Phonon anomalies in pure and underdoped $R_{1-x}K_xFe_2As_2$ ($R=$Ba, Sr) investigated by Raman light scattering

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We present a detailed temperature dependent Raman light scattering study of optical phonons in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ ($x \sim 0.28$, superconducting $T_c \sim 29$ K), Sr$_{1-x}$K$_x$Fe$_2$As$_2$ ($x \sim 0.15$, $T_c \sim 29$ K) and non-superconducting BaFe$_2$As$_2$ single crystals. In all samples we observe a strong continuous narrowing of the Raman-active Fe and As vibrations upon cooling below the spin-density-wave transition $T_s$. We attribute this effect to the opening of the spin-density-wave gap. The electron-phonon linewidths inferred from these data greatly exceed the predictions of ab-initio density functional calculations without spin polarization, which may imply that local magnetic moments survive well above $T_s$. A first-order structural transition accompanying the spin-density-wave transition induces discontinuous jumps in the phonon frequencies. These anomalies are increasingly suppressed for higher potassium concentrations. We also observe subtle phonon anomalies at the superconducting transition temperature $T_c$, with a behavior qualitatively similar to that in the cuprate superconductors.

PACS numbers:

The recent discovery of superconductivity in iron arsenides has triggered a large-scale research effort to explore the physical properties of these materials. After first reports on LaFeAs(O$_{1-x}$F$_x$) with critical temperatures of $T_c = 26$ K [1] and 43 K under pressure [2], even higher transition temperatures up to 56 K were discovered in related compounds [3, 4]. LaFeAsO crystallizes in the ZrCuSiAs-type crystal structure [5] consisting of alternating (LaO)$^+$ and (FeAs)$^-$ layers with one (FeAs)$^-$ layer per formula unit. In LaFeAsO, superconductivity is usually induced by substitution of F$^-$ for O$^{2-}$, introducing electrons into the (FeAs)$^-$ layers. It was recently shown that hole doping by substitution of La$^{3+}$ for Sr$^{2+}$ can also induce superconductivity with $T_c = 25$ K [6].

More recently a second class of iron arsenide superconductors crystallizing in the ThCr$_2$Si$_2$-type crystal structure with two (FeAs)$^-$ layers per formula unit was discovered [7]. The ternary iron arsenide BaFe$_2$As$_2$ (BFA) becomes superconducting after substitution of K$^+$ for Ba$^{2+}$, with $T_c = 38$ K at optimal doping ($x \sim 0.4 - 0.5$) [7, 8]. This system is a hole-doped superconductor. Isostructural compounds with Ca ($T_c = 20$ K) [9], Eu ($T_c = 32$ K) [10], and Sr ($T_c \sim 38$ K) [11, 12] instead of Ba followed soon thereafter. A first example of electron doping in a ternary iron arsenide, induced by substitution of Co$^{2+}$ for Fe$^{2+}$ in BaFe$_2$As$_2$ with $T_c = 22$ K, was reported as well [13]. In contrast to the oxypnictides, large highly-quality single crystals are available for this class of compounds.

Common features of the undoped iron arsenide parent compounds are a structural phase transition from a high temperature tetragonal to a low temperature orthorhombic or monoclinic phase, and an antiferromagnetic spin-density-wave (SDW) transition. While for the electron-doped compounds both phase transitions were found at slightly different temperatures [14, 15], they occur at a same temperature $T_c$ for hole-doped BKFA [8]. Undoped BaFe$_2$As$_2$ and SrFe$_2$As$_2$ show combined transitions at $T_c \sim 140$ K [10] and $T_s \sim 203$ K [17], respectively. Doping with electrons or holes suppresses $T_s$ and induces superconductivity at lower temperatures. In hole-doped RFe$_2$As$_2$ ($R=$Ba, Sr) strong indications exist for a distinct doping range where the superconducting and SDW phases coexist [8, 18]. In the coexistence regime of underdoped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ (BKFA), there is evidence for a weaker structural transition at $T_s$ without macroscopic change of the crystal symmetry, but with an increase of microstrains, that was attributed to a magnetically induced lattice softening in combination with electronic phase separation [19].

Raman light scattering offers a powerful tool to detect subtle changes in the phonon spectrum at structural or electronic phase transitions. In this work we present a detailed temperature dependent Raman light scattering study of the optical phonons in superconducting BKFA and Sr$_{1-x}$K$_x$Fe$_2$As$_2$ (SKFA) single crystals. We observe pronounced narrowing in the phonon linewidths at the combined phase transition temperature $T_s$, as well as more subtle phonon anomalies at the superconducting phase transition temperature $T_c$.

