

## Temperature dependence and resonance effects in Raman scattering of phonons in NdFeAsO<sub>x</sub>F<sub>1-x</sub> single crystals

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We report plane-polarized Raman-scattering spectra of iron oxypnictide superconductor NdFeAsO<sub>1-x</sub>F<sub>x</sub> single crystals with varying fluorine  $x$  content. The spectra exhibit sharp and symmetrical phonon lines with a weak dependence on fluorine doping  $x$ . The temperature dependence does not show any phonon anomaly at the superconducting transition. The Fe related phonon intensity shows a strong resonant enhancement below 2 eV. We associate the resonant enhancement to the presence of an interband transition around 2 eV observed in optical conductivity. Our results point to a rather weak coupling between Raman-active phonons and electronic excitations in iron oxypnictides superconductors.

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The discovery of a new class of high-temperature superconductors belonging to the family of iron oxypnictides raises the possibility of a new route to high  $T_c$  superconductivity besides the one of the cuprates.<sup>1</sup> Most of the compounds discovered up to now have the formula ReFeAsO<sub>1-x</sub>F<sub>x</sub>, where Re is rare-earth atom (La, Nd, Sm). Superconductivity is believed to take place in the conducting FeAs layer where the Fe and As atoms are tetrahedrally coordinated and the Fe atoms form a two-dimensional square lattice. The chemical substitution of O with fluorine F allows electron doping of the FeAs planes and increases  $T_c$  up to 55 K in SmFeAsO<sub>0.9</sub>F<sub>0.1</sub>.<sup>2</sup>

While there are similarities with the cuprates, two dimensionality and the close proximity of high-temperature superconductivity with magnetic order for example, it is becoming increasingly clear that these compounds also bear significant differences with them: the undoped compound is not a Mott insulator but a bad metal with antiferromagnetic spin-density wave (SDW) order arising from the Fe moments.<sup>3,4</sup> The SDW order is associated with a structural transition<sup>3-5</sup> and both the magnetic order and the structural phase transition are suppressed with fluorine doping, leading to the emergence of superconductivity.<sup>3,5</sup> The role of doping in these compounds appears to be quite different than in the cuprates. In iron oxypnictides, doping may in fact be just one of the different ways of tuning and/or suppressing various competing itinerant magnetic orders.<sup>6</sup> For example pressure was already shown to be an alternative tuning parameter.<sup>7,8</sup>

Whether superconductivity in these compounds arises from strong electronic correlations as is believed in the cuprates, from a more conventional phononic mechanism or from a completely different route, remains an open question. A peculiarity of the oxypnictides is the interplay between strong repulsion due to the localized character of the Fe  $3d$  bands and the orbital degrees of freedom.<sup>9</sup> This interplay may provide a completely new mechanism of strongly correlated high-temperature superconductivity.

Determination of the order-parameter symmetry is crucial to understand the nature of the superconducting mechanism but measurements of the gap anisotropy are still very preliminary. The multiband nature of these compounds which

arises from the various Fe related bands crossing the Fermi level complicates further the determination of the order-parameter symmetry.<sup>10,11</sup> On the other hand, the determination of the phonon dynamics may shed light on the possible role of phononic degrees of freedom in the superconductivity of oxypnictides. *Ab initio* calculations give an electron-phonon coupling constant seemingly too weak to explain high  $T_c$  superconductivity in these compounds.<sup>12</sup> Nevertheless recent reports of a nodeless gap via angle-resolved photoemission spectroscopy (Refs. 13 and 14) and the strong sensitivity of the calculated band structures near the Fermi level to the distortion of the FeAs tetrahedra indicate the possible role of vibrational degrees of freedom.<sup>12,15-18</sup> Therefore the role of phonons and their coupling to electronic degrees of freedom deserved to be scrutinized.

In this Brief Report we report plane-polarized Raman-scattering measurements of zone-center phonons in NdFeAsO<sub>1-x</sub>F<sub>x</sub> single crystals. The crystals have a superconducting  $T_c$  of about 50 K for  $x=0.18$  and 48 K for  $x=0.30$ . The undoped crystals  $x=0$  are nonsuperconducting. The single crystals have been grown by a flux method at ambient pressure and have a nominal composition of  $x=0$ ,  $x=0.18$ , and  $x=0.30$ , respectively.<sup>19</sup> The typical lateral size of the crystals studied here is about  $20 \times 20 \mu\text{m}^2$ .

