Signatures of the spin-phonon coupling in Fe$_{1+y}$Te$_{1-x}$Se$_x$ alloys

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Abstract

Raman scattering spectra of Fe$_{1+y}$Te$_{1-x}$Se$_x$ (x=0, y=0.07; x=0.1, y=0.05 and x=0.4, y=0.02) alloys are measured in a temperature range between 20 K and 300 K. The A$_{1g}$ and B$_{1g}$ Raman active modes have been experimentally observed at energies 156 and 198 cm$^{-1}$, which is in rather good agreement with the lattice dynamics calculation. The antiferromagnetic spin ordering below 70 K in Fe$_{1+y}$Te leaves a fingerprint only in the B$_{1g}$ phonon mode linewidth and energy, whose temperature dependence follows the normalized magnetic susceptibility, indicating the presence of the spin-phonon coupling. The frequency and the linewidth of the A$_{1g}$ mode assume a conventional anharmonic temperature dependence in all measured samples, which is also the case for the B$_{1g}$ mode in the Se doped samples. The linewidth (energy) of the A$_{1g}$ mode decreases (increases) with doping, whereas the opposite is seen for the B$_{1g}$ mode.

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1. Introduction

The discovery of a new LaFeAsO$_{1−x}$F$_x$ superconductor family with $T_c=24$ K spurred the research in the field of iron-based superconductors [1–3]. Among these compounds, iron-chalcogenides have the simplest crystal structure of the PbO type including only Fe and Ch atoms (Ch=S, Se and Te) [4,5]. This structure consists of Fe square planar sheets with Ch ions forming distorted tetrahedra around the Fe ions, analogous to the structure of the FeAs planes in LaFeAsO, BaFe$_2$As$_2$, and LiFeAs, which are prototypes of the known families of Fe–As based high-$T_c$ superconductors [6–8]. In fact, these structures match the reported structure of K$_x$Fe$_2$−$_y$Se$_2$, with interspersed FeSe stacked along the c-axis [9,10].

FeTe crystallizes in the tetragonal system of the P4/mmm space group [11]. By lowering the temperature below 70 K, there is a structural transition from the tetragonal to the monoclinic lattice (P2$_1$/m space group), accompanied by the antiferromagnetic spin ordering [12]. Partial substitution of Te with Se progressively suppresses the magnetic ordering temperature and structural transition [13], and leads to the superconductivity at low temperatures [11]. The $T_c$ of the Fe$_{1+y}$Te$_{1-x}$Se$_x$ system can reach up to 14 K at ambient pressure for $x=0.5$ [14] and 27 K at a pressure of 1.46 GPa [15].

The mechanism for superconductivity in the iron-based materials is still under debate [16]. In particular, the magnetic ordering and spin fluctuations are expected to have an important impact on the phonon dynamics and lead to the increase of the electron-phonon coupling [17] which is, however, still insufficient to explain high $T_c$ in these compounds.

Raman scattering is an excellent tool for a study of the phonon properties of materials and its coupling to the electronic charge and spin excitations. Although the Raman scattering spectra in Fe$_{1+y}$Te$_{1-x}$Se$_x$ alloys were analyzed in Refs. [18–21], there are several features in the spectra that have not been fully resolved and understood. Two modes at about 155(±4) and 199(±3) cm$^{-1}$ are experimentally observed and assigned as the A$_{1g}$ (Te-ions vibration along the z-axis) and the B$_{1g}$ (Fe-ions vibration along the z-axis) modes, respectively. Calculated phonon frequencies of these modes agree with the experimental data within 10%, see Table 1. The temperature dependence of the phonon mode linewidth and energy of undoped FeTe sample is, however, controversial. Gnezdilov et al. [20] found an increase of the A$_{1g}$ mode linewidth from 28 to 31.4 cm$^{-1}$ by lowering the temperature from 200 K to 5 K. This A$_{1g}$ mode temperature dependence deviates from the anharmonic picture. In addition, they found the A$_{1g}$ mode energy change about the phase transition temperature...
of $T_N = 70$ K. Um et al. [21], on the other hand, found only minor $A_{1g}$ mode broadening (from 19 to 21 cm$^{-1}$ by lowering the temperature to 5 K) without the energy change at the phase transition temperature. The $B_{1g}$ mode hardens and broadens with decreasing temperature down to $T_N$ and then softens and narrows down to 5 K in both papers [20,21]. This feature is, however, suppressed in the excess-Fe rich sample Fe$_{1.07}$Te [21]. One additional mode at about 136 cm$^{-1}$ for undoped FeTe sample is observed in Refs. [18,21], which origin is related to the sample decomposition.

