Raman spectra in iron-based quaternary CeO$_{1-x}$F$_x$FeAs and LaO$_{1-x}$F$_x$FeAs

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Abstract
Raman spectra have been measured on iron-based quaternary CeO$_{1-x}$F$_x$FeAs and LaO$_{1-x}$F$_x$FeAs with different amounts of fluorine doping at room temperatures. A group analysis has been made to clarify the optical modes. Based on first-principle calculations, the observed phonon modes can be assigned accordingly. In LaO$_{1-x}$F$_x$FeAs, the $E_g$ and $A_{1g}$ modes related to the vibrations of La are suppressed with increasing F doping. However, F doping only has a small effect on the $E_g$ and $A_{1g}$ modes of Fe and As. The Raman modes of La and As are absent in rare-earth substituted CeO$_{1-x}$F$_x$FeAs, and the $E_g$ mode of oxygen, corresponding to the in-plane vibration of oxygen, moves to around 450 cm$^{-1}$ and shows a very sharp peak. The electronic scattering background is low, and electron–phonon coupling is not evident for the observed phonon modes. Three features are found above 500 cm$^{-1}$, which may be associated with multi-phonon processes. Nevertheless, it is also possible that they are related to magnetic fluctuations or interband transitions of d orbitals, considering their energies.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The discovery of iron-based superconductors has stimulated much interest in searching for higher-$T_c$ superconductors without copper oxide planes. Soon after the first LaO$_{1-x}$F$_x$FeAs was reported with $T_c = 26$ K [1], rare-earth substitution compounds SmO$_{1-x}$F$_x$FeAs and CeO$_{1-x}$F$_x$FeAs were synthesized, and their $T_c$ values can go up to above 40 K [2, 3]. For LaO$_{1-x}$F$_x$FeAs, $T_c$ can be raised to above 40 K under high pressure [4]. A higher $T_c$ of 52 K in Fe-based series superconductors was reported in PrO$_{1-x}$F$_x$FeAs which was synthesized under high pressure [5]. The measurements of Hall coefficients indicates that the carriers in the superconductors are electron like [6]. On the other hand, hole-doped (La, Sr)O$_{1-x}$F$_x$FeAs was synthesized successfully with $T_c = 26$ K [7]. Transition-metal substituted LaO$_{1-x}$F$_x$NiAs was also reported with $T_c = 4$ K and an extremely sharp superconducting transition [8]. Most recently, a very exciting result shows that a maximum $T_c$ of 55 K can be obtained even without F doping in the Fe-based superconductors [9]. Up to now the highest $T_c$ of 56.5 K in iron-based superconductors was recorded in Gd$_{1-x}$Th$_x$OFeAs without F doping [10]. It is believed that electrons are transferred into FeAs conducting layers effectively by Th$^{4+}$ substitution of Gd$^{3+}$, just like F doping. This means that the carrier concentration and superconducting transition temperature can be controlled and tuned by the oxygen content and rare-earth substitution, which is very similar to the case of cuprate superconductors. A very high upper critical field over 100 T was estimated by resistance measurements under high magnetic field, even exceeding that of cuprate superconductors [11].

The electronic structure study of iron-based superconductors started from LaOFeP [12], followed by the recent focusing on LaOFeAs. The early band structure calculations suggested that the pure LaOFeAs compound is a nonmagnetic metal but with strong ferromagnetic or antiferromagnetic...
ABON iron-based materials has been done on the collective excitations. In fact, a nice Raman scattering study provided additional information about magnetic, electronic and other modes of vibrations in the compounds. Raman scattering is known as a unique technique in studying optical phonon modes. So it is important and requires a basic knowledge of some important interactions such as electron–phonon coupling. Nevertheless, the spectra only covered 100–400 cm$^{-1}$ and in-plane vibrations were not resolved due to the limitation of the ab plane.

