Anharmonic softening of Raman active phonons in Iron-Pnictides; estimating the Fe isotope effect due to anharmonic expansion.

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We present Raman measurements on the iron-pnictide superconductors CeFeAsO$_{1-x}$F$_x$ and NdFeAsO$_{1-x}$F$_x$. Modeling the Fe-As plane in terms of harmonic and a cubic anharmonic Fe-As interaction we calculate the temperature dependence of the energy and lifetime of the Raman active Fe $B_{1g}$ mode and fit to the observed energy shift. The shifts and lifetimes are in good agreement with those measured also in other Raman studies which demonstrate that the phonon spectrum, at least at small wave numbers, is well represented by phonon-phonon interactions without any significant electronic contribution. Even at zero temperature there is a non negligible effect of interactions on the phonon energy, which for the Fe $B_{1g}$ mode corresponds to 6 cm$^{-1}$, or 3% of the total energy of the mode. We also estimate the anharmonic expansion from Fe (56 → 54) isotope substitution to $\Delta \alpha \approx 5.1 \cdot 10^{-4} \AA$ and $\Delta d_{Fe-As} \approx 2.5 \cdot 10^{-4} \AA$ and the shift of harmonic zero point fluctuations of bond lengths $<\Delta r^2> \approx 3 \cdot 10^{-3} \AA^2$, giving a total relative average decrease of electronic hopping integrals of $|\delta t|/t \lesssim 3 \cdot 10^{-4}$. For a non-phonon mediated weak coupling superconductor this gives an isotope exponent $\alpha \sim 10^{-2}$. The results pose a serious challenge for any theory of superconductivity in the pnictides that does not include electron-phonon interactions to produce a sizable Fe-isotope effect.

I. INTRODUCTION

The recently discovered iron-pnictide high temperature superconductor$^{[2]}$ have several features in common with the much studied cuprate superconductors. In addition to their overall quasi-two dimensional nature such features include commensurate antiferromagnetism in close proximity to or even coexisting with superconductivity. Intriguingly, there is also a common tendency for breaking of the fourfold rotational symmetry of the crystal$^{[3]}$ which in the case of the cuprates is most likely an intrinsic electronic property related to the strong correlations. For the pnictides (as well as in some cases for the cuprates) there is at low doping a crystal symmetry breaking from tetragonal to orthorhombic which is closely connected to an accompanying spin density wave (SDW) order$^{[4]}$. This interplay between atomic and electronic degrees of freedom naturally leads to the question: What is the role of phonons for the electronic properties of these systems? Focusing on the pnictides, results from density functional theory (DFT$^{[5]}$) are credible as they give an electronic spectral distribution consistent with photoemission experiments$^{[6]}$ but have also found that the electron-phonon coupling is much too weak to explain the high $T_c$. Challenging these findings was the recent report of an isotope shift of $T_c$ (and $T_{SDW}$) when substituting $^{56}$Fe with $^{54}$Fe with an exponent of $\alpha = -\frac{\Delta \ln T_c}{\Delta m} = 0.4$ close to the BCS value of 0.5 for a pure iron mode$^{[7]}$. The mechanism for superconductivity in the pnictides is a major unresolved issue and it is clearly essential to understand better the lattice-electron interplay.

In this paper we measure and model one particular Raman active phonon which lives primarily on Fe atoms and thus common to all iron-pnictide superconductors. The purpose is to study the anharmonic structure of the Fe-As plane with two main objectives: First, to investigate whether any non-phonon contributions are necessary to describe the temperature dependence of the phonon energy and lifetime. Second, to estimate the magnitude of the lattice expansion that follows from substitution with a lighter mass and the corresponding changes in electronic hopping integrals, thus investigating the plausibility of a non-phonon related isotope effect in the pnictides$^{[8,9,10]}$.

