Temperature dependence and resonance effects in Raman scattering of phonons in NdFeAsO$_x$F$_{1-x}$ single crystals

Y. Gallais$^1$, A. Sacuto$^1$, M. Cazayous$^1$, P. Cheng$^2$, L. Fang$^2$, and H. H. Wen$^2$

MPQ CNRS UMR 7622 Université Paris 7-Paris Diderot, Bâtiment Condorcet, 75205 Paris Cedex 13, France

$^2$Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

We report plane-polarized Raman scattering spectra of iron oxypnictide superconductor NdFeAsO$_{1-x}$F$_x$ 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.

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 [1]. Most of the compounds discovered up to now have the formula ReFeAsO$_{1-x}$F$_x$ 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 $T_c$ with fluorine F. This mechanism of strongly correlated high temperature superconductivity besides the one of the cuprates [1]. Most of the compounds which arise from the various Fe related bands crossing the Fermi level complicates further the determination of the order parameter symmetry [10, 11]. On the other hand, 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 [14]. Nevertheless recent reports of a nodeless gap via ARPES [12, 13] and the strong sensitivity of the calculated band structures near the Fermi level to the distortions the FeAs tetrahedra indicate the possible role of vibrational degrees of freedom [14, 15, 16, 17, 18]. Therefore the role of phonons and their coupling to electronic degrees of freedom deserved to be scrutinized.

In this communication we report plane-polarized Raman scattering measurements of zone-center phonons in NdFeAsO$_{1-x}$F$_x$ 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 non-superconducting. 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 [19]. The typical lateral size of the crystals studied here is about 20x20µm.

The measurements were performed using a micro-Raman set-up in back scattering geometry. Several excitation lines of an Ar/Kr laser were used ranging from 1.9 eV to 2.7 eV. The scattered light was collected and analyzed by a triple grating spectrometer (JY T64000) and a back-illuminated nitrogen cooled CCD camera. The room temperature measurements were performed with a x50 objective. For the low temperature measurement the crystals were mounted on the cold finger of cryostat and...
a long working distance x50 objective was used.

Special care was taken in order to avoid overheating the crystals and power densities were kept below 10³ W/cm². 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 used yielding an estimated heating of 20 K. All the temperatures displayed have been corrected for the laser heating. Since the crystals have plate-like shapes, only the scattering configuration in which polarizations are in the ab plane could be measured. All the spectra were corrected for the optical properties of NdFeAsO₁₋ₓFₓ.

Figure 1 shows the Raman spectra in different polarization configurations for x=0, x=0.18 and x=0.30 using λ=514.52 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 [−10] directions respectively. NdFeAsO₁₋xFₓ 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. The xy configuration probes the B₂g symmetry, the x′y′B₁g symmetry while the xx and x′x′ probe the A₁g+B₁g and A₁g+B₂g symmetries respectively.

In agreement with the data and analysis of Hadjiev et al. for undoped SmFeAsO, four zone centered Raman active phonons are found. Two have B₁g symmetry and two have A₁g symmetry. Their assignment was reported by Hadjiev et al.: the A₁g modes at 167 cm⁻¹ and 205 cm⁻¹ arise from the out of plane motions of the Nd and As atoms respectively and the B₁g modes at 209 cm⁻¹ (206 cm⁻¹ for x=0 and 210 cm⁻¹ for x=0.30) and 339 cm⁻¹ arise from the out of plane motions of the Fe and O atoms respectively. Except for the Fe mode the phonons 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. 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 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 cm⁻¹. In addition, in the cuprates, several phonon lines exhibit strong coupling with the electronic continuum and show a distinctive asymmetrical Fano lineshape. Corresponingly, except for a broadening of the Nd phonon line upon increasing x, fluorine doping has a very limited impact on the phonons lineshapes (linewidths and positions), again in contrast with cuprates like Y-123, or to a lesser extent Bi-2212, where phonon lines shows large renormalizations upon doping. 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 but this mode is only accessible using polarization along the c-axis and is therefore not reported here.