In this paper we have measured the Raman scattering spectra of Fe$_{1+x}$Te$_{1-x}$Se$_y$ ($x=0$, $y=0.07$; $x=0.1$, $y=0.05$ and $x=0.4$, $y=0.02$) alloys in the temperature range from room temperature down to 20 K in the spectral range from 90 up to 300 cm$^{-1}$. In the optical phonon region of FeTe we have observed two optical phonons of the $A_{1g}$ (156 cm$^{-1}$) and the $B_{1g}$ (198 cm$^{-1}$) symmetries. The observed frequencies are in rather good agreement with our lattice dynamics calculations. The temperature dependence of the energy and linewidth of the $B_{1g}$ mode in Fe$_{1.07}$Te has a maximum at about $T_N$ and follows the lineshape of the normalized magnetic susceptibility as seen in our magnetization measurements. Doping with Se suppresses $T_N$ and a conventional temperature dependence is observed for the $B_{1g}$ mode. We find that the energy and the linewidth of the $A_{1g}$ mode assume a conventional anharmonic temperature dependence in all three samples. Phonon mode at 136 cm$^{-1}$ is not observed in our samples. In Se doped samples the $A_{1g}$ mode hardens and narrows, whereas the $B_{1g}$ mode softens and broadens. These features cannot be simply explained just as a consequence of the substitution of Te by lighter and smaller Se ions and the disorder effect.

2. Experiment and numerical method

Single crystals of Fe$_{1+x}$Te$_{1-x}$Se$_y$ ($x=0$, $y=0.07$; $x=0.1$, $y=0.05$ and $x=0.4$, $y=0.02$) alloys were grown using self-flux method, as described in Ref. [22], Raman scattering measurements were performed on freshly cleaved (001)-oriented samples using JY T64000 and Tri-Vista 557 Raman systems 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$^2$. Low temperature measurements were performed using KONTI CryoVac continuous flow cryostat with 0.5 mm thick window. Magnetization measurements were carried out in Quantum Design MPMS-XL5 system.

We have calculated the lattice dynamics of both FeTe phases: the room temperature phase (tetragonal symmetry) and the low temperature phase (monoclinic symmetry). The lattice dynamics calculations are performed within the density functional perturbation theory (DFPT) [23] as implemented in the QUANTUM ESPRESSO package [24] using the generalized gradient approximation with the PW91 exchange-correlation functional which is used to obtain ultra-soft pseudo-potentials. Iron (tellurium) pseudo-potential includes $3s^2$ $4s^2$ $3p^6$ $4p^6$ $3d^5$ ($5s^2$ $5p^4$ $4d^{10}$) electron states for the valence electrons. The Brillouin zone is sampled with a Monkhorst-Pack $16 \times 16 \times 10$ k-space mesh for higher-symmetry phase ($P4/nmm$ space group) and $16 \times 16 \times 8$ k-space mesh for lower-symmetry phase ($P2_1/m$ space group). Unit cell is constructed using experimental values of the lattices parameters [25] ($P4/nmm$ phase: $a=0.38219$ nm, $c=0.62851$ nm; $P2_1/m$ phase: $a=0.38312$ nm, $b=0.37830$ nm, $c=0.62643$ nm and $\beta=89.17$degr). The Energy cutoffs for the wave functions and the electron densities are 64 Ry and 762 Ry, respectively, which are the highest suggested radii for the chosen pseudo-potentials. We have used Gaussian smearing of 0.001 Ry.
observed at frequencies of about 156 and 198 cm$^{-1}$ from the (001) plane of the sample, only the A$_{1g}$ and the B$_{1g}$ modes can be observed. In the parallel polarization configuration $e_1||e_s$, the A$_{1g}$ could be seen for an arbitrary orientation of the sample, whereas the B$_{1g}$ mode vanishes for the sample orientation in which $e_1||e_s$ for $\Theta=0^\circ$. By rotating the sample, we were able to find the orientation in which the peak around 198 cm$^{-1}$ vanishes. Consequently, this peak is assigned as the B$_{1g}$ symmetry mode, whereas the peak at around 156 cm$^{-1}$ is assigned as the A$_{1g}$ mode. This is in agreement with the previous assignment [18–21] and our lattice dynamics calculation (Table 1). The additional mode at about 136 cm$^{-1}$, as found in Ref. [21] for nearly stoichiometric Fe$_{1.07}$Te sample, has not been observed in the spectra.

