Raman-scattering study of K$_{x}$Sr$_{1-x}$Fe$_2$As$_2$ ($x=0.0, 0.4$)

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Polarized Raman spectra of nonsuperconducting SrFe$_2$As$_2$ and superconducting K$_{0.4}$Sr$_{0.6}$Fe$_2$As$_2$ ($T_c$ = 37 K) microcrystals are reported. All four-phonon modes ($A_1g + B_{1g} + 2E_{g}$) allowed by symmetry are found and identified. Shell model gives reasonable description of the spectra. No detectable anomalies are observed near the tetragonal-to-orthorhombic transition in SrFe$_2$As$_2$ or the superconducting transition in K$_{0.4}$Sr$_{0.6}$Fe$_2$As$_2$.

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The renewed interest in superconductors was sparked recently by the discovery of a class of iron-arsenide-based oxypnictides $R$FeAsO$_x$-$F_y$ (where $R$ is a rare-earth element). 1-5 Similarly to the cuprate superconductors, doping of superconducting FeAs planes in oxypnictides determines one of the key characteristics of a given material (its superconducting transition temperature), which reaches values as high as $T_c$ = 54 K. Oxypnictides were shown to exhibit $n$-type conductivity. More recently a series of compounds with similarly structured FeAs planes, but with different charge reservoir block $A_xM_y$Fe$_2$As$_2$ (where $A$ is an alkali element and $M$ is Sr or Ba), was found to exhibit superconducting properties. 6 Unlike oxypnictides these superconductors clearly show $p$-type conductivity. 7 Optimal material doping is achieved in this latter system at $x$ = 0.4–0.5 when the critical temperature reaches $T_c$ = 38 K. 8

First-principles electronic band-structure calculations of oxypnictides point toward unconventional superconductivity that is mediated by antiferromagnetic spin fluctuations. 9-11 Due to rather weak electron-phonon interactions, it is generally believed that the phonons do not contribute substantially to the superconductivity. Despite this fact, it is important to experimentally identify the symmetry and frequency of phonon excitations and search for specific features in the Raman-scattering spectra, which could shed light onto the properties of the superconducting state. In this Rapid Communication we report the results of polarized Raman-scattering studies of K$_x$Sr$_{1-x}$Fe$_2$As$_2$ microcrystals for the parent $x=0$ compound and superconducting material with $x$ =0.4. We also present the results of shell-model lattice dynamics calculations, which are in a good agreement with the experimental data.

The compounds under investigation were prepared by high-temperature solid-state reactions of high-purity K and Sr with FeAs as described elsewhere. 8 For the mixed-metal samples K$_x$Sr$_{1-x}$Fe$_2$As$_2$, stoichiometric amounts of the ternary iron arsenides were thoroughly mixed, pressed, and then annealed within welded Nb containers (jacketed in quartz) at about 900 °C for 70–120 h. The bulk samples containing microcrystals of typical size of 50×50 ×2 μm$^3$ were characterized by x-ray diffraction, resistivity, magnetic-susceptibility, Hall, and thermoelectric power measurements. 8,12

Raman-scattering measurements were performed with a triple Horiba JY T64000 spectrometer equipped with an optical microscope, microcrystal, and liquid-nitrogen-cooled CCD detector. At room temperature a ×100 objective was used to both focus the laser beam ($λ$$_l$=638.2 nm) at a spot 1–2 μm in diameter on selected $ab$ or $ac$/$bc$ microcrystal surfaces oriented in an exact scattering configuration and collect the scattered light. For low-temperature measurements the sample was mounted in an optical Microstost$^{16}$ (Oxford Instruments) and long-focus objective (∼50) and spot size 2–4 μm, still much smaller than the microcrystal dimensions) was used. The spectra in this case were obtained from crystal surfaces with such orientation that the two strongest phonon modes could simultaneously be observed. The excitation power density did not exceed 10$^4$ W/cm$^2$ in order to minimize heating of the sample. Similarly to the case of RA$S$FeO (Ref. 13), the Raman intensities were very low and long acquisition times were needed.

