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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 $\mathrm{CeFeAsO}_{1-x}\mathrm{F}_x$ and $\mathrm{NdFeAsO}_{1-x}\mathrm{F}_x$. Modeling the Fe-As plane in terms of harmonic and a cubic anharmonic Fe-As interactions, 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-negligent 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 $(56\rightarrow 54)$ isotope substitution to $\Delta a \approx 5.1\times 10^{-4}$ Å and $\Delta d_{\text{Fe-As}} \approx 2.5\times 10^{-4}$ Å and the shift of harmonic zero-point fluctuations of bond lengths $\langle \Delta x^2\rangle \lesssim 3\times 10^{-5}$ Å^2, giving a total relative average decrease in electronic hopping integrals of $|\delta t|/t \lesssim 2.0\times 10^{-4}$. For a nonphonon-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.

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I. INTRODUCTION

The recently discovered iron-pnictide high-temperature superconductors (SC) (Ref. 1) 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[2] which in the case of the cuprates is most likely an intrinsic electronic property related to the strong correlations.[3] For the pnictides (as well as in some cases for the cuprates), there is at low doping a crystal symmetry breaking from tetragonal to orthorombic which is closely connected to an accompanying spin-density wave (SDW) order.[4,5] This interplay between atomic and electronic degrees of freedom naturally leads to the question of what is the role of phonons for the electronic properties of these systems? Focusing on the pnictides, results from density-functional theory (DFT) (Refs. 6 and 7) are credible as they give an electronic spectral distribution consistent with photoemission experiments[8] but have also found that the electron-phonon coupling is much too weak to explain the high T_c.[7] 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 $\alpha = -\frac{d \ln T_c}{d \ln m} = 0.4$ close to the BCS value of 0.5 for a pure iron mode.[9] 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 nonphonon 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 nonphonon-related isotope effect in the pnictides.[10,11]

In short, we model the harmonic spectrum of the As-Fe plane and use the standard Green's 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 $(\mathrm{Nd},\mathrm{Ce})\mathrm{FeAsO}_{1-x}\mathrm{F}_x$ 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 $\mathrm{CaFe}_2\mathrm{As}_2$,[12] thus effectively ruling out any significant electronic contribution to the broadening. Based on the magnitude of the anharmonic coupling we estimate the isotope $(^{56}\mathrm{Fe}\rightarrow {}^{54}\mathrm{Fe})$ shift of the lattice parameters to $\lesssim 2\times 10^{-4}$ and calculate a similar relative decrease in interatomic hopping integrals. Harmonic zero-point fluctuations give an even smaller isotope shift of hopping integrals. In weak-coupling theory correspondingly small changes in the electronic density of states (DOS) is expected to give an isotope exponent $\alpha \sim 10^{-2}$.

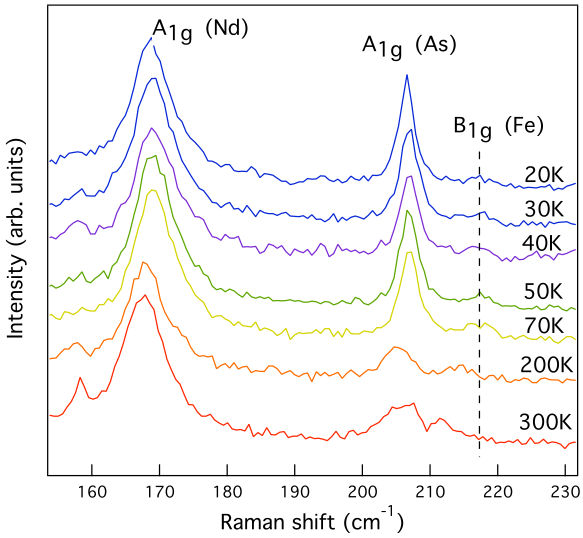

FIG. 1. (Color online) Temperature-dependent Raman spectra for $NdFeAsO_{1-x}F_x$ ($x=0.12$) showing three Raman active phonon modes labeled by their symmetry and main atomic displacement.

II. RAMAN SPECTRA

Raman spectra between 100 and 400 cm^{-1} were collected at temperatures ranging from 20 to 300 K for polycrystalline samples of $CeFeAsO_{1-x}F_x$ ($x=0.16$) and $NdFeAsO_{1-x}F_x$ ($x=0.12$).[13] For sample preparation and characterization see Ref. 14. 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 1 mW was focused onto the samples with a spot size of less than 2 μm. The samples were installed in a liquid He (LHe)-cooled cryostat. We observe three Raman active modes with energies around 170, 210, and 220 cm^{-1} (see Figs. 1 and 2), in agreement with other Raman studies[15] 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 ($T_c=35$ K/45 K for Ce/Nd). As discussed in Sec. I we will be interested in analyzing 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.

