Rapid Communication

Evolution of the 251 cm^{-1} infrared phonon mode with temperature in $Ba_{0.6}K_{0.4}Fe_2As_2$*

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The far-infrared optical reflectivity of an optimally doped $Ba_{1-x}K_xFe_2As_2$ ($x = 0.4$) single crystal is measured from room temperature down to 4 K. We study the temperature dependence of the in-plane infrared-active phonon at 251 cm^{-1}. This phonon exhibits a symmetric line shape in the optical conductivity, suggesting that the coupling between the phonon and the electronic background is weak. Upon cooling down, the frequency of this phonon continuously increases, following the conventional temperature dependence expected in the absence of a structural or magnetic transition. The intensity of this phonon is temperature independent within the measurement accuracy. These observations indicate that the structural and magnetic phase transition might be completely suppressed by chemical doping in the optimally doped $Ba_{0.6}K_{0.4}Fe_2As_2$ compound.

Keywords: iron-based superconductor, phonon mode, infrared spectroscopy

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1. Introduction

Since the discovery of superconductivity with a transition temperature up to 26 K in $LaFeAsO_{1-x}F_x$,[1] six systems of iron-based superconductors have been reported. $LaFeAsO_{1-x}F_x$, which has a ZrCuSiAs-type layered structure, is categorized as the 1111 system; $Ba_{1-x}K_xFe_2As_2$[2] and $Ba(Fe_{1-x}Co_x)_2As_2$[3] derived from $BaFe_2As_2$ represent the 122 system; LiFeAs[4] and NaFeAs[5] are classified as the 111 system; FeSe[6] and $Fe(Se_{1-x}Te_x)_{0.82}$[7] are representative of the 11 system; and materials with more complex layered structures like $(Sr_3Sc_2O_5)Fe_2As_2$[8] and $(Sr_4V_2O_6)Fe_2As_2$[9] are categorized as the 32522 and the 21311 systems, respectively. Among these six systems of iron-pnictides, the Ba122 system is one of the most extensively studied. Unlike the cuprates, the parent compound of this system, $BaFe_2As_2$, is a poor Pauli-paramagnetic metal with a structural and magnetic phase transition at 140 K.[10] The superconductivity arises with the suppression of the structural and magnetic phase transition, which can be achieved by doping or pressure. The Ba atoms can be partially substituted with K atoms, resulting in hole-doped materials[2] with a maximum $T_c \approx 38$ K, while the substitution of Fe atoms with Co or Ni atoms produces electron doped materials[3,11] with a maximum $T_c \approx 25$ K. In the parent compound $BaFe_2As_2$, the structural and magnetic phase transition is accompanied by an infrared phonon anomaly, which might be associated with the orbital ordering in the Fe–As layers.[12] In this sense, investigations into the temperature dependence of the infrared phonon in optimally doped Ba122 materials is highly desired. The Fourier transform infrared (FTIR) spectrometer is a standard tool used to probe the infrared phonons.[13,14] In this paper, we study the evolution of the in-plane infrared-active phonon mode at about 251 cm^{-1} with temperature in optimally doped $Ba_{1-x}K_xFe_2As_2$ ($x = 0.4$)

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single crystals. We find that, with the decreasing temperature, this phonon frequency hardens whereas its intensity (spectral weight) remains a constant. These observations suggest that the structural and magnetic phase transition might be completely suppressed by the chemical substitution in $Ba_{0.6}K_{0.4}Fe_2As_2$.

2. Experiments

High quality $Ba_{0.6}K_{0.4}Fe_2As_2$ single crystals were grown by using the FeAs flux method.[15] The resistivity of the crystal exhibited a very sharp superconducting transition at $T_c = 39.1$ K with a width $\Delta T_c \sim 0.5$ K. Near normal incidence reflectivity from 20 cm^{-1} to 12000 cm^{-1} was measured by using Bruker IFS113 and IFS66v spectrometers at 19 different temperatures ranging from room temperature down to 4 K. The *in situ* gold overfilling technique[16] was used to obtain the absolute reflectivity of the sample. The sample was cleaved prior to each temperature run. In order to calculate the optical conductivity via the Kramers–Kronig relations, the data were extended to the visible and UV range (10000–55000 cm^{-1}) at room temperature with an AvaSpec-2048 × 14 model fiber optic spectrometer.