$AFe_2As_2$ crystallizes in the tetragonal ThCr$_2$Si$_2$-type structure with space group $I4/mmm$ ($D_{4h}^{15}$). 14 The unit cell parameters and atomic positions were obtained from powder-diffraction data using Rietveld refinement. The atomic positions were consistent with the literature values. The cell parameters for SrFe$_2$As$_2$ are $a=0.39259(2)$ nm and $c=1.2375(1)$ nm. For K$_{0.40}$Sr$_{0.60}$Fe$_2$As$_2$, $a=0.38898(2)$ nm and $c=1.2948(1)$ nm; ε$_{as}$=0.3516 for both compounds. The structure features individual FeAs layers identical to those in RFeAsO but with a different layer stacking sequence (AA in RFeAsO and AB in the ThCr$_2$Si$_2$-type structure).

From symmetry considerations 15 one expects four Raman-active phonons: $A_{1g}(As)$, $B_{1g}(Fe)$, $E_{g}(As)$, and $E_{g}(Fe)$ (Table I). Using the polarization selection rules and the fact that the $ab$ surfaces could easily be visually recognized, the identification of the Raman line symmetry is straightforward. In particular, in the spectra obtained from the $ab$ plane, the intensity of the $A_{1g}$ mode will remain constant for any orientation of the incident polarization $ε_i$; given that the scattered polarization $ε_i$ is parallel to it ($ε_i||ε_i$) and will be zero in any crossed polarization configuration ($ε_i \perp ε_i$). The intensity of the $B_{1g}$ mode, however, depends on the angle $α$ between $ε_i$ and the $a$ axis being proportional to $cos^2 2α$ for parallel and $sin^2 2α$ for crossed configuration.
SrFe$_2$As$_2$ obtained from the oxides in particular, which yield Brillouin-zone-center modes. Lower part of the table lists experimental and calculated mode frequencies and their activity.

| Atom    | Wyckoff position | \( \Gamma \)-point phonon modes |
|---------|------------------|---------------------------------|
| Sr      | 2a               | \( A_{2u} + E_g \)              |
| Fe      | 4d               | \( A_{2u} + B_{1g} + E_g + E_u \) |
| As      | 4e               | \( A_{1g} + A_{2u} + E_g + E_u \) |

Modes classification

\[
\begin{align*}
\Gamma_{\text{Raman}} &= A_{1g} + B_{1g} + 2E_g \\
\Gamma_{\text{IR}} &= 2A_{2u} + 2E_u \\
\Gamma_{\text{ACoustic}} &= A_{2u} + E_u
\end{align*}
\]

Raman tensors

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

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

\[
E_g(xz), E_g(yz) &\rightarrow \\
&\begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & e \\
-e & 0 & 0
\end{bmatrix}
\]

| Mode   | Type  | Expt. cm\(^{-1}\) | LDC cm\(^{-1}\) | Main atomic displacements | Allowed polarizations |
|--------|-------|-----------------|----------------|--------------------------|----------------------|
| \( A_{1g} \) | Raman | 182             | 183            | As\((z)\)                 | XX, YY, ZZ           |
| \( B_{1g} \) | Raman | 204             | 203            | Fe\((z)\)                 | XX, YY, X'Y'         |
| \( E_g \) | Raman | 114             | 111            | As\((xy)\), Fe\((xy)\)   | XZ, YZ               |
| \( E_g \) | Raman | 264             | 335            | Fe\((xy)\), As\((xy)\)   | XZ, YZ               |
| \( A_{2u} \) | IR    | 198             | 263            | Sr\((z)\), As\((-z)\)    | Z                    |
| \( A_{2u} \) | IR    | 322             |                | Fe\((z)\), Sr\((-z)\)    | Z                    |
| \( E_u \) | IR    | 135             |                | Sr\((xy)\)               | X, Y                 |
| \( E_u \) | IR    | 263             |                | Fe\((xy)\), As\((-xy)\) | X, Y                 |

Figure 1 shows the variations with \( \alpha \) of the Raman spectra of SrFe$_2$As$_2$ obtained from the \( ab \) plane. Only one line at 204 cm\(^{-1}\) is clearly pronounced in the spectra and its intensity follows the angular dependence expected for the \( B_{1g} \) mode. Obviously, the intensity of the \( A_{1g} \) mode is negligible for incident light propagating along the \( c \) axis and polarized in the \( ab \) plane. However, all Raman-active phonons are clearly seen in the spectra taken from \( ac(bc) \) surface as illustrated in Fig. 2. These observations suggest the following relations between the elements of the Raman tensor in Table I: \( |b| \gg |a| \) and \( |c| \gg |a| \). The experimental phonon frequencies are listed in Table I.