Fig. 1. (Color online) (a) Room temperature polarized Raman scattering spectra of the FeTe crystal (the tetragonal phase, space group P4/nmm) measured for different sample orientations together with normal modes. (b) The normal modes of lattice vibrations of the low temperature monoclinic phase of FeTe (the P2$_1$/m space group). The length of the arrows is proportional to the square roots of the vibration amplitudes.

3. Results and discussion

The results of the lattice dynamics calculations, together with the experimental data are presented in Table 1. Normal modes of Raman active phonons of both FeTe phases are given in Fig. 1.

Fig. 1(a) shows the polarized Raman scattering spectra of Fe$_{1.07}$Te crystal measured from the (001) plane at room temperature in the spectral range from 90 to 300 cm$^{-1}$. Two peaks are observed at frequencies of about 156 and 198 cm$^{-1}$. According to the selection rules, when Raman scattering spectrum is measured from the (001) plane of the sample, only the A$_{1g}$ and the B$_{1g}$ modes can be observed. In the parallel polarization configuration $e_1||e_s$, the A$_{1g}$ could be seen for an arbitrary orientation of the sample, whereas the B$_{1g}$ mode vanishes for the sample orientation in which $e_1||e_s$ for $\Theta=0^\circ$. By rotating the sample, we were able to find the orientation in which the peak around 198 cm$^{-1}$ vanishes. Consequently, this peak is assigned as the B$_{1g}$ symmetry mode, whereas the peak at around 156 cm$^{-1}$ is assigned as the A$_{1g}$ mode. This is in agreement with the previous assignment [18–21] and our lattice dynamics calculation (Table 1). The additional mode at about 136 cm$^{-1}$, as found in Ref. [21] for nearly stoichiometric Fe$_{1.07}$Te sample, has not been observed in the spectra.

Fig. 2 shows the unpolarized Raman scattering spectra of Fe$_1$$_{1.07}$Te$_{1.0}$Se$_{0.4}$ sample measured at room temperature. Replacing Te with Se ions leads to the A$_{1g}$ (the B$_{1g}$) mode hardening (softening), which is indicated in Fig. 2 where the vertical dashed lines denote the energies for the undoped sample. A significant reduction (for about 10 cm$^{-1}$) of the A$_{1g}$ mode linewidth, as well as an increase of the B$_{1g}$ mode linewidth (for about 2.4 cm$^{-1}$) is found in the Fe$_{1.02}$Te$_{0.6}$Se$_{0.4}$ sample. The A$_{1g}$ mode hardening is a consequence of the replacement of heavier Te ions with lighter Se ions (the mass effect) and the unit-cell contraction (c-axis reduction) upon doping [26]. On the other hand, an introduction of substitutional impurities (disorder) should in general induce the linewidth increase in doped compounds [27], as it was observed for the B$_{1g}$ mode. In the case of the A$_{1g}$ mode, the phonon mode linewidth decrease can be related to the decrease of the electron–phonon interaction upon doping [28]. This assumption is also supported by the DFT calculations of the electron–phonon coupling constant in the nonmagnetic solution, which shows a significant decrease of $\lambda$ as the Te atoms are replaced with the Se atoms ($\lambda$(FeTe) = 0.30 [29], $\lambda$(FeTe$_{0.5}$Se$_{0.5}$) = 0.22 [30], and $\lambda$(FeSe) = 0.17 [31]). At this point we can not exclude the possibility that excess Fe ions may play role in the behaviour of the A$_{1g}$ mode. The excess Fe ions are located within Te layer [32] and may produce qualitatively different effects from those induced by the substitutional disorder.