In Fig. 2 is displayed the Raman spectrum in xx configuration for x=0.18 at room temperature as a function of the incident laser energy. Compared to the Nd mode, the Fe mode shows a significant increase in intensity towards when excited using near infra-red 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 eV 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 predicts an interband transition between As-4p and Fe-3d related bands around 2 eV. A recent optical study of LaFeAsOF also found a weak interband transition in the same energy range. 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 between 320 K and 30 K for x=0.18 is shown in Fig. 3. The Nd, Fe and As modes 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 Tc for all three modes. The same behavior was reported by Litvinchuk et al. in related, oxygen-free KₓSr₁₋ₓFe₂As₂ single crystals. This is in sharp contrast with the cuprates where anomalies in phonon frequencies and linewidths are often observed upon crossing Tc. In the entire temperature range, the phonon frequencies can be reproduced by a standard anharmonic decay model 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 absence of phonon anomalies at Tc 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 NdFeAsO₁₋xFₓ. The doping dependence and the temperature dependence of the phonon modes sug-
gest a weak coupling between Raman-active modes and electronic excitations. The situation is in contrast with the cuprates where several phonons line exhibits strong lineshape 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 was done in the cuprates. 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.

[1] Y. Kamihara, T. Watanabe, M. Hirano and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
[2] Z.-A. Ren, L. Wei, J. Yang, W. Yi, X.-L. Shen, Z.-C. Li, G.-C. Che, X.-L. Dong, L.-L. Sun, F. Zhou and Z.-X. Zhao, Chin. Phys. Lett. 25, 2215 (2008).
[3] C. de la Cruz, Q. Huang, J.W. Lynn, J. Li, W. Ratcliff II, J.L. Zarestky, H.A. Mook, G.F. Chen, J.L. Luo, N.L. Wang, and P. Dai, Nature 453, 899 (2008).
[4] Y. Chen, J.W. Lynn, J. Li, G.F. Chen, J.L. Luo, N.L. Wang, P. Dai, C. de la Cruz and H.A. Mook, Phys. Rev. B 78, 064515 (2008).
[5] Y. Qui, W. Bao, Q. Huang, T. Yildrim, J. Simmons, J.W. Lynn, Y.C. Gasparovic, J. Li, M. Green, T. Wu, G. Wu and X.H. Chen, arXiv:08062195.
[6] I.I. Mazin and M.D. Johannes, arXiv:0807.3737.
[7] T. Park, E. Park, H. Lee, T. Klimczuk, E.D. Bauer, F. Ronning and J.D. Thompson, J. Phys. Condens. Matter 20, 322204 (2008).
[8] P.L. Alireza, J. Gillett, Y.T. Chris Ko, S.E. Sebastian and G.G. Lonzarich, arXiv: 0807.1896.
[9] K. Haule, J.H. Shim and G. Kotliar, Phys. Rev. Lett. 100, 226402 (2008).
[10] S. Lebegue, Phys. Rev. B 75, 035110 (2007).
[11] C. Liu, T. Kondo, M. Tillman, G.D. Samolyuk, Y. Lee, J.L. McCchesney, S. Bud’ko, M. Tanatar, E. Rotenberg, P. Canfield, R. Prozorov, B. Harmon and A. Kaminski. arXiv:0806.2147 (2008).