In brief, we model the harmonic spectrum of the As-Fe plane and use standard Greens function methods to calculate the self energy of the Fe $B_{1g}$ Raman phonon to second order in the cubic anharmonic Fe-As interatomic coupling. The harmonic spectrum is based on a minimal parameter fit to spectra derived within the local density approximation (LDA) of DFT but the calculation of the temperature dependent contribution from phonon-phonon interactions is beyond the capabilities of that method. We present Raman results on (Nd,Ce)FeAsO$_{1-x}$F$_x$ and estimate the anharmonic coupling strength by fitting our model calculations to the measured temperature dependent energy shift. Also the width agrees well with Raman measurements on CaFe$_2$As$_2$ thus effectively ruling out any significant electronic contribution to the broadening. Based on the magnitude of the anharmonic coupling we estimate the isotope ($^{56}$Fe→$^{54}$Fe) shift of the lattice parameters to $\lesssim 2 \cdot 10^{-4}$ and calculate a similar relative decrease of interatomic hopping integrals. Harmonic zero point fluctuations give an even smaller isotope shift of hopping.
FIG. 1: (Color online) Temperature dependent Raman spectra for NdFeAsO$_{1-x}$F$_x$ ($x = 0.12$) showing three Raman active phonon modes labeled by their symmetry and main atomic displacement.

integrals. In weak coupling theory correspondingly small changes in the electronic density of states (DOS) is expected to give an isotope exponent $\alpha \sim 10^{-2}$.

II. RAMAN SPECTRA

Raman spectra between 100cm$^{-1}$ and 400cm$^{-1}$ were collected at temperatures ranging from 20K to 300K for polycrystalline samples of CeFeAsO$_{1-x}$F$_x$ ($x = 0.16$) and NdFeAsO$_{1-x}$F$_x$ ($x = 0.12$). For sample preparation and characterization see Chen at al. All spectra were recorded using a Dilor-XY800 spectrometer in double subtractive mode. In all scans the 514.5 nm line from a Ar$^+$ laser used with a power of less than 1mW was focused onto the samples with a spot size less than 2 $\mu$m. The samples were installed in a LHe cooled cryostat. We observe three Raman active modes with energies around 170, 210 and 220 cm$^{-1}$, see Fig. 1 and Fig. 2 in agreement with other Raman studies that are identified as (Ce/Nd)-$A_{1g}$, As-$A_{1g}$, and Fe-$B_{1g}$ modes respectively. Also in agreement with earlier studies we found no effect on the phonon energies from crossing into the superconducting phase ($T_c = 35K/45K$ for Ce/Nd). As discussed in the introduction we will be interested in analysing the temperature dependence of the energy as extracted in Fig. 3 and for modeling purposes we consider only the Fe-$B_{1g}$ ($x^2 - y^2$) mode which lives primarily in the Fe-As plane.

FIG. 2: (Color online) Raman spectra for CeFeAsO$_{1-x}$F$_x$ ($x = 0.16$).

FIG. 3: (Color online) Temperature dependence of the phonon peak position for NdFeAsO$_{0.88}$F$_{0.12}$ (red) as extracted from Fig. 1 and correspondingly for CeFeAsO$_{0.84}$F$_{0.16}$ (blue) from Fig. 2.

III. MODELING

The temperature dependence of the lifetime and energy of a phonon is ordinarily due to phonon-phonon interactions that arise from anharmonic interatomic potentials. In general the cubic anharmonicity is the dominant term and we consider only this. The Raman ($\vec{q} = 0$) intensity for Stokes scattering for the mode $j$ at frequency
\( \omega \) is given by \( I_S(j, \omega) \propto -(1 + n(\omega))(n D_{ret}(\vec{q} = 0, j, \omega)_{\perp}) \)

where \( D_{ret} \) is the retarded phonon Greens function which to linear order in the self energy \( \Pi = \Delta - i \Gamma \) (minus sign by convention) gives

\[
I_S(j, \omega) \propto \frac{(1 + n(\omega))\Gamma(\vec{0}, j, \omega)}{[\omega_0(\vec{0}, j) + \Delta(\vec{0}, j, \omega) - \omega]^2 + \Gamma^2(\vec{0}, j, \omega)}
\]

where \( n(\omega) = (e^{\hbar \omega/k_B T} - 1)^{-1} \) is the Bose occupation factor. The measured width (FWHM) is thus ideally given by \( \Gamma \) and the shift by \( \Delta \). We calculate the self energy to second order in the interaction \( H_A = \frac{1}{6} \sum_{(\vec{q}_i, j_i)} V(\vec{q}_i, j_1; \vec{q}_2, j_2; \vec{q}_3, j_3) A_{\vec{q}_i, j_i} A_{\vec{q}_2, j_2} A_{\vec{q}_3, j_3} \delta_{\vec{q}_i, 0} \)

where \( A_{\vec{q}, j} = a_{\vec{q}, j} + a_{\vec{q}, j}^\dagger \) is the phonon operator. \( V \) are the matrix elements