The measurements were performed using a micro-Raman setup in back scattering geometry. Several excitation lines of an Ar/Kr laser were used ranging from 1.9 to 2.7 eV. The scattered light was collected and analyzed by a triple grating spectrometer (JY T64000) and a back-illuminated nitrogen-cooled charge coupled device (CCD) camera. The room-temperature measurements were performed with a  $\times 50$  objective. For the low-temperature measurement the crystals were mounted on the cold finger of cryostat and a long working distance  $\times 50$  objective was used.

Special care was taken in order to avoid overheating the crystals and power densities were kept below  $10^3 \text{ W/cm}^2$ . The local heating at the laser spot was estimated by comparing both the temperature and the power dependences of the Raman spectra. For most of the measurements reported here the heating was estimated to be 30 K except for the lowest temperature measurement where a lower power density was

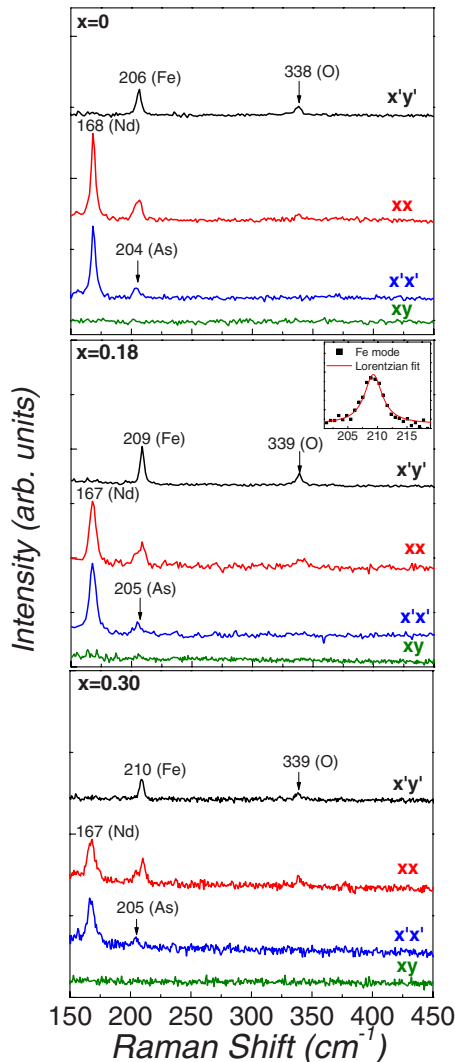


FIG. 1. (Color online) Room-temperature Raman spectra of  $\text{NdFeAsO}_{1-x}\text{F}_x$  with incident and scattered lights polarized in the  $ab$  plane for three different fluorine concentrations ( $x=0$ ,  $x=0.18$ , and  $x=0.30$ ). The polarization configuration of each spectra is indicated in Porto notation. The frequency of each phonon and the atom involved are indicated. The inset shows a Lorentzian fit of the Fe mode for  $x=0.18$  showing a half width at half maximum of about  $2 \text{ cm}^{-1}$ .

used yielding an estimated heating of 20 K. All the temperatures displayed have been corrected for the laser heating. Since the crystals have platelike shapes, only the scattering configuration in which polarizations are in the  $ab$  plane could be measured. All the spectra were corrected for the spectral response of the spectrometer and the CCD detector. They were not corrected for the optical properties of  $\text{NdFeAsO}_{1-x}\text{F}_x$ .

Figure 1 shows the Raman spectra in different polarization configurations for  $x=0$ ,  $x=0.18$ , and  $x=0.30$  using  $\lambda_{\text{exc}}=514.52 \text{ nm}$  (2.4 eV). The Porto notation is used: the first letters refer to the direction of the incoming polarization with respect to crystallographic directions while the second one refers to the direction of the outgoing polarization.  $x$  and  $y$  refer to  $[100]$  and  $[010]$  directions, respectively, while  $x'$  and

$y'$  refer to  $[110]$  and  $[1-10]$  directions, respectively.  $\text{NdFeAsO}_{1-x}\text{F}_x$  has tetragonal symmetry at room temperature and fluorine doping is believed to suppress the orthorhombic distortion that occurs at low temperature in the undoped compound.<sup>3,5</sup> The  $xy$  configuration probes the  $B_{2g}$  symmetry, the  $x'y'$  the  $B_{1g}$  symmetry, while the  $xx$  and  $x'x'$  probe the  $A_{1g}+B_{1g}$  and  $A_{1g}+B_{2g}$  symmetries, respectively.

