fe2−x}Se_{2} single crystals, in the spectral range between 150 and 325 cm\(^{-1}\), measured from the (0 0 1) plane of the sample at various temperatures. The observed Raman modes are assigned according to [19] (see figure 2(a)) and in agreement with previously discussed selection rules for the high-symmetry (I4/mmm) and low-symmetry (I4/m) phases of this phase-separated sample [11]. The Raman active mode appearing in crossed polarization configuration at about 206 cm\(^{-1}\) (marked by an arrow in figure 3) could be assigned as the B_{1g} symmetry mode [19]. However, a high-intensity A_g phonon is present in the parallel polarization configuration at almost the same frequency (see figure 3). Due to the possible leakage of the A_g^6 mode, unambiguous assignment of the marked Raman mode cannot be made here.

Figure 2(b) shows temperature-dependent Raman spectra of K_{Fe1.8Co0.2}Se_{2} single crystals, measured from the (0 0 1) plane of the sample at various temperatures, are presented in figure 2(b). Energies of Raman active phonons are close to the energies of the corresponding modes in K_{Fe2−x}Se_{2}. Based on this, it can be concluded that doping of a K_{Fe2−x}Se_{2} single crystal with a small amount of Co does not have a significant impact on the phonon spectrum in the normal state.

Ignatov et al [20] argued that the Raman active mode at about 203 cm\(^{-1}\) in K_{Fe2−x}Se_{2} (at 3 K) disappears above 250 K, together with two other modes at about 163 and 210 cm\(^{-1}\). They concluded that these modes belong to the 14 space group. As can be seen in figure 2, this phonon (206 cm\(^{-1}\)) is clearly visible in our Raman spectra of both compounds up to room temperature, and it is assigned in [19] as the B_{1g} mode, originating from the I4/mmm phase. Due to the absence of new Raman modes below 250 K, there are no indications of a structural phase transition in our samples.
The behavior of the phonon modes with temperature can be properly described in terms of the phonon self-energy [27]:

\[ \Sigma_i(T) = \Delta_i(T) + i\Gamma_i(T), \]

(1)

where \( \Delta_i(T) \) represents the change in the Raman mode energy and \( \Gamma_i(T) \) is the mode linewidth, which is inversely proportional to the phonon lifetime \( \tau \).

Therefore, the temperature dependence of the Raman mode energy can be described using

\[ \omega_i(T) = \omega_{0,i} + \Delta_i(T), \]

(2)

where \( \omega_{0,i} \) is the temperature-independent contribution to the energy of the phonon mode \( i \) and \( \Delta_i(T) \) can be decomposed as [27, 28]

\[ \Delta_i(T) = \Delta_i^\nu + \Delta_i^A. \]

(3)

The first term in (3) represents the change in phonon energy due to the thermal expansion of the crystal lattice, and is given by [27]

\[ \Delta_i^\nu = \omega_{0,i} \int_0^T \alpha(T)dT + \frac{\omega_{0,i} \gamma}{2}. \]

(4)

where \( \gamma \) is the Grüneisen parameter of a given mode and \( \alpha(T) \) is the thermal expansion coefficient of the material under investigation.

The second term in (3) describes the contribution of phonon–phonon scattering (lattice anharmonicity) to the Raman mode energy. If we describe anharmonic effects by three-phonon processes, it follows [28] that

\[ \Delta_i^A = -C_i \left( 1 + 4\lambda_{ph-ph-ph}^{i} \right) \frac{1}{\omega_{0,i}}. \]

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\[ \Delta_i^A = -C_i \left( 1 + 4\lambda_{ph-ph-ph}^{i} \right) \frac{1}{\omega_{0,i}}. \]

(5)

The temperature dependence of the Raman mode linewidth is caused only by phonon anharmonicity [28]:

\[ \Gamma_i(T) = \Gamma_0,i \left( 1 + \frac{2\lambda_{ph-ph}^{i}}{\omega_{0,i}^2} \right), \]

(6)

where \( \Gamma_0 \) is the anharmonic constant.