The experiments were performed on thin platelets of BKFA and SKFA single crystals (thickness $\sim 20$ µm) with the crystallographic c-axis perpendicular to the surface. The samples were grown from tin flux, as described previously [20, 21, 22]. They were underdoped with $x \sim 0.28$ and $x \sim 0.15$ (determined by energy-dispersive x-ray analysis and inductively-coupled plasma spectroscopy), respectively. From measurements of the electrical resistivity in the FeAs planes (Fig. 1) and the magnetization (Fig. 2) on samples from the same batch as the ones used for the Raman measurements, we infer superconducting transition temperatures $T_c \sim 29$ K.
in both cases. In particular, the diamagnetic signal of SKFA shown in Fig. 2 is characterized by an onset of 32 K, a midpoint of 29 K, and a 10%–90% width of 4 K. Similar data were previously reported for BKFA crystals from the same batch as ours [22]. The combined structural-SDW transition temperature in SKF A was determined as $T_s \sim 178$ K by a decrease of the in-plane resistivity on SKF A samples from the same batch [21], while $T_s \sim 75$ K was determined by neutron scattering and muon spin rotation experiments on BKF A samples from the same batch [22]. Furthermore, we used a non-superconducting sample of BF A with thickness $\sim 50 \mu m$ grown in self-flux [21, 23], and $T_s \sim 138$ K inferred from the in-plane resistivity (Fig. 1).

The Raman measurements were performed using a micro-Raman setup. The samples were mounted in a helium-flow cryostat, and the spectra were taken in backscattering geometry using the linearly polarized 632.817 nm line of a He$^+/Ne^+$-mixed gas laser for excitation. The laser beam was focused through a 50× microscope objective to a $\sim 5 \mu m$ diameter spot on the sample surface. In order to avoid sample heating through the laser beam, we used an incident laser power of less than 1.5 mW. The scattered light was analyzed by a JobinYvon LabRam single-grating spectrometer equipped with a notch filter and a Peltier-cooled CCD camera. For each Raman spectrum an additional calibration spectrum of a nearby neon line was measured in order to determine the precise frequency and linewidth of the different phonons. For data analysis, all phonon peaks were fitted to Voigt profiles, which result from a convolution of the Lorentzian phonon line-shape with the instrumental resolution of $\sim 2$ cm$^{-1}$ (full width at half maximum).
$I4/mmm$ ($D_{4h}^{17}$) one expects four Raman-active modes with symmetries $A_{1g} + 2B_{1g} + 2E_g$. According to the mode assignment of Litvinchuk et al. [24], the peaks at 182 cm$^{-1}$ and 206 cm$^{-1}$ can be identified with the $A_{1g}$ and $B_{1g}$ vibrations of the As- and Fe-atoms, respectively. The $A_{1g}$ mode is strong for $(zu)$ and weak for $(xu)$ polarization, respectively. The $B_{1g}$ mode cannot be observed for $(zu)$ polarization in accordance with the Raman selection rules. The two $E_g$ modes are weak and are observed at 117 cm$^{-1}$ and 268 cm$^{-1}$ in the $(yzu)y$ polarization configuration. The insets show the corresponding Raman spectra at 5 and 300 K. All modes show a clear shift to lower energies upon heating from 5 to 300 K.

Figure 4 shows the frequency and full width at half maximum (FWHM) of the $A_{1g}$ and $B_{1g}$ modes of underdoped BKFA in the $(yzu)y$ and $(xu)y$ polarization configurations as a function of temperature. The vertical lines correspond to the critical temperatures $T_c$ and $T_s$ for the superconducting and the combined structural-SDW transitions, respectively. Figure 5 shows corresponding Raman measurements on non-superconducting BF A samples. The solid line through the data is the result of a fit to the normal state data according to anharmonic phonon decay processes (see text for details). The dashed lines indicate the superconducting $T_c \sim 29$ K and the SDW transition temperature $T_s \sim 75$ K as obtained from Ref. [24].

The solid line through the $B_{1g}$ data is the result of a fit to an expression based on phonon-phonon interactions, i.e. the anharmonic decay of phonons [25]. For simplicity we assumed a symmetric phonon decay according to:

$$\omega_{ph}(T) = -A \left( 1 + \frac{2a}{\exp(h\omega_0/2k_BT) - 1} \right) + \omega_0,$$

where $A$ is a positive constant and $a$ corrects for terms arising from non-symmetric phonon decay processes. While the frequency of the $B_{1g}$ mode follows nearly perfectly the expression for anharmonic decay, significant deviations from this behavior are observed for the $A_{1g}$ mode at both $T_c$ and $T_s$. We first discuss the relatively subtle lineshape anomalies at $T_c$, and later turn to the stronger anomalies at $T_s$ in the context of analogous measurements on non-superconducting BFA samples.

In contrast to the low-temperature saturation of the frequency of the $B_{1g}$ modes, the $A_{1g}$ modes of both BKFA and SKF A exhibit a distinct hardening by $\sim 0.3$ cm$^{-1}$ upon cooling below $T_c$. Moreover, the linewidth of the $A_{1g}$ mode in SKF A (Fig. 5) shows a kink in its temperature dependence at $T_c$, which can be described as a slight superconductivity-induced broadening superposed on a continuous decrease upon cooling below the spin-density-wave transition at $T_s$ (to be discussed further below). While the latter trend is already nearly saturated at $T = T_c$ in SKF A, it is much more pronounced in BKFA, where $T_s$ is considerably lower, and overshadows the superconductivity-induced linewidth anomaly (Fig. 4).

