Effect of K Doping on Phonons in Ba$_{1-x}$K$_x$Fe$_2$As$_2$

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The lattice dynamics of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ ($x = 0.00, 0.27$) have been studied by inelastic X-ray scattering measurement at room temperature. K doping induces the softening and broadening of phonon modes in the energy range $E = 10$–$15$ meV. Analysis with a Born-von Kármán force-constant model indicates that the softening results from reduced interatomic force constants around (Ba,K) sites following the displacement of divalent Ba by monovalent K. The phonon broadening may be explained by the local distortions induced by the K substitution. Extra phonon modes are observed around the wave vector $q = (0.5,0,0)$ at $E = 16.5$ meV for the $x = 0.27$ sample. These modes may arise either from the local disorder induced by K doping or from electron-phonon coupling.

**KEYWORDS:** Fe-based superconductor, inelastic X-ray scattering, phonon dispersion

1. Introduction

Since the discovery of Fe-based superconductors with superconducting transition temperatures ($T_c$) of up to 55 K$^{1-5}$, intensive studies have been conducted to clarify the mechanism of Cooper pair formation and to improve their $T_c$ values. For example, the possibility of phonon-mediated superconductivity has been studied intensively.$^{5-15}$ Calculations using the density functional perturbation theory, however, revealed very weak electron-phonon coupling constants, suggesting that, within those simplified models, conventional phonon-mediated superconductivity is unlikely.$^{14,15}$ Nevertheless, a mechanism involving phonons remains possible. In fact, both $T_c$ and the band structure of Fe-based superconductors are sensitive to the crystal structure,$^{16-18}$ suggesting the importance of electron-lattice coupling. For example, the coupling between lattice and magnetism$^{19}$ or Fermi surface nesting$^{20}$ may induce high-$T_c$ superconductivity. Recently, the results of neutron scattering measurements on CaFe$_2$As$_2$ have been interpreted as evidence for strong electron-phonon coupling.$^{11}$ Inelastic X-ray scattering measurements on NdFeAsO$_{1-y}$F$_y$ powder samples revealed softening in the phonon density of states under F doping.$^{12}$ In contrast, recent studies on doped and undoped BaFe$_2$As$_2$ single crystals by inelastic X-ray scattering measurement revealed no significant doping-induced phonon softening.$^{13}$ Further studies on phonon dynamics using single crystals are essential for identifying relevant phonon modes and elucidating the role of phonons in the appearance of superconductivity in Fe-based superconductors.

$M$Fe$_2$As$_2$ ($M =$ Ba, Ca, or Sr) is a parent compound of Fe-based superconductors. A maximum $T_c$ of 38 K is observed for Ba$_{1-x}$K$_x$Fe$_2$As$_2$ ($x = 0.40$).$^{21}$

Undoped $M$Fe$_2$As$_2$ shows a tetragonal-to-orthorhombic structural phase transition accompanied by the appearance of antiferromagnetic long-range ordering, which can be attributed to the nesting of the Fermi surface along $(0.5,0.5,0)$ in tetragonal notation. Although its $T_c$ is lower than the maximum $T_c$ of the $R$FeAsO ($R =$ rare-earth) system, $M$Fe$_2$As$_2$ offers the advantages of a simpler crystal structure and the availability of large single crystals. Both systems share layers formed by FeAs tetrahedrons. Between these FeAs layers, $R$FeAsO exhibits blocks consisting of two atoms, i.e., $R$ and O, while $M$Fe$_2$As$_2$ exhibits blocks consisting of only one atom, i.e., $M$ (Fig. 1(a)). The simpler crystal structure of $M$Fe$_2$As$_2$ facili-
Fig. 2. Energy spectra of phonons observed at \( Q = (2.5,2.5,0) \) for \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) \((x = 0.00, 0.27)\). Solid lines show the results of fits with three Lorentzian components.

Fig. 3. Energy spectra of phonons observed at \( Q = (4.48,0,0) \) for \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) \((x = 0.00, 0.27)\). Solid lines show the results of fits with four Lorentzian components.