The parameter \( C_i \) is connected with \( \omega_0 \) and \( \Gamma_0,i \) via the relation [28]

\[ C_i = \frac{\Gamma_0,i^2}{2\omega_{0,i}}. \]

(7)

The temperature dependences of the energy and linewidth of the \( A_6^g \) and \( A_7^g \) modes of \( K_xFe_{2-y}Se_2 \) and \( K_{0.8}Fe_{1.8}Co_{0.2}Se_2 \) single crystals as functions of temperature. Solid lines represent theoretical dependences, according to (2) and (6), with \( \Delta_i^A \) neglected. The dependence of the \( A_6^g \) and \( A_7^g \) mode energies on temperature with only anharmonic contributions included is shown by dash–dot lines.

C and \( \lambda_{ph-ph} \) are the anharmonic constant and phonon–phonon interaction constant, respectively.

The temperature dependence of the Raman mode linewidth is caused only by phonon anharmonicity [28]:

\[ \Gamma_i(T) = \Gamma_0,i \left( 1 + \frac{2\lambda_{ph-ph}^{i}}{\omega_{0,i}^2} \right), \]

(6)

where \( \Gamma_0,i \) is the anharmonic constant.

C and \( \lambda_{ph-ph} \) are the anharmonic constant and phonon–phonon interaction constant, respectively.

The parameter \( C_i \) is connected with \( \omega_0,i \) and \( \Gamma_0,i \) via the relation [28]

\[ C_i = \frac{\Gamma_0,i^2}{2\omega_{0,i}}. \]

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The parameter \( C_i \) is connected with \( \omega_0,i \) and \( \Gamma_0,i \) via the relation [28]

\[ C_i = \frac{\Gamma_0,i^2}{2\omega_{0,i}}. \]

(7)
single crystals are presented in figure 4. Using (2), (4), (6) and (7), and following the previously described procedure, we have obtained best fit parameters, which are shown in table 1. It can be seen that the parameter $C$ has very small values for both modes, thus the contribution to the Raman mode energy from the phonon–phonon interaction (as can be seen in figures 4(a), (b), (e) and (f)) can be neglected. For this reason, the change in the Raman mode energy with temperature is properly described only by the thermal expansion term $\Delta'\gamma$ (solid lines in figures 4(a), (b), (e) and (f)).

Figure 5 shows the energy and linewidth of the $B^6_g$ and $B^8_g$ phonon modes of $K_{Fe_2\ldots2Se_2}$ and $K_{Fe_1\ldotsCo_2Se_2}$ single crystals as functions of temperature. Analysis of the temperature dependence of energy and linewidth for these modes was carried out as in the case of the $A^g$ phonons. Best fit parameters are listed in table 1. Small values of the parameter $C$ allow us to omit the contribution from the lattice anharmonicity to the phonon mode energy. Good agreement of the theoretical curves with experimental data justifies our assumption. The Grüneisen parameter is close to the conventional value $\gamma \sim 2$ for $B_g$ modes, as well as for the other analyzed Raman active phonons.

The dependence of the $A_{ig}$ and $B_{ig}(A^6_g)$ mode energy of $K_{Fe_2\ldots2Se_2}$ and $K_{Fe_1\ldotsCo_2Se_2}$ single crystals on temperature is given in figure 6. Rather small values of intrinsic linewidth for both modes ($\Gamma_0 \sim 2 \text{ cm}^{-1}$) give negligible values of parameter $C$. Therefore, the temperature dependence of $A_{ig}$ and $B_{ig}(A^6_g)$ phonon energy is analyzed using (2) with only the $\Delta'$ term included. The $B_{ig}(A^6_g)$ mode energy of both single crystals exhibits a good agreement between experimental data and expected behavior (represented by solid lines in figure 6) over the whole temperature range. However, the temperature dependence of the $A_{ig}$ mode energy is well described by the proposed model only in the case of the Co-doped (non-superconducting) sample. An abrupt change in the $A_{ig}$ mode energy around $T_C$ in the superconducting sample (see inset of figure 6) has been observed. This results in a clear deviation from the expected behavior described with (2) and is governed by some other interaction.

