We report the polarized Raman spectra of undoped ReOF\textsubscript{e}As (Re = Sm, La) collected at room temperature from \textit{ab} surfaces of impurity free microcrystals. The spectra exhibit sharp phonon lines on very weak electronic background. The frequency and symmetry of the four Raman phonons involving out-of-plane atomic vibrations are found at 170 cm\textsuperscript{-1} (\textit{A}\textsubscript{1\text{g}}, Sm), 201 cm\textsuperscript{-1} (\textit{A}\textsubscript{1\text{g}}, As), 208 cm\textsuperscript{-1} (\textit{B}\textsubscript{1\text{g}}, Fe), 345 cm\textsuperscript{-1} (\textit{B}\textsubscript{1\text{g}}, O) for SmOF\textsubscript{e}As, and 162 cm\textsuperscript{-1} (\textit{A}\textsubscript{1\text{g}}, La), 208 cm\textsuperscript{-1} (\textit{A}\textsubscript{1\text{g}}, As), 201 cm\textsuperscript{-1} (\textit{B}\textsubscript{1\text{g}}, Fe), 316 cm\textsuperscript{-1} (\textit{B}\textsubscript{1\text{g}}, O) for LaOF\textsubscript{e}As.

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### Table I: Wyckoff positions and irreducible representations (Γ-point phonon modes) for ReOF\textsubscript{e}As (space group P4/\textit{nmnm}, No.129, origin choice 2, \(Z=2\)). The Raman tensors are given in an orthogonal system with \(z\) and \(x\) directions along the \(C\textsubscript{4}\) and \(C\textsubscript{4}^{'\text{v}}\) axes, respectively.

| Atom   | Wickoff position | Γ-point phonon modes |
|--------|-----------------|----------------------|
| Sm/La  | 2c              | \(A\textsubscript{1\text{g}} + A\textsubscript{2\text{u}} + E\textsubscript{g} + E\textsubscript{u}\) |
| O      | 2a              | \(B\textsubscript{1\text{g}} + A\textsubscript{2\text{u}} + E\textsubscript{g} + E\textsubscript{u}\) |
| Fe     | 2b              | \(B\textsubscript{1\text{g}} + A\textsubscript{2\text{u}} + E\textsubscript{g} + E\textsubscript{u}\) |
| As     | 2c              | \(A\textsubscript{1\text{g}} + A\textsubscript{2\text{u}} + E\textsubscript{g} + E\textsubscript{u}\) |

Modes classification:
\(\Gamma\text{Raman} = 2A\textsubscript{1\text{g}} + 2B\textsubscript{1\text{g}} + 4E\textsubscript{g}\)
\(\Gamma\text{Acoustic} = A\textsubscript{2\text{u}} + E\textsubscript{u}\)

Raman tensors:
\(A\textsubscript{1\text{g}}(x^2 + y^2, z^2) \rightarrow \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}\)
\(B\textsubscript{1\text{g}}(x^2 - y^2) \rightarrow \begin{bmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{bmatrix}\)
\(E\textsubscript{g}\text{(xz), E\textsubscript{g}\text{(yz)}} \rightarrow \begin{bmatrix} 0 & 0 & -c \\ 0 & 0 & e \\ -c & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & e \\ 0 & e & 0 \end{bmatrix}\)

Recent report of superconductivity at 26 K in LaO\textsubscript{1-x}F\textsubscript{2}As (\(x=0.05\) - 0.12)\cite{1} has triggered an intense wave of research activities comparable to that in the early days of the superconducting cuprates and MgB\textsubscript{2}. Soon after, other members of the Fe-As oxypnictides family were found superconducting at even higher temperatures.\cite{2} The calculated electron-phonon coupling\cite{3, 4} is found weak to produce a superconducting state within the Eliashberg theory at the experimentally measured \(T_c\), and unconventional origin of superconductivity mediated by antiferromagnetic spin fluctuations is suggested.\cite{5} Although the phonons may play little role in mediating the superconducting state in oxypnictides, their study using Raman spectroscopy can provide important information on the superconducting state through phonon coupling to the Raman active electronic excitations.\cite{6, 7}