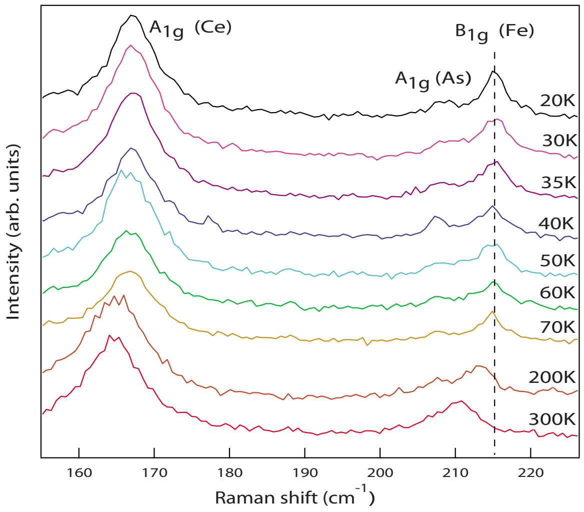

FIG. 2. (Color online) Raman spectra for $CeFeAsO_{1-x}F_x$ ($x=0.16$).

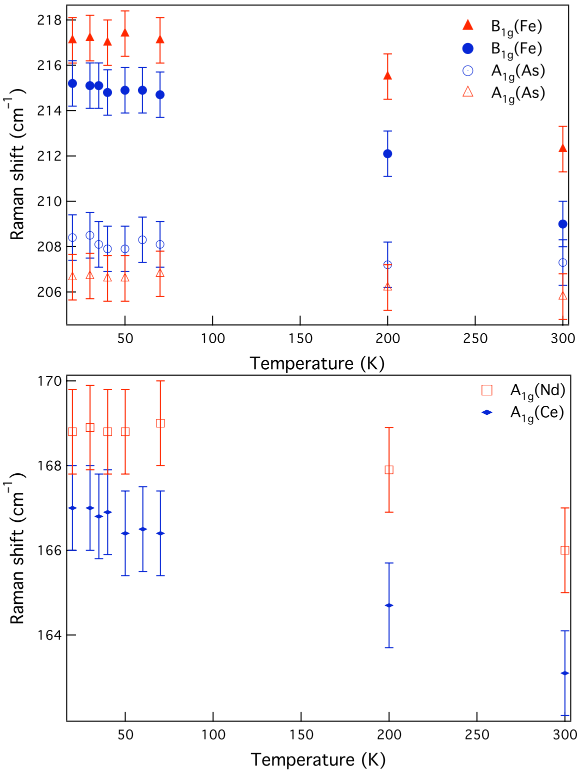

FIG. 3. (Color online) Temperature dependence of the phonon peak position for $NdFeAsO_{0.88}F_{0.12}$ (triangles and boxes) as extracted from Fig. 1 and correspondingly for $CeFeAsO_{0.84}F_{0.16}$ (circles and diamonds) from Fig. 2.

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[16] and we consider only this. The Raman ($\vec{q}=0$) intensity for Stokes scattering for the mode j at frequency ω is given by $I_S(j,\omega)\propto-[1+n(\omega)]\mathrm{Im}\,\mathcal{D}_{ret}(\vec{q}=0,j,\omega)$,[17] where $\mathcal{D}_{ret}$ is the retarded phonon Green's function which to linear order in the self-energy $\Pi=\Delta-i\Gamma$ (minus sign by convention) gives

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

where $n(\omega)=(e^{\hbar\omega/k_BT}-1)^{-1}$ is the Bose occupation factor. The measured width [full width at half maximum (FWHM)] is thus ideally given by Γ and the shift by Δ. We calculate the self-energy to second order in the interaction $H_A=\frac{1}{6}\sum_{\{\vec{q}_i\},\{j_i\}}V(\vec{q}_1,j_1;\vec{q}_2,j_2;\vec{q}_3,j_3)A_{\vec{q}_1,j_1}A_{\vec{q}_2,j_2}A_{\vec{q}_3,j_3}\delta_{\Sigma\vec{q}_i,0}$, where $A_{\vec{q},j}=a_{\vec{q},j}+a^{\dagger}_{-\vec{q},j}$ is the phonon operator.[16] V are the matrix elements