It is well established that, upon entering the superconducting state, some of the phonons are renormalized due to the change in electronic structure with the opening of the superconducting gap, and therefore electron–phonon coupling. Depending on the values of the corresponding phonon energies and the magnitude of the superconducting gap, this may result in hardening or softening of the phonons [30]. Recently, the superconductivity-induced self-energy effect has also been reported in some iron arsenides [31–33]. We believe that the $A_{ig}$ mode hardening around $T_C$, observed for the superconducting sample and absent for the non-superconducting one (see inset of figure 6), is caused by superconductivity-induced phonon renormalization. Moreover, the hardening around $T_C$ has been observed only for the mode corresponding to the vibrations of the superconducting high-symmetry (I$4/mmm$) phase in the superconducting $K_{Fe_2\ldots2Se_2}$ sample, and it is in agreement with the expected behavior ($2\Delta < \omega_{\Delta}$, $2\Delta \sim 130 \text{ cm}^{-1}$) [9, 11, 30].

Table 1. Best fit parameters for the temperature dependence of energy and linewidth for the observed Raman modes ($\omega_{\phi}$—temperature-independent phonon energy, $\gamma$—Grüneisen parameter, $\Gamma_0$, $C$—anharmonic constants, $\lambda_{ph-ph}$—phonon–phonon interaction constant).

| $K_{Fe_2\ldots2Se_2}$ | $A^g_{ig}$ | $A^6_g$ | $A^7_g$ | $B^6_g$ | $B^7_g$ | $B^8_g$ |
|-----------------------|-------------|---------|---------|---------|---------|---------|
| $\omega_0$ (cm$^{-1}$) | 182.2(2)    | 205.43(6) | 242.06(9) | 195.15(5) | 205.34(9) | 215.62(7) | 275.79(6) |
| $\gamma$              | 1.6(1)      | 1.74(5)   | 1.52(6)   | 1.57(4)   | 1.63(8)   | 2.10(5)   | 1.42(4)   |
| $\Gamma_0$ (cm$^{-1}$) | 2.8(1)      | 7.2(2)    | 1.9(1)    | 3.2(1)    | 6.3(1)    |
| $\lambda_{ph-ph}$     | 0.29(3)     | 0.13(2)   | 0.42(5)   | 0.36(3)   | 0.25(2)   |
| $C$ (cm$^{-1}$)        | 0.018(2)    | 0.106(4)  | 0.009(1)  | 0.023(2)  | 0.072(2)  |

Note: The temperature dependence of the linewidth has not been analyzed for the $A_{ig}$ and $B_{ig}$ modes due to large relative errors.
4. Conclusion

In this article a Raman scattering study of superconducting K$_x$Fe$_{2-x}$Se$_2$ and non-superconducting K$_{0.8}$Fe$_{1.8}$Co$_{0.2}$Se$_2$ single crystals has been presented. Two Raman active modes from the superconducting (I$_4$/mmm) phase and seven phonon modes from the insulating (I$_4$/m) phase are observed in the investigated frequency range. The same number of observed modes in these two compounds, together with their similar energies, suggests that phase separation is also present in a K$_{0.8}$Fe$_{1.8}$Co$_{0.2}$Se$_2$ single crystal. The temperature-induced change of Raman mode linewidth is in good agreement with the lattice anharmonicity model. The behavior of the Raman mode energy as a function of temperature for all the analyzed modes is well described by the contribution from the lattice thermal expansion alone. The sudden change in the A$_{1g}$ mode energy near $T_C$ in K$_x$Fe$_{2-x}$Se$_2$ is due to the rearrangement of the electronic states to which this mode couples as the superconducting gap opens. A rather small electron–phonon coupling constant at the Γ-point is obtained from the superconductivity-induced A$_{1g}$ phonon energy renormalization.

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