\[
V(\vec{q}_1, j_1; \vec{q}_2, j_2; \vec{q}_3, j_3) = \sum_{r_1, r_2, r_3, \vec{R}_1, \vec{R}_2, \vec{R}_3} \left[ \prod_{i=1}^3 \left( \frac{\hbar}{2M_{r_i} \omega(\vec{q}_i, j_i)} \right)^\frac{3}{2} e^{i \vec{q}_i \cdot \vec{R}_i} e^{-i \vec{R}_i \cdot (r_i) \cdot \nabla} \right] \phi(r_1, r_2, r_3, \vec{R}_1, \vec{R}_2, \vec{R}_3)
\]

with the numerical value \( \kappa = 0.10 \).

FIG. 4: (Color online) Schematic of the Fe-As plane with in-plane lattice parameter \( a \). The harmonic interatomic couplings are \( k \), \( k' \) and \( k'' \) and cubic coupling \( g \) as described in the text. Arrows indicate the Fe B\(_{1g}\) mode.

A. Phonon self energy

Now we are ready to address the frequency shift by calculating the self-energy to second order in \( V_0 \). The self energy is given by the bubble diagram with imaginary part.
dependence $\Gamma(\omega) \sim (1 + 2n(\omega/2))$. As discussed previously we find instead that the scattering is approximately isotropic between modes and we need to do a more careful analysis. In principle we could calculate this expression numerically at each temperature using our numerical phonon spectrum but instead we will use an approximate Lorentzian fit for the phonon DOS with the advantage of giving an analytic expression for both $\Gamma$ and $\Delta$ including the full temperature dependence. The calculated phonon DOS, plotted in Fig. 5 consists of three regions of high density centered around $w_1 \approx 100\text{cm}^{-1}$, $w_2 \approx 200\text{cm}^{-1}$, $w_3 \approx 300\text{cm}^{-1}$. The lower part contains $m_1 = 4$ modes, the intermediate part contains $m_2 = 3$ modes and the upper part $m_3 = 5$ modes giving

$$\rho(\omega) \approx \frac{N}{\pi} \sum_{i=1}^{3} m_i \left(\frac{\gamma}{(w - \omega_j)^2 + \gamma^2}\right) = \sum_i \rho_i(\omega),$$ (5)

which is thus normalized by $\int_{-\infty}^{\infty} \rho(\omega) = 12N$ and where we estimate $\gamma = 25\text{cm}^{-1}$. To proceed we evaluate the occupation factor $n(\omega)$ at the peak position of the respective DOS and assume a q-independent spectral weight giving $\Gamma$ as an integral over all pairs of peaks of the spectral weight with the result

$$\Gamma_0(\omega) = \frac{1}{2\hbar^2} V_0^2 \sum_{i,j=1}^{3} m_i m_j \left[(1 + n(\omega_i) + n(\omega_j)) \frac{2\gamma}{(\omega - \omega_i - \omega_j)^2 + 4\gamma^2} - \frac{2\gamma}{(\omega + \omega_i + \omega_j)^2 + 4\gamma^2}\right]$$

$$+ (n(\omega_i) - n(\omega_j)) \frac{2\gamma}{(\omega + \omega_i - \omega_j)^2 + 4\gamma^2} - \frac{2\gamma}{(\omega - \omega_i + \omega_j)^2 + 4\gamma^2}].$$ (6)

The expression is naturally understood as the scattering of the mode at $\omega$ into two modes within the same or different DOS peaks (or the corresponding difference process). Note that $\Gamma_0(\omega_{B_{1g}})$ will be dominated by scattering into the low-energy peak ($i = j = 1$) which will give

$$\Delta_0(\omega) = \frac{1}{2\hbar^2} V_0^2 \sum_{i,j=1}^{3} m_i m_j \left[(1 + n(\omega_i) + n(\omega_j)) \frac{(\omega - \omega_i - \omega_j)}{(\omega - \omega_i - \omega_j)^2 + 4\gamma^2} - \frac{(\omega + \omega_i + \omega_j)}{(\omega + \omega_i + \omega_j)^2 + 4\gamma^2}\right]$$

$$+ (n(\omega_i) - n(\omega_j)) \frac{(\omega + \omega_i - \omega_j)}{(\omega + \omega_i - \omega_j)^2 + 4\gamma^2} - \frac{(\omega - \omega_i + \omega_j)}{(\omega - \omega_i + \omega_j)^2 + 4\gamma^2}].$$ (7)

FIG. 5: (Color online) Phonon density of states of the isolated Fe-As plane calculated within the harmonic model discussed in the text and its approximation in terms of three Lorentzians (solid curve) that contain 4,3,5 modes with increasing energy respectively.