In this study, Raman scattering measurements at room temperature from 30 to 2000 cm$^{-1}$ have been performed on two kinds of iron-based material, CeO$_{1-x}$Fe$_x$As with $x = 0$ ($T_c = 0$ K) and 0.16 ($T_c = 41$ K), and LaO$_{1-x}$Fe$_x$As with $x = 0$ ($T_c = 0$ K), 0.04 ($T_c = 17$ K) and $x = 0.08$ ($T_c = 26$ K), respectively. Six Raman phonon modes were observed below 500 cm$^{-1}$. Based on the structural data obtained by neutron scattering and x-ray diffraction, a group analysis was made to classify the optical modes. Then first-principle calculations were carried out to calculate the optical modes at the $\Gamma$-point. By comparison with the calculations and group analysis, the observed phonon modes were assigned accordingly. The changes of some modes with F doping and rare-earth substitution are discussed. The electron–phonon coupling was found to be small. Three weak features were observed above 500 cm$^{-1}$, which may be associated with multi-phonon processes, magnetic fluctuations or interband transitions.

2. Experimental details

Polycrystal samples of CeO$_{1-x}$Fe$_x$As and LaO$_{1-x}$Fe$_x$As were synthesized by the solid state reaction method. As precursor materials, CeAs or LaAs were presynthesized by reacting Ce or La chips and As pieces in an evacuated quartz tube. Then FeAs was obtained with a similar process. Using CeAs/LaAs, Fe, CeO$_2$/La$_2$O$_3$, CeF$_3$/LaF$_3$, and FeAs as starting materials, the raw materials with stoichiometric ratio were mixed thoroughly and pressed into pellets. The pellets were wrapped with Ta foil and sealed in an evacuated quartz tube. Almost pure phase polycrystal samples were obtained after annealing. The detailed procedure for preparing the samples can be found elsewhere [3]. The temperature dependence of the susceptibility and resistivity of the polycrystal used in the present Raman study is shown in figure 1. The transition temperature width shows the high quality of the samples. For CeO$_{1-x}$Fe$_x$As, many shining single crystal grains can be seen even without a microscope. After polishing, a flat alloy-like surface can be obtained. Unfortunately the Raman signal is too weak to be detected because most intensities of the excitation light are reflected back by the alloy-like surface. In order to increase the intensities of incident light effectively and to resolve more phonon modes beyond the ab plane, the present Raman measurements were done with finely ground powder, in which the sizes of the crystal grains are several microns in diameter, estimated with a microscope.

The Raman measurements were performed with a triple-grating monochromator (Jobin Yvon T64000), which works with a microscopic Raman configuration. A 50× objective microscopic lens with a working distance of 10.6 mm was used to focus the incident light on the sample and collect the scattered light from the sample. The detector was a back-illuminated CCD cooled by liquid nitrogen. An solid state laser (Laser Quantum Torus 532) with high stability and very narrow width of the laser line was used with an excitation wavelength of 532 nm. The laser beam, of 3 mW, was focused into a spot of less than 10 μm in diameter on the sample surface.

Figure 1. Temperature dependence of resistivity for (a) CeO$_{1-x}$F$_x$FeAs and (b) LaO$_{1-x}$F$_x$FeAs used in the present Raman measurements. The sharp superconducting transitions indicate the high quality of samples. Especially for the superconducting CeO$_{1-x}$F$_x$FeAs, a quite small residual resistivity is shown by extrapolation.
3. Assignment of Raman phonons

The refined structure parameters of LaOFeAs were obtained by neutron scattering and x-ray diffraction. It has a tetragonal ZrCuSiAs-type structure with space group $P4/nmm$ (No. 129, origin choice 2) and point group $D_{4h}$. Atoms La, O, Fe and As occupy Wyckoff positions 2c, 2a, 2b and 2c, respectively. Symmetry analysis shows that there are eight Raman-active modes and six infrared (IR)-active modes, as classified in table 1.

