Raman spectroscopy of $R\text{FeAsO}$ ($R=\text{Sm}, \text{La}$)V. G. Hadjiev,¹ M. N. Iliev,² K. Sasmal,² Y.-Y. Sun,² and C. W. Chu^{2,3,4}¹Texas Center for Superconductivity and Department of Mechanical Engineering, University of Houston, Texas 77204-5002, USA²Texas Center for Superconductivity and Department of Physics, University of Houston, Houston, Texas 77204-5002, USA³Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong⁴Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA

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We report the polarized Raman spectra of undoped $R\text{FeAsO}$ ($R=\text{Sm}, \text{La}$) collected at room temperature from ab surfaces of impurity-free microcrystals. The spectra exhibit sharp phonon lines on very weak electronic scattering background. The frequency and symmetry of the four Raman phonons involving out-of-plane atomic vibrations are found at 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 SmFeAsO ; and 162 cm^{-1} (A_{1g} , La), 208 cm^{-1} (A_{1g} , As), 201 cm^{-1} (B_{1g} , Fe), and 316 cm^{-1} (B_{1g} , O) for LaFeAsO .

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A recent report of superconductivity at 26 K in $\text{LaFeAsO}_{1-x}\text{F}_x$ ($x=0.05-0.12$) (Ref. 1) has triggered an intense wave of research activities comparable to that in the early days of the superconducting cuprates and MgB_2 . Soon after, superconductivity at even higher temperatures was reported for other members of the Fe-As oxypnictides family.^{2,3} The calculated electron-phonon coupling^{4,5} is found to be too weak to produce a superconducting state within the Eliashberg theory at the experimentally measured T_c , and an unconventional origin of superconductivity mediated by antiferromagnetic spin fluctuations is suggested.⁶ Although the phonons may play little role in mediating the superconductivity in oxypnictides, using Raman spectroscopy to study them can provide important information on the superconducting state through phonon coupling to the Raman active electronic excitations.^{7,8}

In this Rapid Communication we present the results of a polarized Raman study of $R\text{FeAsO}$ ($R=\text{Sm}, \text{La}$). The Raman spectra were obtained under a microscope from very small platelike single crystals within polycrystalline samples, which allowed reliable measurements only of the nondegenerate Raman modes in $R\text{FeAsO}$. 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 *ab initio* calculations.^{4,5,9}

LaFeAsO and SmFeAsO crystallize in the $P4/nmm$ (space group No. 129) structure.^{1,2} Presented in Table I are the number of the expected Γ phonons, their symmetry, and the corresponding Raman tensors.¹⁰ The eigenvectors of the A_{1g} and B_{1g} modes are displayed in Fig. 1. These nondegenerate modes involve predominantly out-of-plane atomic vibrations. The E_g modes eigenvectors (not shown in Fig. 1) are parallel to the ab plane.

The polycrystalline pellets of LaFeAsO and SmFeAsO used in our experiment were prepared by solid state sintering. First, La (Sm) metal powders and As chips were mixed and pressed into pellets, sealed in a vacuumed quartz tube, and heated at 1000°C for 20–50 h. The formed LaAs (SmAs) was then mixed with Fe powder and Fe_2O_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 h. The powder x-ray diffraction of the LaFeAsO phase revealed a tetragonal structure with the room temperature lattice constants of $a=0.4021\text{ nm}$ and $c=0.8723\text{ nm}$. The lattice constants of the SmFeAsO phase were $a=0.3942\text{ nm}$ and $c=0.8498\text{ nm}$.

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, SmFeAsO and LaFeAsO , were measured with incident laser power density below 10^4 W/cm^2 to avoid local overheating

TABLE I. Wyckoff positions and irreducible representations (Γ -point phonon modes) for $R\text{FeAsO}$ (space group $P4/nmm$, No. 129, $Z=2$). The Raman tensors are given in an orthogonal system with z and x directions along the C_4 and C_2' axes, respectively.

Atom	Wyckoff position	Γ -point phonon modes
Sm/La	$2c$	$A_{1g} + A_{2u} + E_g + E_u$
O	$2a$	$B_{1g} + A_{2u} + E_g + E_u$
Fe	$2b$	$B_{1g} + A_{2u} + E_g + E_u$
As	$2c$	$A_{1g} + A_{2u} + E_g + E_u$

Modes classification:

$$\Gamma_{\text{Raman}} = 2A_{1g} + 2B_{1g} + 4E_g$$

$$\Gamma_{\text{IR}} = 3A_{2u} + 3E_u$$

$$\Gamma_{\text{Acoustic}} = A_{2u} + E_u$$

Raman tensors:

$$A_{1g}(x^2 + y^2, z^2) \rightarrow \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}$$

$$B_{1g}(x^2 - y^2) \rightarrow \begin{bmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$E_{g1}(xz), E_{g2}(yz) \rightarrow \begin{bmatrix} 0 & 0 & -e \\ 0 & 0 & 0 \\ -e & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & e \\ 0 & e & 0 \end{bmatrix}$$

FIG. 1. (Color online) Eigenvectors of all nondegenerated Raman phonons of $R\text{FeAsO}$ ($R=\text{Sm}, \text{La}$).

and burning the samples. 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 SmFeAsO and LaFeAsO microcrystals have platelike forms, which, by analogy with other layered compounds, suggests that the larger faces are most likely parallel to the crystallographic ab plane, (001). Under this assumption and considering the Raman tensors $\mathbf{R}$ given in Table I, one should expect the Raman mode intensity $I(\varphi) \propto [\vec{e}_s \mathbf{R} \vec{e}_i]^2$ ($\vec{e}_i$ and $\vec{e}_s$ are the incident and scattered light polarizations, respectively) to vary with the angle φ 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.