(The phonon-difference process, the second term, vanishes at zero temperature but can give a significant contribution at finite temperature.) The simplest standard way to evaluate this expression is to assume that the scattering is diagonal in the modes $V_0 \sim \delta_{j_1, j_2}$, the Klemens model\cite{13} which gives a characteristic temperature dependence $\Gamma(\omega) \sim (1 + 2n(\omega/2))$.
FIG. 6: (Color online) Fit of the model frequency shift ($\Delta_0$) to data for $NdFeAsO_{0.86}F_{1.2}$ (boxes) and $CeFeAsO_{0.84}F_{1.16}$ (diamonds). Inset are the corresponding model lifetimes ($\Gamma_0$) together with linewidth data (triangles) on CaFe$_2$As$_2$ from Choi et al.[2]

IV. DISCUSSION

Figure 6 shows the fit from equation [7] to the experimental values using $\omega = \omega_0 + \Delta_0(\omega_{Bi})$, with fitting parameters $\omega_0$ and $g$ ($\Delta_0 \sim g^2$). For the Nd sample we find $\omega_0 = 221.7 cm^{-1}$ and $g = 103 eV/A^2$ and for the Ce sample $\omega_0 = 221.0 cm^{-1}$ and $g = 116 eV/A^2$, where $\omega_0$ is close to the assumed harmonic value $\omega_{Bi} = 220 cm^{-1}$.[13]

It is interesting to note that we find $\Delta_0(T = 0) \approx 6 cm^{-1}$, i.e. even at zero temperature phonon-phonon interactions give a finite (here 3%) contribution to the phonon energy, an effect which LDA calculations of phonon energies based on linear response neglects.

Due to the polycrystalline nature of our samples we are not able to find reliable phonon widths and compare instead our theoretical results to Raman studies by Choi et al.[12] on CaFe$_2$As$_2$. In that material the $B_{1g}$ mode has lower energy but the temperature dependence is similar and the width correspond well with our calculations without any additional fit. The temperature dependence is in fact just the Klemens model but the strength of the calculation is that only one parameter $g$ gives both the shift and the width. In Ref.[12] the linewidth variations were tentatively assigned to changes in the electronic scattering below $T_{SDW}$. These speculations we can quite definitely rule out; the anharmonic contribution accounts to good accuracy for both the shift and linewidth variations of this mode.[12]

A. Lattice expansion

The cubic coupling will give rise to an expansion of the lattice that we estimate by considering an isolated Fe-As bond for which $< 0|\delta r|0 > = \frac{h_0}{2(\omega_{Bi})^2} \delta r^2$ with $m^* = Mm/(m + M)$. We include also a nearest neighbor Fe-Fe anharmonic coupling $g'$ with the same relative strength $(g' = g(k/k)^{3/2})$. With this the isotope substitution $^{56}$Fe$\rightarrow$ $^{54}$Fe gives an expansion of the in-plane lattice parameter $\Delta a = 5.1 \times 10^{-4} \AA$ and Fe-As distance $\Delta d_{Fe-As} = 2.5 \times 10^{-4} \AA$, which compared to $\omega \approx 4 \AA$ and $d_{Fe-As} \approx 2.5 \AA$ gives a relative expansion $\lesssim 2 \cdot 10^{-4}$.

What is the possible effect of a small lattice expansion on $T_\epsilon$ and $T_{SDW}$? There is a direct effect on the electronic hopping integrals $t$, and theories of an isotope effect based on this has been suggested for the cuprates and $C_{60}$ as well the pnictides.[16,18-20] Assuming $t = t_0 e^{-q(r/r_0-1)}$ with $q \approx 1$[22] and where $\vec{r} = r_0\vec{r} + \delta$ with small displacement $\delta$ we find $\frac{\delta t}{t_0} = -q\frac{\delta r}{r_0} - \frac{2}{2}\delta r + \frac{2}{2}\delta r^2$ where $\delta_r = \delta \cdot \vec{r}$ and $\delta_{\perp} = \delta \times \vec{r}$. The linear term has only an anharmonic contribution whereas the quadratic terms will get contributions from zero point fluctuations in the harmonic approximation. We estimate $\delta^2$ from the ground state energy per atom $\epsilon_0 = 38.9 meV$ and $\epsilon_0 = 39.2 meV$ for $^{56}$Fe and $^{54}$Fe respectively and energy $\epsilon_0/2$ per Fe-As bond. The fluctuation along a bond is given by $\frac{\delta^2 \delta r^2}{2} \approx \epsilon_0/4 (k = 8.7 eV/A^2)$, giving the difference $\delta t^2 \approx \epsilon_0/(2k) \approx 2.3 \cdot 10^{-3} A^2$ and for the transverse fluctuations $\delta_{\perp}^2 \approx 2 \delta r^2 \approx 4.6 \cdot 10^{-5} A^2$.[20] The contribution to the shift of the hopping integrals is partially canceled by the different signs and in total smaller by an order of magnitude compared to the anharmonic contribution.