3. Results and discussion

Figure 1 shows the optical reflectivity of optimally doped $Ba_{1-x}K_xFe_2As_2$ ($x = 0.4$) single crystal at different temperatures in the infrared frequency range. In the normal state, the material exhibits a metallic response, which is characterized by a very high reflectivity at low frequencies and a tendency to approach unity at zero frequency. At 4 K, the low frequency reflectivity increases and reaches a flat unity response below 160 cm^{-1}. This behavior is associated with a fully open superconducting gap.[17,18] The weak feature observed at ∼251 cm^{-1} (shown by the arrow) is the in-plane infrared-active phonon mode. $Ba_{0.6}K_{0.4}Fe_2As_2$ has the tetragonal $I4/mmm$ space group, the same as the parent $BaFe_2As_2$ above T_N. Two E_u modes are expected in the *ab*-plane response. In $BaFe_2As_2$, both modes (at ∼94 and 253 cm^{-1}) are observed.[12] Nevertheless, in the optimally doped $Ba_{0.6}K_{0.4}Fe_2As_2$, the one at ∼94 cm^{-1} has a very small intensity and does not show a clear feature in the reflectivity spectrum. This might be due to the increase of the electronic screening with more carriers doped into the material. Nevertheless, it is the highest frequency phonon renormalized when the material undergoes the magenetic and structural phase transition.[12]

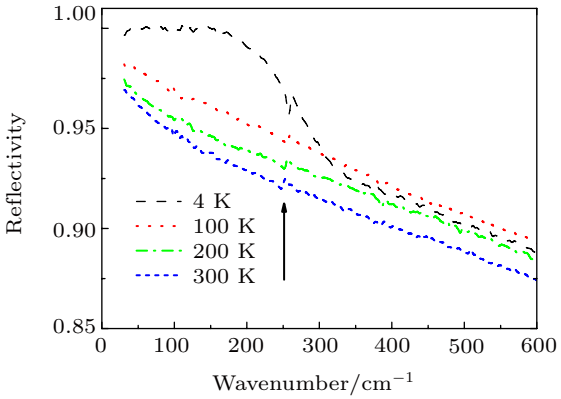

Fig. 1. (colour online) Infrared reflectivity of optimally doped $Ba_{1-x}K_xFe_2As_2$ ($x = 0.4$) at selected temperatures.

The real part of optical conductivity is derived from the reflectivity via the Kramers–Kronig analysis and is shown in the main panel of Fig. 2 as dashed lines. A prominent in-plane infrared-active phonon mode at 251 cm^{-1} is observed at 300 K (short dashed line). At 4 K (dashed line), this phonon mode shifts to 259 cm^{-1}, but does not show any obvious change in its intensity. This phonon sits on a high conductivity background due to the Drude-like behavior of the conducting carriers.

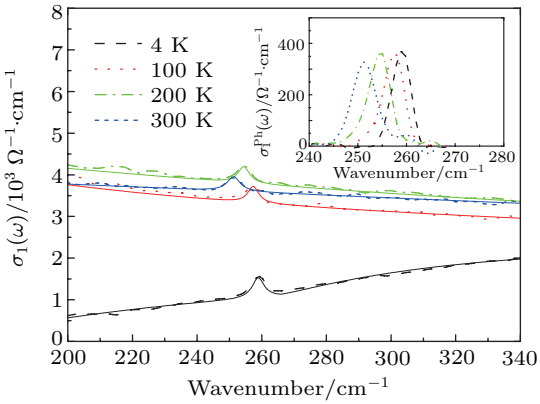

Fig. 2. (colour online) Optical conductivity of $Ba_{1-x}K_xFe_2As_2$ ($x = 0.4$) at different temperatures in the frequency range from 200 cm^{-1} to 340 cm^{-1}. The thin solid lines through the data are corresponding fits with the Drude–Lorentz model. An in-plane infrared-active phonon mode can be seen at about 250 cm^{-1}, which can be reproduced by a Lorentz oscillator. The inset shows the optical conductivity of the phonon at several selected temperatures, the background has been subtracted from the total optical conductivity.

In order to quantitatively study the evolution of this phonon mode with temperature, we fit the optical conductivity to a Drude–Lorentz model, which is

written as

$$\sigma_1(\omega) = \frac{2\pi}{Z_0}\sum_k \Big[\frac{\Omega_{\mathrm{p},k}^2}{\tau_k(\omega^2+\tau_k^{-2})} + \frac{\gamma_k\omega^2 S_k^2}{(\Omega_k^2-\omega^2)^2+\gamma_k^2\omega^2}\Big], \quad (1)$$

where Z_0 is the vacuum impedance. The first term in Eq. (1) corresponds to a sum of free-carrier Drude responses each characterized by a plasma frequency $\Omega_{\mathrm{p},k}$ and a scattering rate τ_k^{-1}. The second term is a sum of Lorentz oscillators each characterized by a resonance frequency Ω_k, a line width γ_k, and a plasma frequency S_k.