In agreement with the data and analysis of Hadjiev *et al.*<sup>20</sup> for undoped  $\text{SmFeAsO}$ , four zone-centered Raman-active phonons are found. Two have  $B_{1g}$  symmetry and two have  $A_{1g}$  symmetry. Their assignment was reported by Hadjiev *et al.*:<sup>20</sup> the  $A_{1g}$  modes at 167 and 205  $\text{cm}^{-1}$  arise from the out of plane motions of the Nd and As atoms, respectively, and the  $B_{1g}$  modes at 209  $\text{cm}^{-1}$  (206  $\text{cm}^{-1}$  for  $x=0$  and 210  $\text{cm}^{-1}$  for  $x=0.30$ ) and 339  $\text{cm}^{-1}$  arise from the out of plane motions of the Fe and O atoms, respectively. Except for the Fe mode the phonon frequencies show only weak changes with varying  $x$  content. The hardening of the Fe mode with increasing  $x$  is consistent with the data of Le Tacon *et al.*<sup>21</sup> which also show a hardening of this mode between  $x=0$  and  $x=0.15$ .

An important aspect of the data reported here is that all the phonons are sharp and symmetrical. In particular the half width at half maximum (HWHM) of the Fe mode is only about  $2 \text{ cm}^{-1}$  at room temperature for all doping  $x$  (see the inset of Fig. 2). This value is considerably lower than in the cuprates where the HWHM of most of the phonon lines at room temperature is at least  $5 \text{ cm}^{-1}$ . In addition, in the cuprates, several phonon lines exhibit strong coupling with the electronic continuum and show a distinctive asymmetrical Fano line shape.<sup>22</sup> Correspondingly, except for a broadening of the Nd phonon line upon increasing  $x$ , fluorine doping has a very limited impact on the phonon line shapes (linewidths and positions), again in contrast with cuprates such as Y-123, or to a lesser extent Bi-2212, where phonon lines show large renormalizations upon doping.<sup>23-26</sup> Altogether, these observations suggest a rather weak coupling between in-plane polarized Raman-active phonons and electronic degrees of freedom in oxypnictides. We note that a strong coupling of the Fe in-plane breathing mode to the electronic continuum has been suggested<sup>15</sup> but this mode is only accessible using polarization along the  $c$ -axis and is therefore not reported here.

The Raman spectrum in  $xx$  configuration for  $x=0.18$  at room temperature as a function of the incident laser energy is displayed in Fig. 2. Compared to the Nd mode, the Fe mode shows a significant increase in intensity toward when excited using near infrared excitation energy (1.9 eV). When normalized to the integrated intensity of the Nd mode, its integrated intensity increases by almost a factor of 3 between 2.2 and 1.9 eV. Such a resonant profile of the Fe mode suggests the presence of an interband transition located around or below 2 eV involving a Fe  $3d$  related band. Recent DMFT calculations indeed predict an interband transition between As  $4p$  and Fe  $3d$  related bands around 2 eV.<sup>9</sup> A recent optical study of  $\text{LaFeAsOF}$  also found a weak interband transition in the same energy range.<sup>27</sup> The reported resonance enhancement may provide a route to explore electronic Raman scattering from quasiparticle excitations arising from Fe  $3d$  related Fermi surfaces.

The temperature dependence of the Raman spectrum be-

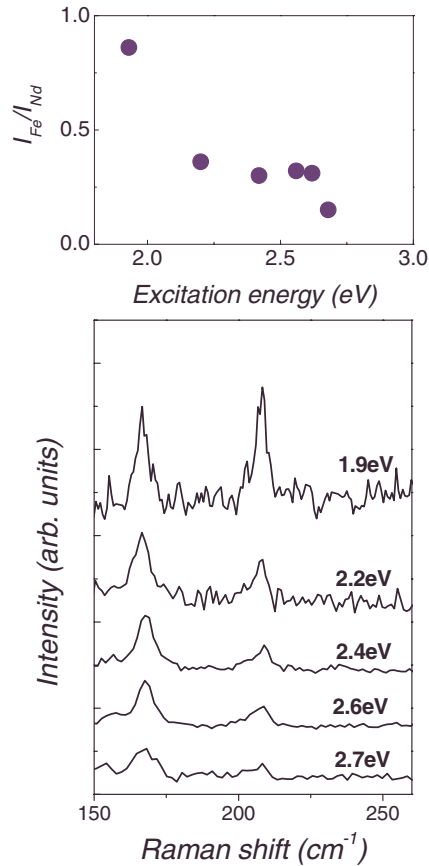


FIG. 2. (Color online) Lower panel: room-temperature Raman spectra as a function of laser excitation energy for the  $xx$  polarization configuration and  $x=0.18$ . The upper panel shows the resonance profile of the Fe mode integrated intensity with respect to the Nd mode integrated intensity.