To assign the phonon modes at the $\Gamma$-point, the phonon frequencies of nonmagnetic LaOFeAs crystal have been calculated in the framework of the density perturbation functional theory (DFPT) using plane-wave pseudopotentials [23] with the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [24] for the exchange–correlation potentials. First, a self-consistent calculation was accomplished using the experimental lattice parameters and the energy minimized internal atomic positions [17], during which the following parameters were adopted: 45 and 360 Ryd cutoffs of kinetic energy for the wavefunction and charge density, respectively; $24 \times 12$ uniform $k$-space for the $k$-point integration; and a Gaussian smearing parameter of 0.002 Ryd. Although it has been mentioned that the optimized heights of As atoms to the nearest Fe layers (or $z_{As}$) vary by as much as 0.1 Å between local density approximation (LDA) and GGA calculations [25], which invokes quantitative discrepancies in the magnetic properties [26, 27], the zone-center phonon frequencies are not much affected in our calculations as the internal forces on atoms are balanced in both cases. Then, by diagonalizing the dynamical matrix generated from the converged potentials, we obtained the eigenvalues, namely the squared phonon frequencies, and the eigenvectors to derive the displacements of each atom in a specific vibration mode.

Eight frequency-distinguishable Raman-active phonon modes were deduced at the $\Gamma$-point, consisting of four two-fold degenerated $E_g$, two non-degenerated $A_{1g}$, and two non-degenerated $B_{1g}$ modes, which is consistent with the group symmetry analysis. Comparing them to the above Raman spectra revealed a fairly good agreement; see figure 2 and table 2. All the Raman-active vibration modes are characterized in figure 3, where the arrows indicate the vibration directions of the corresponding atoms, with their lengths representing the relative vibration amplitude compared with those of other atoms in the same mode.

4. Discussion

In figure 2, at first glance the LaOFeAs system has a similar phonon spectrum for different amounts of F doping. There is no obvious frequency shift or change of peak shape for the three samples. However, there still exist some small changes with varying F doping. Both the $E_g$ mode at 96 cm$^{-1}$ and the $A_{1g}$ mode at 161 cm$^{-1}$ of La are suppressed gradually with increasing F doping. This can be naturally understood as the effect of F dopants entering the LaO layer. The sensitivity of La phonon modes to F doping may be considered as an alternative way to characterize the concentration of F doping.

F doping has little effect on the Fe- and As-dominated phonon modes, such as the $B_{1g}$ mode at 214 cm$^{-1}$ and the $E_g$ mode at 278 cm$^{-1}$ of Fe, and the $E_g$ mode at 137 cm$^{-1}$ of As. This can be easily explained because the F dopants are far away from the FeAs layer and thus have little effect on Fe- and As-related vibrations. These three modes have a special significance in exploring the mechanism of the magnetic phase transition near 140 K revealed by some experiments. As suggested by neutron scattering and other measurements, there also exists a structural changes just above the temperature of the magnetic phase transition. For iron-based superconductors, it is still a key issue to make clear whether there is a connection between the magnetic transition and the structural change or not. The modes related to Fe and As would play an important role in answering the above question in further Raman scattering measurements at various temperatures and with applied magnetic field.

A relatively broad $E_g$ mode of oxygen was observed near 423 cm$^{-1}$ for LaOFeAs. We will come back to this point in combination with the results for CeOFeAs in the following.

A striking change in the Raman spectra of CeOFeAs is that the $E_g$ phonon of oxygen becomes very strong and moves to 450 cm$^{-1}$. The reason for the sharper oxygen $E_g$ mode can be attributed to the better sample quality of CeOFeAs, as described above. Interestingly, infrared measurements also revealed a mode with quite high intensities near 430 cm$^{-1}$ in both LaOFeAs and CeOFeAs, which moves to higher frequencies with decreasing temperatures, showing a typical phonon behavior [3, 18]. However, the first-principle calculations show that there should be no IR-active mode above

| Atom | Wyckoff position | Raman modes | IR modes |
|------|------------------|-------------|----------|
| La   | 2c               | $A_{1g} + E_g$ | $A_{2u} + E_u$ |
| O/F  | 2a               | $B_{1g} + E_g$ | $A_{2u} + E_u$ |
| Fe   | 2b               | $B_{1g} + E_g$ | $A_{2u} + E_u$ |
| As   | 2c               | $A_{1g} + E_g$ | $A_{2u} + E_u$ |
400 cm$^{-1}$. It is speculated that an inversion symmetry breaking can cause an intensity leakage of the oxygen E$_g$ mode into the IR channel. If this is true, it means that a subtle structural distortion could occur even at room temperatures.