Fig. 4. Energy spectra of phonons observed at \( Q = (4.48,0,0) \) \((x = 0.00, 0.27)\) and \((0.51,1,19)\) for \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) \((x = 0.00 \text{ (a)}, 0.27 \text{ (b)})\). Solid lines depict Lorentzian fits. Spectra at \( Q = (4.48,0,0) \) are shifted vertically for ease of viewing with the zero level shown by horizontal dashed lines.

tates phonon analysis for deriving the nature of superconducting FeAs layers. In this study, we therefore analyze the phonon dispersion of \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) by inelastic X-ray scattering measurement on single crystals.

2. Experimental Procedure

Single crystals of \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) were grown by the self-flux method. For the \( x = 0.00 \) sample, the FeAs precursor was prepared from Fe and As at 900 °C for 10 h in an evacuated atmosphere and then mixed with Ba in the atomic ratio \( \text{Ba}:\text{FeAs} = 1:4 \). For the K-doped sample, the starting materials of Ba, K, Fe, and As were mixed in the atomic ratio \( 0.6:0.4:2:2 \). All mixtures were placed in a BN-coated quartz or \( \text{Al}_2\text{O}_3 \) crucible and sealed in a quartz tube. For the \( x = 0.00 \) sample, the tube was heated to 1140 °C, whereas for the K-doped sample, the tube was preheated to 600 °C, maintained at that temperature for 10 h, and then heated to 1140 °C. All samples were maintained at the maximum temperature for 10 h and cooled to 1040 °C at a rate of 0.4-1 °C/h, followed by decanting the flux.

The compositions of the single crystals were confirmed by lattice-constant measurements with a laboratory X-ray diffractometer (RINT-1000, RIGAKU) at room temperature. The lattice constant of the K-doped sample was \( c = 13.22 \) Å, corresponding to a composition of \( x = 0.27 \). The \( T_c \) of the K-doped single crystal was measured using a SQUID magnetometer at a magnetic field of 10 Oe after zero-field cooling. The \( T_c \) onset for the \( x = 0.27 \) sample is 37 K, close to the maximum \( T_c \) of the \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) system.

Inelastic X-ray scattering measurements were carried out using synchrotron radiation at BL35XU in SPring-8. The incident X-ray energy was fixed at 21.75 keV using the Si(11,11,11) reflection as a monochromator in the backscattering setup. The energy resolution was about \( \Delta E = 1.5 \) meV. Single crystals were mounted on a thin carbon fiber attached to a thin glass capillary. All measurements were conducted at room temperature.

Phonon dispersion was analyzed using a Born-von Kármán force-constant model. The longitudinal and transverse force constants of 11 atomic pairs were chosen as fitting parameters (Table I and Fig. 1(a)), and the calculated energies were fitted to the measured data. For the \( x = 0.27 \) sample, we assumed a virtual atom with an averaged atomic mass corresponding to the mixed occupation of this site by Ba and K.

3. Results and Discussion

Figure 2 shows the energy spectra of the \( x = 0.00 \) and \( 0.27 \) samples at the scattering vector \( Q = (2.5,2.5,0) \), where the wave vector \( \mathbf{q} = (0.5,0.5,0) \) is the same as the nesting vector of the Fermi surface. The solid lines depict Lorentzian fits. Comparing the \( x = 0.00 \) and \( 0.27 \) samples, the well-defined peak around \( E = 12 \) meV softens about 1 meV and the linewidth broadens upon K doping. For the other peaks, the doping-induced energy shifts amount to less than 0.5 meV. These observed phonon spectra are almost consistent with previous data reported in ref. 13, except for the softening and broadening. Note that the phonon mode at \( E = 22 \) meV, which has been...
Fig. 5. Phonon dispersion curves of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($x = 0.00, 0.27$). Solid and dashed lines depict results of calculations based on the Born-von Kármán model for $x = 0.00$ and $0.27$, respectively. Light-colored lines depict modes that are unobservable with the chosen scattering vectors. (a) Phonon modes along $(\zeta,0,0)$ observed at $Q = (4+\zeta,0,0)$ and $(\zeta,1,19)$, (b) at $Q = (\zeta,4,0)$, (c) dispersion along $(\zeta,\zeta,0)$ at $Q = (2+\zeta,2+\zeta,0)$ and (d) dispersion along $(0,0,\zeta)$ at $Q = (0,0,16+\zeta)$. Squares and circles depict results of measurements for $x = 0.00$ and $0.27$, respectively.
predicted to couple strongly with the static magnetic moment,\textsuperscript{11,13} exhibits only a weak K doping dependence, although magnetic long-range ordering of $x = 0.00$ disappears with K doping.