B. Isotope effect

Consider a weak coupling (non phonon mediated) SC or SDW transition with $T_\epsilon \sim \Omega e^{-1/N(0)V}$, where $\Omega$ is the relevant energy cut-off, which may be the magnon energy for spin fluctuation mediated pairing, $V$ is the effective interaction and $N(0)$ the relevant electronic DOS at the Fermi energy. Focusing on the contribution from the DOS, $N(0) \approx 1/t$ gives the isotope exponent $\alpha = -\frac{d \ln T_\epsilon}{d \ln \Omega} \approx -N(0)/\Omega \approx 5.5 \cdot 10^{-2} \approx 10^{-2}$. (Assuming $N(0)V \approx 0.5$. It cannot be much smaller to get a high $T_c$.) The interaction strength and $\Omega$ may also depend on the hopping integrals and give isotope shifts of similar magnitude. Although this is a simple analysis we expect the order of magnitude estimate to be relevant to any purely electronic microscopic model containing inter and intra orbital hopping integrals and interactions that only depend indirectly on the lattice parameters.

Alternatively, we may relate the change of lattice parameter to a corresponding pressure of $dP = \frac{3\Delta a}{a} / \beta \approx 0.4 kbar$ through the compressibility $\beta = -\frac{d \ln V}{d \ln P} \approx 1.0 \cdot 10^{-3}/kbar$.[20] (We have no estimate of the c-axis change related to the in-plane expansion but only assume that this is of similar relative magnitude.) Pressure dependence of $T_\epsilon$ of around 0.2K/kbar has been reported in several materials at different dopings although close to
optimal doping it appears that the effect is generally significantly smaller.\textsuperscript{22} Nevertheless, from these considerations we find an upper estimate of the isotope exponent $\alpha \approx 0.06$.

Clearly something more sophisticated is needed to produce $\alpha = 0.4$ as found experimentally in Ref.\textsuperscript{9}. Encouraging perhaps, the sign from the naive weak coupling analysis based on a change in the electronic DOS does agree with experiments and would naturally imply a similar exponent for both SC and SDW.\textsuperscript{25}

V. SUMMARY

In summary, we find that the temperature dependent shift and width of a Raman active phonon is well represented by the anharmonic contribution, consistent with weak electron-phonon interactions. At the same time, we estimate the change of electronic hopping integrals due to weak electron-phonon interactions. The anharmonic contribution, consistent with changes in the lattice parameter of isotope substituted samples, are the same within the experimental error of $\sim 1 \cdot 10^{-3}$ Å, which is greater than the change $\Delta a \approx 5 \cdot 10^{-4}$ Å calculated here. There also appeared a report of a negative Fe-isotope effect with $\alpha = -0.18$\textsuperscript{26} Again, XRD data find the same in-plane lattice parameter within experimental error of $\sim 1 \cdot 10^{-3}$ Å\textsuperscript{10}.

VI. ACKNOWLEDGEMENT

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Note added After the submission of this work x-ray diffraction (XRD) data on the samples used for the isotope experiments appeared (Ref. 9 supplemental). Changes in the lattice parameter of isotope substituted samples are the same within the experimental error of $\sim 1 \cdot 10^{-3}$ Å, which is greater than the value $\Delta a \approx 5 \cdot 10^{-4}$ Å calculated here. There also appeared a report of a negative Fe-isotope effect with $\alpha = -0.18$\textsuperscript{26} Again, XRD data find the same in-plane lattice parameter within experimental error of $\sim 1 \cdot 10^{-3}$ Å\textsuperscript{10}.

[Footnotes]

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