We also performed shell-model calculations of the lattice dynamics using the general utility lattice program (GULP),\(^{16}\) which is known to reasonably describe a wide class of ionic materials (oxides in particular).\(^{17,18}\) In the shell model each ion is considered as a point core with charge \( Y \) surrounded by a massless shell with charge \( Q \). The free-ion polarizability is accounted for by the force constant \( k \). The short-range potentials \( V(r) \) are chosen in the Born-Mayer-Buckingham form

\[
V(r) = a \exp(-r/r_0) - cr^{-6}.
\]

The model parameters of Fe$^{2+}$, Sr$^{2+}$, and As$^{3-}$ were tuned in order to achieve the best agreement with experimental even-parity phonon modes (to the best of our knowledge, there is no experimental information on odd-parity infrared-active phonons); they are listed in Table II. The displacement patterns of all four Raman-active modes are shown in Fig. 3. It is worth noting here that, while the \( A_{1g} \) and \( B_{1g} \) modes can be considered as “pure” modes (involving displacements...
along the c axis of either As or Fe, the two Eg modes are strongly mixed. As expected, the A1g and B1g modes of SrFe2As2 are very close in frequency to the corresponding modes of same symmetry in RFeAsO.13 Indeed, the individual FeAs layers in both compounds are practically identical in terms of bond lengths and angles.

Due to the long acquisition time, the Raman spectra of superconducting K0.4Sr0.6Fe2As2 (Tc = 37 K) microcrystals were taken from the surface where both A1g and B1g modes were observed (Fig. 4). Their frequency is practically the same as in the parent compound, the linewidth being somewhat larger. Upon lowering temperature these two modes show standard anharmonic behavior in both materials with
the high-frequency might expect splitting of the modes by about 0.8%. Even for 2.1 cm\(^{-1}\), which is small compared to the linewidth and is frequency /H9275, the main effect of the structural transition should be a splitting of A\(_0\) 0.55%. Following a simple expression for the phonon of Fe-As bond lengths within SrFe\(_2\)As\(_2\) at near the tetragonal-to-orthorhombic structural transition of SrFe\(_2\)As\(_2\) and superconducting transition in K\(_{0.4}\)Sr\(_{0.6}\)Fe\(_2\)As\(_2\) were observed within the accuracy of our experiments for the A\(_{1g}\) and B\(_{1g}\) modes. In principle, the main effect of the structural transition should be a splitting of the E\(_g\) modes, which position was difficult to follow in the temperature-dependent experiments. The reported anisotropy of Fe-As bond lengths within ab plane, however, is only 0.55%. Following a simple expression for the phonon frequency \(\omega_{ph}\) as a function of bond length \(l / (\omega_{ph}^2 \sim 1/l^3)\), one might expect splitting of the modes by about 0.8%. Even for the high-frequency E\(_g\) mode at 264 cm\(^{-1}\) this yields 2.1 cm\(^{-1}\), which is small compared to the linewidth and is challenging to be observed experimentally.

In conclusion, all four Raman-active phonons in SrFe\(_2\)As\(_2\) have been observed experimentally. The substitution of K for Sr has little effect on the frequencies of Raman modes involving As and Fe vibrations. The structural transition in SrFe\(_2\)As\(_2\) and superconducting transition in K\(_{0.4}\)Sr\(_{0.6}\)Fe\(_2\)As\(_2\) do not produce detectable anomalies in the parameters of A\(_{1g}\) and B\(_{1g}\) modes.

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| Ion | \(Y(|e|)\) | \(Q(|e|)\) | \(k(\text{eV} \times \text{Å}^{-2})\) | Ion pair | \(a\) (eV) | \(r_0\) (Å) | \(c(\text{eV} \times \text{Å}^6)\) |
|-----|-----------|-------------|-----------------|-----------|---------|----------|----------------|
| Sr  | 2.40      | -0.50       | 10.0            | Sr-As     | 1226    | 0.482    | 0              |
| Fe  | 2.40      | -0.50       | 19.9            | Fe-As     | 2399    | 0.350    | 0              |
| As  | 0.15      | -3.00       | 15.2            | As-As     | 2000    | 0.209    | 2500           |

TABLE II. Shell-model parameters and the short-range potentials for SrFe\(_2\)As\(_2\). We used structural parameters reported in Ref. 8 and listed in the text.

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