To clarify whether the softening and broadening are associated with nesting or a magnetic interaction, we measured phonon spectra at a different Q position of approximately (4.5,0,0), where Q is tilted at 45$^\circ$ to the nesting vector (Fig. 3). The solid lines depict Lorentzian fits. As shown, the well-defined peak around $E = 14$ meV softens about 1 meV upon K doping accompanied by a broadening similar to the observation at $Q = (2.5,2.5,0)$. Since similar softening and broadening are observed along different $q$ directions, it appears unlikely that these effects are caused by Fermi surface nesting or a magnetic interaction. A displacement pattern of the well-defined peaks around $E = 14$ meV is shown in Fig. 1(b). These modes are characterized by large (Ba,K) amplitudes, rendering them very sensitive to K doping. The broadening may be due to distortion induced by K doping.

Phonon modes with energies around $E = 16-20$ meV at $Q = (4.48,0,0)$ also show softening from $E = 19.5$ to 16.5 meV with K doping (Fig. 3). Since the corresponding phonon intensity is weak owing to the small dynamical structure factor and disturbing peaks present around $E = 14$ meV, we have confirmed the spectra around $Q = (0.5,1,19)$ where q is identical and the lattice-dynamics model predicts a higher intensity for the mode around $E = 16-20$ meV (Fig. 4). The displacement pattern of the corresponding phonon mode is shown in Fig. 1(c). For the $x = 0.00$ sample, a well-defined peak is observed at $E = 19.5$ meV around $Q = (0.5,1,19)$, which agrees well with the energy observed around $Q = (4.5,0,0)$ (Fig. 4(a)). On the other hand, for the $x = 0.27$ sample, the peak observed at $E = 16.5$ meV around $Q = (4.5,0,0)$ is not observable around $Q = (0.5,1,19)$ (Fig. 4(b)). However, a well-defined peak is observed at $E = 19.5$ meV, which is the same energy as that observed for the $x = 0.00$ sample. Therefore, the peak observed at $E = 16.5$ meV around $Q = (4.5,0,0)$ in the doped sample is unlikely to be associated with the $E = 19.5$ meV signals; it appears to be associated with the additional mode at the lower energy appearing in only the doped sample.

Figure 5 shows the observed and calculated dispersion curves for the $x = 0.00$ and 0.27 samples. The phonon modes shown in Figs. 3 and 4 are indicated in Fig. 5(a), and those shown in Fig. 2 are indicated in Fig. 5(c). The extra phonon modes appearing around $Q = (4.5,0,0)$ in the $x = 0.27$ sample are depicted by open squares in Fig. 5(a). Doping-induced phonon softening is observed in the energy range $E = 10-15$ meV at $Q = (4+\zeta,0,0)$ and $(2+\zeta,2+\zeta,0)$. The energies of all the other phonon modes studied are almost identical for the $x = 0.00$ and 0.27 samples. All data, except the extra modes, are reasonably well described by the calculation. The obtained interatomic force constants are shown in Table I.