The thin solid lines in Fig. 2 are fittings of the data to Eq. (1). The data are adjusted in the whole measured range up to 10000 cm^{-1}, and we utilize two Drude peaks, one Lorentzian for the phonon and the other for the mid-infrared absorption. To better observe the phonon behavior, we subtract from our data the Drude and the mid-infrared contributions to $\sigma_1(\omega)$. The result is shown in the inset of Fig. 2. This panel shows the measured optical conductivity for the phonon alone. We can see that the phonon peak shifts to upper frequencies at lower temperatures and that the line shapes are symmetric. In a solid, if a lattice mode couples to the spins or to the electronic background, it exhibits an asymmetric Fano line shape.[19] However, we note that the phonon mode line shape in the optical conductivity is symmetric and can be well described by a Lorentz oscillator, which indicates a very weak coupling between the phonon mode and the electronic background. To pursue our analysis on this phonon, we will utilize the phonon parameters obtained from the fittings. These parameters are listed in Table 1 for 300 K and 4 K, where Ω_0 represents the resonant frequency of the phonon. The intensity of the phonon is proportional to S^2.

Table 1. Fitting parameters of the phonon mode at 300 K and 4 K.

Temperature/K	$\Omega_0/\mathrm{cm}^{-1}$	γ/cm^{-1}	S/cm^{-1}
300	251.3	4.9	320.4
4	258.9	4.6	364.5

In Fig. 3(a), the resonant frequency of the phonon is displayed as a function of temperature. With decreasing temperature, the frequency of the phonon continuously increases. If no structural or magnetic phase transition occurs in a solid, the frequency of the lattice vibration mode as a function of temperature $\Omega(T)$ is given by[20]

$$\Omega(T) = \Omega(0)\exp\Big[-3\gamma_{\mathrm{G}}\int_0^T \alpha(T')\,\mathrm{d}T'\Big], \quad (2)$$

where $\Omega(0)$ represents the frequency of the phonon at zero temperature, γ_{G} is the Grüneisen parameter, and α is the coefficient of linear thermal expansion. The temperature dependence of the phonon mode frequency given by the above expression closely approximates to a quadratic behavior. In the parent compound $BaFe_2As_2$, the phonon mode at $\sim$ 253 cm^{-1} shows a clear frequency renormaliztion at the structural and magnetic transition.[12] However, in $Ba_{0.6}K_{0.4}Fe_2As_2$, we find that the temperature dependence of the phonon frequency can be fit to a quadratic behavior very well from room temperature down to 4 K, as shown by the dashed line in Fig. 3(a). This fact excludes the presence of a structural or magnetic transition in the optimally doped $Ba_{0.6}K_{0.4}Fe_2As_2$.

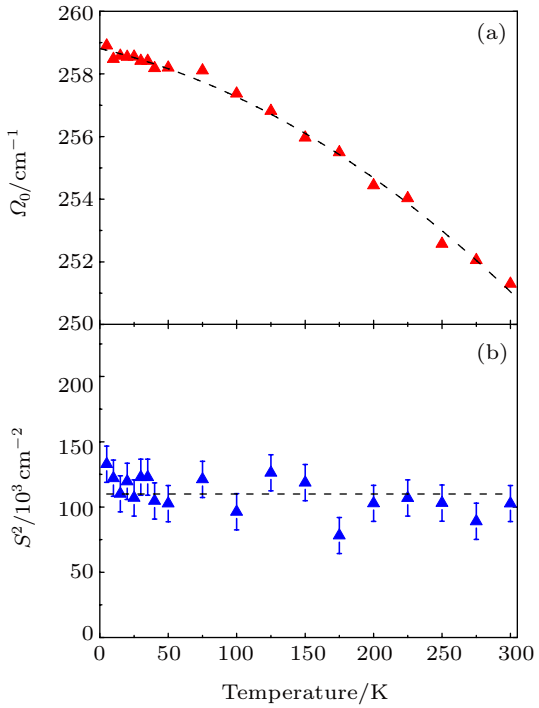

Fig. 3. (colour online) Panel (a) shows the phonon mode frequency as a function of temperature, the dashed line represents the temperature dependence of phonon frequency in the absence of structural or magnetic transition. Panel (b) shows the intensities of the phonon at different temperatures.