tween 320 and 30 K for  $x=0.18$  is shown in Fig. 3. The Nd, Fe, and As mode frequencies show modest temperature dependences. The Fe mode shows a slightly more pronounced hardening upon cooling. This results in an enhanced splitting of the As and Fe modes which become clearly resolved upon lowering temperature. No anomaly in linewidths and positions is detected when crossing  $T_c$  for all three modes. The same behavior was reported by Litvinchuk *et al.*<sup>29</sup> in related, oxygen-free  $K_x\text{Sr}_{1-x}\text{Fe}_2\text{As}_2$  single crystals. This is in sharp contrast with the cuprates where anomalies in phonon frequencies and linewidths are often observed upon crossing  $T_c$ .<sup>23,26,30–34</sup> In the entire temperature range, the phonon frequencies can be reproduced by a standard anharmonic decay model<sup>28</sup> in which a zone-centered optical phonon decays into two lower-frequency acoustical phonons. The result of the fit is shown in Fig. 3 for the Nd, As, and Fe modes. Again the

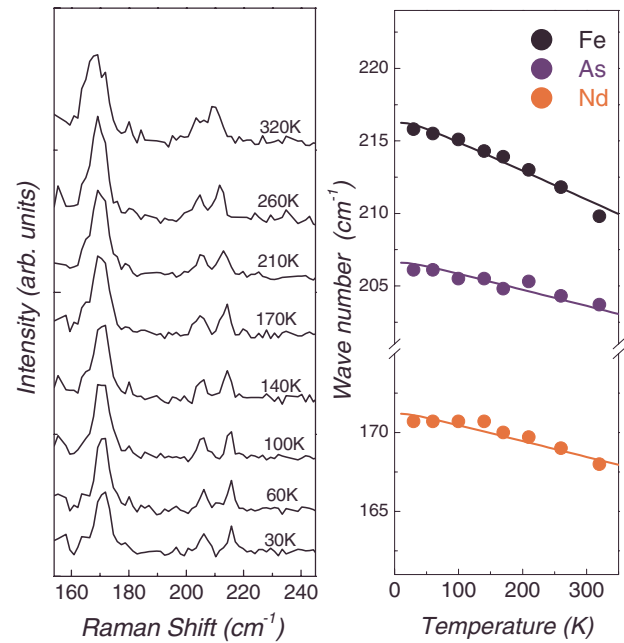


FIG. 3. (Color online) Left panel: Temperature dependence of the Raman spectra in  $xx$  polarization configuration for  $x=0.18$ . The evolution of the phonon frequencies as a function of temperature is reported in the right panel. The solid lines show a fit with a standard anharmonic behavior using the following expression for the phonon frequency:  $\omega(T) = \omega_0 + C \left( 1 + \frac{2}{\exp\left(\frac{\hbar\omega_0}{2k_B T}\right)} \right)$ , where  $\omega_0$  is the bare phonon frequency and  $C$  a temperature independent fitting parameter (Ref. 28).

absence of phonon anomalies at  $T_c$  highlights the absence of a significant coupling between the Raman-active phonons and the electronic degrees of freedom.

In conclusion we have reported plane-polarized Raman spectra of  $\text{NdFeAsO}_{1-x}\text{F}_x$ . The doping dependence and the temperature dependence of the phonon modes suggest a weak coupling between Raman-active modes and electronic excitations. The situation is in contrast with the cuprates where several phonon line exhibits strong line shape renormalizations due to electron-phonon coupling. This weak electron-phonon coupling may prevent the use of phonons to gain insight into the electronic degrees of freedom as done in the cuprates.<sup>34</sup> The direct observation of electronic Raman scattering will likely require larger single crystals but the strong enhancement of the Fe phonon mode intensity below 2 eV reported here suggests the possibility of resonantly enhancing the electronic Raman-scattering cross section. This may shed light into the symmetry of the superconducting order parameter in iron oxypnictides.

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