The other change is that the modes below 200 cm$^{-1}$, contributed by La and As, cannot be observed. This may be caused by the distortion of the LaO layer due to the substitution of La by smaller Ce ions. Raman results based on single crystals are needed to confirm this point.

Besides the above first-order Raman phonons, there exist some common features above 500 cm$^{-1}$ in both LaOFeAs and CeOFeAs, which are located at 590, 846, and 1300 cm$^{-1}$. Generally, these features originate from multi-phonon processes. For instance, the feature at 846 cm$^{-1}$ can be contributed by two E$_g$ phonons of oxygen simply considering its frequency. On the other hand, the energies of features correspond to 73, 105, and 161 meV, respectively. Theses are close to the interband differences of d orbitals [28], and also the

Figure 3. Raman-active modes of LaOFeAs: (a) E$_g$ of La (96 cm$^{-1}$); (b) E$_g$ of As and Fe (137 cm$^{-1}$); (c) A$_{1g}$ of La (161 cm$^{-1}$); (d) A$_{1g}$ of As (not observed); (e) B$_{1g}$ of Fe (214 cm$^{-1}$); (f) E$_g$ of Fe (278 cm$^{-1}$); (g) B$_{1g}$ of O (not observed); (h) E$_g$ of O (423 cm$^{-1}$).
ferromagnetic/antiferromagnetic exchange energies according to electronic structure calculations [17, 21]. At present it cannot be ruled out that some of the features are associated with interband transitions or magnetic fluctuations. Further Raman experiments under applied magnetic field could be helpful to answer this question.

Although polycrystal samples were used in the present measurements, it can be seen that electronic scattering background is low. And for the observed modes, especially those of Fe and As, it is not easy to distinguish evident features of electron–phonon coupling. Measurements on single crystals cannot be ruled out that some of the features are associated with phonons, more features found at higher frequencies may be related to magnetic excitations or interband transitions. Further Raman experiments under applied magnetic field could be helpful to answer this question.

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Table 2. Assignment of optical phonons in comparison with the first-principle calculations. The cited data of IR phonons comes from [15]. Only the dominant atoms involved in a specific mode are listed here. The last column describes the approximate direction and phase of vibration, where [001], [010], and [001] are parallel to the a, b, and c crystal axes, respectively. See figure 3 for the crystal coordinate system.

| Experimental (cm⁻¹) | Calculated (cm⁻¹) | Symmetry | Active | Atom | Vibration |
|--------------------|------------------|----------|--------|------|-----------|
| 97                 | 60.956 57        | E_g      | IR     | La, As, Fe | [010] or [001] |
| 96                 | 80.731 06        | A_2g     | IR     | La, As, Fe | [001] |
| 137                | 111.022 50       | E_g      | Raman  | La    | [001] or [010], out-of-phase |
| 161                | 138.062 64       | E_g      | Raman  | As, Fe | [110] or [110], out-of-phase |
| 203.741 54         | 180.567 08       | A_1g     | Raman  | La    | [001], out-of-phase |
| 214                | 203.741 54       | A_1g     | Raman  | As    | [001], out-of-phase |
| 248                | 218.219 30       | B_1g     | Raman  | Fe    | [001], out-of-phase |
| 266                | 248.158 52       | A_2u     | IR     | Fe, As| [001] |
| 266                | 268.087 70       | E_g      | IR     | Fe, As| [010] or [010] |
| 278                | 279.246 77       | E_g      | Raman  | Fe    | [110] or [110], out-of-phase |
| 338                | 280.216 50       | E_g      | IR     | O     | [010] or [010], in-phase |
| 338                | 282.449 46       | B_1g     | Raman  | O     | [001], out-of-phase |
| 423                | 338.454 20       | A_2u     | IR     | O     | [001], in-phase |
| 423                | 388.805 67       | E_g      | Raman  | O     | [001] or [010], out-of-phase |