[12] H. Ding, P. Richard, K. Nakayama, T. Sugarawa, T. Arakane, Y. Sekiba, A. Takayama, S. Souma, T. Sato, T. Takahashi, Z. Wang, X. Dai, Z. Fang, G.F. Chen, J.L. Luo and N.L. Wang, Europhys. Lett. 83, 47001 (2008).
[13] T. Kondo, A.F. Santadner-Syro, O. Copie, C. Liu, M. Tillman, E.D. Mun, J. Schmalian, S.L. Bud’ko, M. Tanatar, P. Canfield and A. Kaminski. arXiv:0807.0815 (2008).
[14] L. Boeri, O.V. Dolgov and A.A. Golubov, Phys. Rev. Lett. 101, 026403 (2008).
[15] H. Eschrig, arXiv:0804.0186.
[16] I.I. Mazin, M.D. Johannes, L. Boeri, K. Koepenik and D.J. Singh, arXiv:0806.1869.
[17] D.J. Singh and M.H. Du, Phys. Rev. Lett. 100, 237003 (2008).
[18] V. Vildosola, L. Prougovskii, S. Biermann and A. Georges, arXiv:0806.3285.
[19] Y. Jia, P. Cheng, L. Fang, H. Luo, H. Yang, C. Ren, L. Shan, C. Gu and H.-H. Wen, Appl. Phys. Lett. 93, 032503 (2008).
[20] V.G. Hadjiev, M.N. Iliev, K. Sasimal, Y.Y. Sun and C. W. Chu, Phys. Rev. B 77, 220505(R) (2008).
[21] M. Le Tacon, M. Krisch, A. Bosak, J.-W.G. Bros and S. Margadonna, to appear in Phys. Rev. B (2008).
[22] S.L. Cooper, F. Slakey, M.V. Klein, J.P. Rice, E.D. Bukowski and D.M. Ginsberg, Phys. Rev. B 38, 11934 (1988).
[23] E. Altendorf, X.K. Chen, J.C. Irwin, R. Liang and W.N. Hardy, Phys. Rev. B 47, 8140 (1993).
[24] X. Zhou, M. Cardona, D. Colson and V. Viallet, Phys. Rev. B 55, 12770 (1997).
[25] V.G. Hadjiev, X. Zhou, T. Strohm, M. Cardona, Q.M. Lin and C.W. Chu, Phys. Rev. B 58, 1043 (1998).
[26] A.A. Martin, J.A. Sanjurjo, K.C. Hewitt, X.-Z. Wang, J.C. Irwin and M.J.G. Lee, Phys. Rev. B 56, 8426 (1997).
[27] M. Opel, R. Hackl, T.P. Devereaux, A. Virostek, A. Zawadowski, A. Erb, E. Walker, H. Berger and L. Forro, Phys. Rev. B 60, 9836 (1999).
[28] K.C. Hewitt, X.K. Chen, C. Roch, J. Chrzanski, J.C. Irwin, E.H. Altendorf, R. Liang, D. Bonn and W.N. Hardy, Phys. Rev. B 69, 064514 (2004).
[29] S.-L. Drechsler, M. Grobosh, K. Koepenik, G. Behr, A. Köhler, J. Werner, A. Kondrat, N. Leps, Ch. Hess, R. Klingeler, R. Schuster, B. Büchner and M. Knupfer, arXiv:0805.1321 (2008).
[30] A.P. Litvinchuk, V.G. Hadjiev, M.N. Iliev, Bing Lv, A.M. Guloy and C.W. Chu, Phys. Rev. B 78, 060503(R) (2008).
[31] R.M. Macfarlane, H.J. Rosen and H. Seki, Solid State Commun. 63, 831 (1987).
[32] R. Zeyher and G. Zwicknagl, Z. Phys. B 69, 175 (1990).
[33] B. Friedl, C. Thomsen and M. Cardona, Phys. Rev. Lett. 65, 915 (1990).
[34] P.G. Klemens, Phys. Rev. 148, 845 (1966).
FIG. 1: (Color online) Room temperature Raman spectra of NdFe$_{1-x}$F$_x$AsO$_1$ with incident and scattered light 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 (HWHM) of about 2 cm$^{-1}$.
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.
FIG. 3: (Color online) Left panel: Temperature dependance 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: $\omega(T)=\omega_0 + C(1+\frac{\omega_0^2}{2\hbar\omega_0^2kB})$ where $\omega_0$ is the bare phonon frequency and $C$ a temperature independent fitting parameter [34].