The solid triangles in Fig. 3(b) denote the intensity of the phonon as a function of temperature. The intensity of the infrared-active phonon mode is proportional to $\sum_i \mu_i^2$, where μ_i represents the net dipole moment. If the bonding or the coordination does not change in the unit cell of a material, i.e. no structural phase transition happens, the intensity of the phonon mode is expected to remain a constant. Here, we note that the intensity of the 251 cm^{-1} phonon

in $Ba_{0.6}K_{0.4}Fe_2As_2$ remains a constant from room temperature to 4 K. This is quite different from the 253 cm^{-1} phonon mode in $BaFe_2As_2$, which doubles in intensity below T_N.[12] Therefore, the phonon effects present at the structural and magnetic transition in the parent compound are absent in the optimally doped $Ba_{0.6}K_{0.4}Fe_2As_2$, indicating that the structural and magnetic phase transition might be completely suppressed by the chemical doping.

4. Conclusion

The infrared optical conductivity of optimally doped $Ba_{1-x}K_xFe_2As_2$ ($x = 0.4$) single crystal is determined at 19 different temperatures from accurate reflectivity measurements. An in-plane infrared-active phonon at 251 cm^{-1} is observed at all temperatures. The symmetric line shape of this phonon in the optical conductivity implies a very weak coupling between the phonon and the electronic background. We fit the phonon to a Lorentz oscillator to quantitatively study its evolution with temperature. As the temperature decreases, the phonon frequency increases continuously, following an almost quadratic temperature dependence, while its intensity remains a constant from room temperature down to 4 K. These observations suggest that the structural and magnetic phase transition is absent in the optimally doped $Ba_{0.6}K_{0.4}Fe_2As_2$ compound and might be completely suppressed by the chemical doping.

References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296

[2] Rotter M, Tegel M and Johrendt D 2008 *Phys. Rev. Lett.* **101** 107006

[3] Sefat A S, Jin R, McGuire M A, Sales B C, Singh D J and Mandrus D 2008 *Phys. Rev. Lett.* **101** 117004

[4] Tapp J H, Tang Z, Lü B, Sasmal K, Lorenz B, Chu P C W and Guloy A M 2008 *Phys. Rev.* B **78** 060505

[5] Parker D R, Pitcher M J, Baker P J, Franke I, Lancaster T, Blundell S J and Clarke S J 2009 *Chem. Commun.* **16** 2189

[6] Hsu F C, Luo J Y, Yeh K W, Chen T K, Huang T W, Wu P M, Lee Y C, Huang Y L, Chu Y Y, Yan D C and Wu M K 2008 *Proc. Natl. Acad. Sci. USA* **105** 14262

[7] Fang M H, Pham H M, Qian B, Liu T J, Vehstedt E K, Liu Y, Spinu L and Mao Z Q 2008 *Phys. Rev.* B **78** 224503

[8] Zhu X Y, Han F, Mu G, Zeng B, Cheng P, Shen B and Wen H H 2009 *Phys. Rev.* B **79** 024516

[9] Zhu X Y, Han F, Mu G, Cheng P, Shen B, Zeng B and Wen H H 2009 *Phys. Rev.* B **79** 220512

[10] Rotter M, Tegel M, Johrendt D, Schellenberg I, Hermes W and Pöttgen R 2008 *Phys. Rev.* B **78** 020503

[11] Li L J, Luo Y K, Wang Q B, Chen H, Ren Z, Tao Q, Li Y K, Lin X, He M, Zhu Z W, Cao G H and Xu Z A 2009 *New J. Phys.* **11** 025008

[12] Akrap A, Tu J J, Li L J, Cao G H, Xu Z A and Homes C C 2009 *Phys. Rev.* B **80** 180502

[13] Ma J Y, Fang X, Muhammad K, Zhao H Y, Bi C Z, Zhao B R and Qiu X G 2008 *Chin. Phys.* B **17** 3313

[14] Lobo R P S M, Moreira R L, Lebeugle D and Colson D 2007 *Phys. Rev.* B **76** 172105

[15] Luo H Q, Wang Z S, Yang H, Cheng P, Zhu X Y and Wen H H 2008 *Superconductor Science and Technology* **21** 125014

[16] Homes C C, Reedyk M, Cradles D A and Timusk T 1993 *Appl. Opt.* **32** 2976

[17] Li G, Hu W Z, Dong J, Li Z, Zheng P, Chen G F, Luo J L and Wang N L 2008 *Phys. Rev. Lett.* **101** 107004

[18] Charnukha A, Dolgov O V, Golubov A A, Matiks Y, Sun D L, Lin C T, Keimer B and Boris A V 2011 *Phys. Rev.* B **84** 174511

[19] Fano U 1961 *Phys. Rev.* **124** 1866

[20] Menéndez J and Cardona M 1984 *Phys. Rev.* B **29** 2051