According to the standard description of superconductivity-induced self-energy anomalies of optical phonons [26, 27], the rearrangement of the electronic density of states below $T_c$ is expected to induce hardening and broadening for phonons with energies above the pair-breaking energy $2\Delta$. Experimental observations on the cuprate high-temperature superconductors are largely consistent with this theory. Angle-resolved photoemission experiments on BKFA samples from the same batch as ours found two superconducting gap energies at $\Delta_1 \sim 9$ meV and $\Delta_2 \sim 4$ meV [28], yielding pair-breaking energies of $2\Delta_1 \sim 150$ cm$^{-1}$ and $2\Delta_2 \sim 65$ cm$^{-1}$. Assuming comparable gap values for the two BKFA and SKF A samples, both the $A_{1g}$ and $B_{1g}$ mode energies are well above the upper $2\Delta_1$-gap.
phonon frequency and linewidth at \( T_s \) are therefore in agreement with the theoretical expectations. The weakness of the observed self-energy renormalization indicates that the superconductivity-induced modification of the electronic density of states is small at the phonon energies monitored experimentally.

We now turn to the phonon anomalies at the combined structural-SDW transition temperature \( T_s \). Beginning with the BKFA sample with the lowest \( T_s \) (Fig. 4), we note a pronounced singularity in the temperature dependence of the linewidths of both \( A_{1g} \) and \( B_{1g} \) modes at \( T_s \), followed by a continuous narrowing upon cooling. This effect is further enhanced in the SKF A sample. The \( A_{1g} \) mode, in particular, narrows by \( \sim 3 \text{ cm}^{-1} \) between \( T_s \) and the lowest temperature, and softens by \( \sim 0.5 \text{ cm}^{-1} \) around \( T_s \). For reference, we have carried out further experiments on pristine BFA, the results of which are shown in Fig. 6. Here the phonon anomalies at \( T_s \) are even stronger. The \( A_{1g} \) mode softens abruptly by \( \sim 1 \text{ cm}^{-1} \) at \( T_s \) and narrows by more than \( \sim 4 \text{ cm}^{-1} \) between \( T_s \) and the lowest temperature. The \( B_{1g} \) mode frequency also shows a small break in its temperature gradient at \( T_s \), as well as a continuous narrowing by \( \sim 2 \text{ cm}^{-1} \) between \( T_s \) and base temperature. Similar behavior was reported before for CaFe\(_2\)As\(_2\) [29].

In conclusion, we have shown that the electron-phonon interaction on the lattice dynamics in the iron arsenides. Ab-initio density functional calculations predict that the \( A_{1g} \) mode, which corresponds to a vibration of the arsenic ions along the c-axis, shows the strongest electron-phonon coupling [36, 57], in qualitative agreement with our observations. However, calculations without spin polarization fail to account quantitatively for the experimentally observed linewidths. The predicted density of states at the Fermi level, \( N(0) \sim 4.42/\text{eV} \), and total electron-phonon coupling parameter (summed over the phonon branches and averaged on the Brillouin zone), \( \lambda \sim 0.21 \), yields a rough estimation for the FWHM of \( \frac{1}{2} N(0) \lambda \omega^2 \sim 0.4 \text{ cm}^{-1} \), about an order of magnitude smaller than observed for the \( A_{1g} \) mode above the SDW transition. This discrepancy is in line with earlier reports of differences between the calculated and observed phonon density of states around the \( A_{1g} \) mode energy [40, 41, 42, 43]. Since the ab-initio calculations also show that the electron-phonon coupling greatly increases in the SDW state [37, 44], this may be a manifestation of local Fe moments that survive well above the SDW transition.

In any case, the strong reduction of the linewidths of both \( A_{1g} \) and \( B_{1g} \) modes below \( T_s \) points to a substantial influence of the electron-phonon interaction on the lattice structure and associated phonon-phonon interactions alone. It can, however, be understood if the difference between the linewidths above and below \( T_s \) is attributed to the electron-phonon interaction, which becomes inoperative at low temperatures due to the opening of the SDW gap [34]. This scenario is further supported by infrared experiments on EuFe\(_2\)As\(_2\) single crystals [35], where the interaction of the Fe-As lattice vibration \( E_A \) with the electronic background was found to be reduced below the SDW transition. The continuous, second-order-like behavior of the linewidth can be reconciled with the abrupt jump in the phonon frequency either if separate first-order structural and second-order SDW transitions take place at slightly different temperatures that are not resolved in the experiment, or if the single, combined transition is weakly first-order so that the jump in linewidth is below the detection limit.
anomalies requires theoretical work beyond the density functional calculations thus far reported.

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Note that the factor of 15 reflects the number of phonon branches in BaFe$_2$As$_2$.

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