In this Communication we present the results of a polarized Raman study of ReOF\textsubscript{e}As (Re = Sm, La). The Raman spectra were obtained under a microscope from very small plate-like single crystals within polycrystalline samples, which allowed reliable measurements only of the non-degenerated Raman modes in ReOF\textsubscript{e}As. The experimentally determined symmetry and frequencies of the Raman active phonons are compared with those predicted by a group-theoretical-analysis of the Γ-point phonon modes and recently reported \textit{ab initio} calculations.\cite{3, 4}

LaOF\textsubscript{e}As and SmOF\textsubscript{e}As crystallize in the \(P4/\text{nmnm}\) (space group No.129) structure.\cite{1, 4} In Table I are given the number of the expected Γ-phonons, their symmetry and the corresponding Raman tensors.\cite{8} The eigenvectors of the \(A\textsubscript{1\text{g}}\) and \(B\textsubscript{1\text{g}}\) modes are displayed in Fig. 1. These non-degenerated modes involve predominantly out-of-plane atomic vibrations. The \(E\textsubscript{g}\) modes eigenvectors (not shown in Fig. 1) are parallel to the \(ab\)-plane.

The polycrystalline pellets of LaOF\textsubscript{e}As and SmOF\textsubscript{e}As used in our experiment were prepared by solid state sintering. Firstly, La (Sm) metal powders and As chips were mixed and pressed into pellet, sealed in vacuumed quartz tube, and heated at 1000° C for 20-50 hrs. The formed LaAs (SmAs) was then mixed with Fe powder and Fe\textsubscript{2}O\textsubscript{3} according to the designed stoichiometry, pressed into pellets and sealed in quartz tubes again. The final reaction was carried out at 1150° C for 60 hrs. The powder X-ray diffraction of the LaOF\textsubscript{e}As phase revealed a
tetragonal structure with room temperature lattice constants of $a = 0.4021$ nm and $c = 0.8723$ nm. The lattice constants of the SmOFeAs phase were $a = 0.3942$ nm and $c = 0.8498$ nm.

The Raman spectra of small single crystals were measured under a microscope ($\times 100$-magnification) attached to a Horiba JY T64000 triple spectrometer. Both compounds, SmOFeAs and LaOFeAs, appeared to be highly absorbing in the visible range and having relatively poor thermal conductivity that required use of incident laser power density below $10^4$ W/cm$^2$. In addition, phonon scattering intensity was found to be relatively weak, about $10^{-3}$ of that of Si. The Raman spectra presented here were excited with the 632.8 nm laser line. Raman measurements with the 514.5 nm excitation confirmed that the collected Raman spectra are intrinsic.

The Raman spectra of small single crystals were measured and considering the Raman tensors $R$ given in Table I, one should expect the Raman mode intensity $I(\varphi) \propto [\vec{e}_i \cdot R \vec{e}_s]^2$ ($\vec{e}_i$ and $\vec{e}_s$ are the incident and scattered light polarizations) to vary with the angle $\varphi$ between the [100] crystallographic direction (along the a-axis) and the incident light polarization as $I_{A_{1g}}^\parallel(\varphi) \propto a^2$ and $I_{A_{1g}}^\perp(\varphi) = 0$ for parallel $\vec{e}_i \parallel \vec{e}_s$ and crossed $\vec{e}_i \perp \vec{e}_s$ scattering configurations, respectively. For the $B_{1g}$ modes the expected intensity dependencies are $I_{B_{1g}}^\parallel(\varphi) \propto c^2 \cos^2 2\varphi$ and $I_{B_{1g}}^\perp(\varphi) \propto c^2 \sin^2 \varphi \cos^2 \varphi$.

No $E_g$ modes should be observable with incident and scattered light polarizations in the $ab$-plane.