Figure 2 compares the polarized Raman spectra of SmFeAsO and LaFeAsO measured at room temperature in backscattering configurations with light polarizations along certain crystallographic directions. The scattering configurations are presented in Porto notation.¹¹ The Z direction is along $[001]$ (c axis), X is 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 ($10 \times 10 \mu\text{m}^2$), 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 nondegenerate modes in SmFeAsO are 170 cm^{-1} (A_{1g} , Sm), 201 cm^{-1} (A_{1g} , As), 208 cm^{-1} (B_{1g} , Fe), and

FIG. 2. (Color online) Polarized Raman spectra of SmFeAsO and LaFeAsO measured in backscattering configuration with incident and scattered light polarizations in the ab plane. Notations: $Z \parallel [001]$, $\bar{Z} \parallel [00\bar{1}]$, $X \parallel [100]$, $Y \parallel [001]$, $X' \parallel [110]$, and $Y' \parallel [\bar{1}10]$.

345 cm^{-1} (B_{1g} , O). For LaFeAsO the corresponding modes are 162 cm^{-1} (A_{1g} , La), 208 cm^{-1} (A_{1g} , As), 201 cm^{-1} (B_{1g} , Fe), and 316 cm^{-1} (B_{1g} , O).

The phonon dispersions and electron-phonon coupling of LaFeAsO have already been reported as calculated using the Quantum Espresso code with ultrasoft pseudopotentials.^{4,5,9} The calculations predict phonon branches with little dispersion in the z direction (c axis), reflecting the layered structure of LaFeAsO , and a phonon spectrum that spreads up to 500 cm^{-1} . The oxygen vibrations are expected between 300 and 500 cm^{-1} , whereas those of La, Fe, and As occupy the range below 300 cm^{-1} . No assignment of the Γ -point phonons is made in Refs. 4 and 5. Reference 9, however, gives explicitly the calculated frequency and symmetry of the Γ phonons in LaFeAsO , which allows us to compare in Table II the measured and calculated nondegenerate Raman phonon symmetry and frequencies for LaFeAsO . The calculated phonon frequencies in Refs. 4 and 5 were taken from those nondegenerate dispersion curves that cross the Γ point of the Brillouin zone between 170 and 320 cm^{-1} . The calculated frequencies are in fairly good agreement (less than 10% deviation) with the experimental ones given that each one of the calculations in Refs. 4, 5, and 9 was done using different lattice parameters.

Further, we briefly compare the Raman phonons of SmFeAsO with those of LaFeAsO as no lattice dynamics

TABLE II. Experimental (this work) and calculated in Refs. 4, 5, and 9 nondegenerate Raman phonon frequencies for SmFeAsO (SFAO) and LaFeAsO (LFAO). The calculated frequencies for LaFeAsO , columns LFAO (Ref. 4) and LFAO (Ref. 5), were taken from the phonon dispersions crossing the Γ point of the Brillouin zone. In Ref. 9, the symmetry and frequencies of the Γ phonons are given explicitly.

Mode symmetry	SFAO (this work) (cm^{-1})	LFAO (this work) (cm^{-1})	LFAO (Ref. 4) (cm^{-1})	LFAO (Ref. 5) (cm^{-1})	LFAO (Ref. 9) (cm^{-1})
A_{1g} (La/Sm)	170	162	180	183	178
A_{1g} (As)	201	208	200	208	201
B_{1g} (Fe)	208	201	217	216	221
B_{1g} (O)	345	316	311	294	284

calculation has been reported so far for SmFeAsO . The only atomic substitution in these isostructural compounds is at the La site. Sm ($m_{\text{Sm}}=150.4$ u) is heavier than La ($m_{\text{La}}=139$ u); however, the smaller ionic radius of Sm^{3+} results in the shortening of the Sm-O distances ($d_{\text{Sm-O}}=2.259$ Å) by $\sim 4\%$ compared to those of La-O ($d_{\text{La-O}}=2.359$ Å) in LaFeAsO .¹² Using the standard dependence of the phonon frequencies on the atomic masses and nearest neighbor distances in isostructural compounds,¹³ we can write $\omega_{\text{Sm}}/\omega_{\text{La}} \approx (m_{\text{La}}/m_{\text{Sm}})^{1/2}(d_{\text{La-O}}/d_{\text{Sm-O}})^{3/2}$. From this expression we find that $\omega_{\text{Sm}} \approx 1.026 \omega_{\text{La}}$, which compares well with the ex-

perimentally established $\omega_{\text{Sm}} \approx 1.049 \omega_{\text{La}}$. The shorter Sm-O distance also causes a higher B_{1g} oxygen mode frequency in SmFeAsO . It should be noted that the Fe and As mode frequencies in both compounds range from 200 to 210 cm^{-1} but, while $\omega_{\text{As}} > \omega_{\text{Fe}}$ for LaFeAsO , this relation is opposite for SmFeAsO . 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 LaFeAsO to SmFeAsO , 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 nondegenerate Raman phonons in undoped $R\text{FeAsO}$ ($R=\text{Sm}, \text{La}$). 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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¹¹ $D_i(P_s P_i)D_s$: D_i and D_s denote the propagation directions of incident and collected scattered light, respectively. P_i and P_s denote the corresponding incident and scattered light polarization directions.

¹²The distances were calculated for crystal structures with the following parameters: $a=0.4021$ nm, $c=0.8723$ nm, $z_{\text{La}}=0.1415$, and $z_{\text{As}}=0.6512$ for LaFeAsO ; $a=0.3942$ nm, $c=0.8498$ nm, $z_{\text{Sm}}=0.1299$, and $z_{\text{As}}=0.6402$ for SmFeAsO .

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