In the case of the B$_{1g}$ mode (Fe ions vibrations) we expected the mode softening due to the unit cell compression with doping by the Se atoms. Instead of the hardening, we observe the mode softening in the Fe$_{1.02}$Te$_{0.6}$Se$_{0.4}$ sample, which is in accordance with the DFT calculations of the electron–phonon interaction upon doping [28]. This assumption is also supported by the DFT calculations of the electron–phonon coupling constant in the nonmagnetic solution, which shows a significant decrease of $\lambda$ as the Te atoms are replaced with the Se atoms ($\lambda$(FeTe) = 0.30 [29], $\lambda$(FeTe$_{0.5}$Se$_{0.5}$) = 0.22 [30], and $\lambda$(FeSe) = 0.17 [31]). At this point we can not exclude the possibility that excess Fe ions may play role in the behaviour of the A$_{1g}$ mode. The excess Fe ions are located within Te layer [32] and may produce qualitatively different effects from those induced by the substitutional disorder.

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with expectations for FeTe$_{1-x}$Se$_x$ solid solution based on a linear fit of the mode energy values of parent crystals FeTe (this work) and FeSe [33], see the inset of Fig. 2. However, one should also have in mind that the change in the excess iron concentration (decrease from $y=0.07$ for the undoped to $y=0.02$ for the 40% Se doped sample) may have significant impact on the B$_{1g}$ mode energy [21].

Upon cooling, no additional Raman lines have been observed although the crystal structure and the crystal symmetry of FeTe are changed at $T < T_N$. By comparing the calculated phonon energies in both phases (see Table 1) it can be seen that the phonon energies do not differ substantially. In fact, the E$_1$g mode of the tetragonal phase splits into A$_{1g}$/B$_{1g}$ (A$_4$/B$_2$) doublets of monoclinic symmetry, which appear at energies very close to the mode energies of tetragonal phase. In the case of the A$_{1g}$ mode there is virtually no energy change between the A$_{1g}$ mode of the tetragonal phase and the A$_{2g}$ mode of the monoclinic phase (see Table 1). The B$_{1g}$ mode of the tetragonal phase changes energy (softens) and symmetry (becomes A$_g$ symmetry one) at the phase transition temperature. The change of the symmetry of this mode in the low temperature phase does not influence the low temperature Raman spectra because the energy of this mode (A$_2^g$) is far enough (40 cm$^{-1}$) from the (A$_4^g$) mode, preventing the phonon mode coupling between them [34]. The lattice vibration normal modes of the low temperature phase are given in Fig. 1(b).

Fig. 3 shows the energy and the linewidth temperature dependence for the A$_{1g}$ and the B$_{1g}$ modes of the Fe$_{1.07}$Te single crystal, which are obtained from the Raman spectra measured at various temperatures using the Lorentzian profile fit. Solid and dashed lines in Fig. 3(c,d) are calculated curves obtained using the well known anharmonicity effect formula, [35,27] which takes into account three-phonon processes for the temperature dependent change of the phonon energy and linewidth:

$$\omega(T) = \omega_0 - C[1 + 2/(e^x - 1)],$$

(1)

$$\Gamma(T) = \Gamma_0 + A[1 + 2/(e^x - 1)],$$

(2)

where $\omega_0$ ($\Gamma_0$) is the temperature independent energy (intrinsic linewidth), $C$ ($A$) is the anharmonic constant and $x = \hbar \omega_0/(2k_BT)$. The best fit parameters are indicated in Fig. 3(c,d). A rather good agreement between the experimental data and fitted curves for the A$_{1g}$ mode is observed in the whole temperature range (above and below $T_N=70$ K). Large value of $\Gamma_0$ parameter in comparison to the anharmonic constant ($24.5 > 1$ cm$^{-1}$) also suggest the importance of the electron–phonon interaction for this mode [36] or the orbital degrees of freedom of Fe ions [20].