FIG. 2: (Color online) Polarized Raman spectra of SmOFeAs and LaOFeAs measured at room temperature in back scattering configurations with light polarizations along certain crystallographic directions. The scattering configurations are presented in Porto notation. The $Z$ direction is along [001] ($c$-axis), $X$ along [100] ($a$-axis), and $X'$ is parallel to [110]. The $Y$ and $Y'$ directions are orthogonal to $X$ and $X'$. The Raman spectra in Fig. 2 were taken from square shaped plates (10 x 10 $\mu$m$^2$), which were found to obey thoroughly the angular dependencies $I_{A_{1g}/B_{1g}}^\parallel(\varphi)$ and $I_{A_{1g}/B_{1g}}^\perp(\varphi)$ for light polarizations in the $ab$-plane. The assignment of the phonon lines in Fig. 2 is straightforward. The measured non-degenerated modes in SmOFeAs are: 170 cm$^{-1}$ ($A_{1g}$, Sm), 201 cm$^{-1}$ ($A_{1g}$, As), 208 cm$^{-1}$ ($B_{1g}$, Fe), and 345 cm$^{-1}$ ($B_{1g}$, O). For LaOFeAs the corresponding modes are 162 cm$^{-1}$ ($A_{1g}$, La), 208 cm$^{-1}$ ($A_{1g}$, As), 201 cm$^{-1}$ ($B_{1g}$, Fe), 316 cm$^{-1}$ ($B_{1g}$, O).

The phonon dispersions and electron-phonon coupling of LaOFeAs have already been reported as calculated using the Quantum Espresso code with ultrasoft pseudopotentials. The calculations predict phonon branches with little dispersion in the z direction ($c$-axis), reflecting the layered structure of LaOFeAs, and phonon spectrum that spreads up to 500 cm$^{-1}$. The oxygen vibrations are expected between 300 cm$^{-1}$ and 500 cm$^{-1}$.
whereas those of La, Fe, and As are occupying the range below 300 cm$^{-1}$. No assignment of the Γ-point phonons, however, is made in Refs. [3, 4]. Given the measured non-degenerated Raman phonon frequencies in LaOF$_2$As are between 150 cm$^{-1}$ and 350 cm$^{-1}$ we can assign them to the four non-degenerated dispersion curves crossing the Γ-point near 180 cm$^{-1}$, 200 cm$^{-1}$, 217 cm$^{-1}$, and 311 cm$^{-1}$ in the calculated phonon dispersion curves. Therefore, the calculated frequencies are in fairly good agreement (less then 10% deviation) with the experimental ones.

Further, we briefly compare the Raman phonons of SmOF$_2$As with those of LaOF$_2$As. The only atomic substitution in these isostructural compounds is at the La site. Sm ($m_{Sm} = 150.4$ u) is heavier than La ($m_{La} = 139$ u), however, the smaller ionic radius of Sm$^{3+}$ results in shortening of the Sm-O distances ($d_{Sm-O} = 2.259$ Å) by 7% compared to those of La-O ($d_{La-O} = 2.359$ Å) in LaOF$_2$As. Using the standard dependence of the phonon frequencies on the atomic masses and nearest neighbor distances in isostructural compounds, we can write $\omega_{Sm}/\omega_{La} \approx (m_{La}/m_{Sm})^{1/2}(d_{La-O}/d_{Sm-O})^{3/2}$. From this expression we find that $\omega_{Sm} \approx 1.026 \omega_{La}$, which is close to the experimentally established $\omega_{Sm} \approx 1.049 \omega_{La}$. The shorter Sm-O distance also causes a higher $B_{1g}$ oxygen mode frequency in SmOF$_2$As. Note that Fe and As mode frequencies are close in both compounds but while $\omega_{As} > \omega_{Fe}$ in LaOF$_2$As, this relation is opposite for SmOF$_2$As. We attribute this behavior of the phonon modes to the particular eigenvector of the As atoms vibrating between Fe and La/Sm sublattices (see Fig. 1), whereas Fe is vibrating only within the As sublattice. It seems that although the Fe-As distance decreases in going from LaOF$_2$As to SmOF$_2$As, the softening of the As mode is due to the compensatory increase in the Sm-As distance.

The Raman detection of the $E_g$ modes was challenging because the laser spot was comparable in size with the dimension of the crystal $ac$-surface and no reliable results were produced.

In conclusion, we measured and assigned the four non-degenerated Raman phonons in undoped ReOF$_2$As (Re = Sm, La). The phonon Raman lines are very sharp indicating small if any renormalization due to interactions with the other excitations in these compounds.

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