The observed phonon softening is reproduced by reducing the (Ba,K)-(Ba,K) and (Ba,K)-Fe force constants. As shown in Fig. 5, the calculated energies of the corresponding $x = 0.00$ phonon modes (solid lines) that soften upon doping decrease toward the dashed lines of the $x = 0.27$ phonon modes. The energies of these phonon modes are sensitive to the force constants involving the (Ba,K) atoms, since these atoms contribute largely to the corresponding polarization pattern (see Fig. 1(b)). The smaller (Ba,K)-(Ba,K) and (Ba,K)-Fe force constants of the K doped sample appear to be reasonable owing to the fact that monovalent K ions exhibit a smaller valency than divalent Ba ions.

The extra modes observed around $Q = (4.5,0,0)$ and $E = 16.5$ meV, on the other hand, cannot be explained by the Born-von Kármán harmonic model. A plausible explanation for the extra modes is the splitting of lower-energy modes near $E = 13$ meV, where (Ba,K) atoms dominate the polarization pattern (Fig. 1(b)). The substitution of Ba by K induces significant local disorder due to the difference in ionic radius thereby allowing for mode splitting as well as for broadening. In addition, the difference in atomic mass by nearly a factor of three may enhance the splitting of phonon frequency. In fact, in Ba$_{1-x}$K$_x$B$_4$O$_7$ superconducting materials, K doping leads to disorder that has been characterized in ref. 24. However, we may not rule out the possibility that extra modes in Ba$_{0.75}$K$_{0.25}$Fe$_2$As$_2$ arise from electron-phonon coupling. Recently, $^{57}$Fe nuclear resonant inelastic scattering measurement has revealed that the Fe partial density of states of Ba$_{1-x}$K$_2$Fe$_2$As$_2$ shows softening around $E = 20$ meV with K doping.\textsuperscript{25} It could be that the extra modes split rather from the modes located at a higher energy, i.e., $E = 19.5$ meV, owing to electron-phonon coupling. NdFeAsO$_{1−y}$F$_y$ powder samples analyzed by inelastic X-ray scattering measurement also show phonon softening at a similar energy of $E = 20$ meV with carrier doping.\textsuperscript{12} Because the present modes around $Q = (4.5,0,0)$ and $E = 16.5$ meV consist mainly of Fe and As atom vibrations (Fig. 1(c)), it is reasonable for the soft phonon modes in NdFeAsO$_{1−y}$F$_y$ to be of comparable energy. It is worth noting that As-Fe-As bond angles that can be associated with $T_c$\textsuperscript{16} vibrate in the corresponding phonon modes.

Table I. Interatomic force constants obtained from analysis based on the Born-von Kármán model. Only the force constants of (Ba,K)-Fe and (Ba,K)-(Ba,K) pairs are reduced under K doping.

| Pair                  | Longitudinal force constant (mdyn/Å) | Transverse force constant (mdyn/Å) |
|----------------------|-------------------------------------|-----------------------------------|
| $f_1$                | Fe-As                               | 0.70                              |
| $f_2$                | Fe-Fe                               | 0.13                              |
| $f_3$                | (Ba,K)-As                            | 0.08                              |
| $f_4$                | As-As                               | 0.02                              |
| $f_5$                | (Ba,K)-Fe                            | 0.10                              |
| $f_6$                | As-As                               | 0.03                              |
| $f_7$                | As-As                               | 0.04                              |
| $f_8$                | (Ba,K)-(Ba,K)                       | 0.08                              |
| $f_9$                | Fe-Fe                               | 0.03                              |
| $f_{10}$             | Fe-As                               | 0.03                              |
| $f_{11}$             | (Ba,K)-(Ba,K)                       | 0.02                              |

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4. Conclusions

We have studied the phonon dynamics of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ ($x = 0.00, 0.27$) by inelastic X-ray scattering measurement. K doping induces phonon softening and broadening for modes in the energy range $E = 10$-$15$ meV. These modes are characterized by large (Ba,K) vibrations. Born-von Kármán analysis indicates that the softening results from a reduction in interatomic force constants. The broadening can be a consequence of the local disorder induced by K substitution. Extra modes observed around $E = 10^{-15}$ meV for the $x = 0.27$ sample appear to arise from the phonon splitting due to either the local disorder or the electron-phonon interaction.

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