Upon cooling, the B$_{1g}$ mode of the undoped sample shows pronounced broadening down to $T_N$, when it suddenly narrows (see Fig. 3(b)). This deviation from the standard anharmonic picture suggests the presence of additional scattering process. The energy and broadening temperature change of the B$_{1g}$ mode closely follows the normalized magnetic susceptibility curve, as can be seen in Fig. 4, indicating that spin-phonon coupling leaves a

![Fig. 3](image)

**Fig. 3.** (Color online) The phonon energy and the linewidth temperature dependence of the A$_{1g}$ (c,d) and the B$_{1g}$ (a,b) modes of Fe$_{1.07}$Te single crystal together with existing literature data [20,21]. The solid and the dashed lines represent calculated curves using Eqs. (1) and (2), respectively.

![Fig. 4](image)

**Fig. 4.** (Color online) Temperature dependence of the normalized frequency and linewidth of the B$_{1g}$ mode together with the normalized magnetic susceptibility (solid line) of Fe$_{1.07}$Te single crystal.
fingerprint in the phonon dynamics of FeTe. This is to be expected because the Bragg mode represents vibrations of Fe-ions which carry the magnetic moments. Softening of the Bragg mode below $T_T$ is a consequence of the antiferromagnetic ordering and structural change (see Table 1).

In the case of the $Fe_{1.02}Te_{0.6}Se_{0.4}$ sample, the temperature dependences of the phonon mode energy and linewidth follow the standard anharmonic picture for both vibrational modes. The absence of the Bragg mode softening in this sample at temperatures below 70 K is a consequence of the suppression of antiferromagnetic ordering with doping [13].

Finally, in Fig. 3 we compared energy and linewidth vs temperature dependence of the $A_{1g}$ and $B_{1g}$ modes with previously published results [20,21]. The $B_{1g}$ mode energy and linewidth (Fig. 3(ab)) show no substantial difference from our results (taking into account that error bar in our case is $\pm 2$ cm$^{-1}$; in Ref. [21] is $\pm 4$ cm$^{-1}$) except of the position of $FWHM(T)$ curve maximum, which is related to the sample composition, i.e., $T_T$. The $A_{1g}$ mode energy temperature dependences follow the same trend (mode hardening) by the temperature lowering in Refs. [20,21] and in this work. The main difference is the linewidth change by the temperature lowering (Fig. 3(d)). We have shown that the linewidth narrows by temperature lowering, but an opposite trend is found in Refs. [20,21]. Our finding is in accordance with an anharmonic picture.

4. Conclusion

In summary, we have measured the Raman scattering spectra of the $Fe_{1+x}Te_{1-x}Se_x$ ($x=0, y=0.07; x=0.1, y=0.05$ and $x=0.4, y=0.02$) alloys at various temperatures. Two out of four Raman-active modes predicted by the factor-group analysis have been experimentally observed and assigned. Energies of these modes are in rather good agreement with our lattice dynamics calculations. The main focus of our work was the temperature and doping dependence of the phonon energies and linewidths, whose features are, to some extent, contradictory in previous works. We have shown that the $A_{1g}$ mode (corresponding to the Te ions vibration along the $z$-axis) follows the standard anharmonic temperature dependence (which originates in the phonon-phonon interaction) both in the doped and the undoped samples. The width of the $A_{1g}$ mode at room temperature is significantly reduced in the doped samples. In the case of the $B_{1g}$ mode, the phonon frequency and the linewidth closely follow the magnetic susceptibility temperature dependence, indicating the presence of the spin-phonon coupling in the undoped $Fe_{1.07}Te$ sample. The antiferromagnetic ordering is suppressed by doping, and $Fe_{1.02}Te_{0.6}Se_{0.4}$ sample follows a conventional temperature dependence in both phonon modes.

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