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

where the derivatives act on ϕ, the interatomic potential, with r_i as the atomic positions within unit cell $\vec{R}_i$ and $\vec{e}_{\vec{q}_i,j_i}(r_i)$ are the displacement vectors of the respective mode. The expression thus amounts to the third derivate with respect to phonon displacements of the atomic positions. The iron atoms are only weakly coupled to the (Ce,Nd)O layer and since the phonon dispersions in the c direction are weak[7] we can model the Fe B_{1g} mode by considering only the Fe-As plane. (This also makes the procedure quasiuniversal as it only depends on the properties of this plane which is common to all iron-pnictide superconductors.) For the harmonic problem we use a minimal spring model (Fig. 4) with nearest-neighbor Fe-As potential $\frac{k}{2}\delta r^2$, nearest-neighbor Fe-Fe potential $\frac{k'}{2}\delta r'^2$, and in-plane As-As coupling $\frac{k''}{2}\delta r''^2$ with δr, $\delta r'$, and $\delta r''$ as the deviations from the respective equilibrium distances. For the Fe-As coupling we also add a cubic term $-\frac{g}{6}\delta r^3$, where the magnitude of g is to be estimated from the experimental fit. The Raman active B_{1g} is here a pure Fe mode as depicted in Fig. 4 with energy $\omega_{B_{1g}}=\sqrt{\frac{4k\sin^2\theta}{m}}$ (m=56u) and to get $\omega_{B_{1g}}$=220 cm^{-1} we take k=8.7 eV/Å^2, using θ=35°.[5] The values k'=0.3k and k''=0.2k give a lower edge of the acoustic branches in good agreement with LDA calculations.[7] Using this phonon spectrum we calculate the interaction matrix elements through Eq. (2) and the cubic potential. Sampling the coupling $V(\vec{0},\mathrm{Fe}_{B1g};\vec{q},j_1;-\vec{q},j_2)\equiv V_0(\vec{q},j_1,j_2)$ over the Brillouin zone shows that except at high symmetry points all 12 modes are coupled quite isotropically and do not vary strongly with $\vec{q}$ if the frequency dependence is included, giving

$$V_0(\vec{q},j_1,j_2) \approx \kappa g\left(\frac{\hbar}{2m\omega_{B_{1g}}}\right)^{3/2} \equiv V_0, \tag{3}$$

with the numerical value κ=0.10.

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[16] with imaginary part

$$\begin{aligned}\Gamma(\omega) = \frac{\pi}{2N\hbar^2}\sum_{\vec{q},j_1,j_2}&|V_0(\vec{q},j_1,j_2)|^2\{[1+n(\omega_{\vec{q},j_1})+n(\omega_{\vec{q},j_2})]\\ &\times[\delta(\omega-\omega_{\vec{q},j_1}-\omega_{\vec{q},j_2})-\delta(\omega+\omega_{\vec{q},j_1}+\omega_{\vec{q},j_2})]\\ &+[n(\omega_{\vec{q},j_1})-n(\omega_{\vec{q},j_2})]\\ &\times[\delta(\omega+\omega_{\vec{q},j_1}-\omega_{\vec{q},j_2})-\delta(\omega-\omega_{\vec{q},j_1}+\omega_{\vec{q},j_2})]\}.\end{aligned} \tag{4}$$

(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,[18] which gives a characteristic temperature 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 analytical expression for both Γ and Δ including the full temperature dependence. The calculated phonon DOS, plotted in Fig. 5, consists of three regions of high density centered on $w_1\approx 100$ cm^{-1}, $w_2\approx 200$ cm^{-1}, and $w_3\approx 300$ cm^{-1}. The lower part contains m_1=4 modes, the intermediate part contains m_2=3 modes, and the upper part contains m_3=5 modes giving

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

which is thus normalized by $\int_{-\infty}^{\infty}\rho(\omega)=12N$ and where we estimate γ=25 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 Γ as an integral over all pairs of peaks of the spectral weight with the result

$$\begin{aligned}\Gamma_0(\omega) = \frac{1}{2\hbar^2}V_0^2\sum_{i,j=1}^{3} m_i m_j\Bigg\{&[1+n(\omega_i)+n(\omega_j)]\\ &\times\left[\frac{2\gamma}{(\omega-\omega_i-\omega_j)^2+4\gamma^2}-\frac{2\gamma}{(\omega+\omega_i+\omega_j)^2+4\gamma^2}\right]\\ &+[n(\omega_i)-n(\omega_j)]\\ &\times\left[\frac{2\gamma}{(\omega+\omega_i-\omega_j)^2+4\gamma^2}-\frac{2\gamma}{(\omega-\omega_i+\omega_j)^2+4\gamma^2}\right]\Bigg\}.\end{aligned} \tag{6}$$

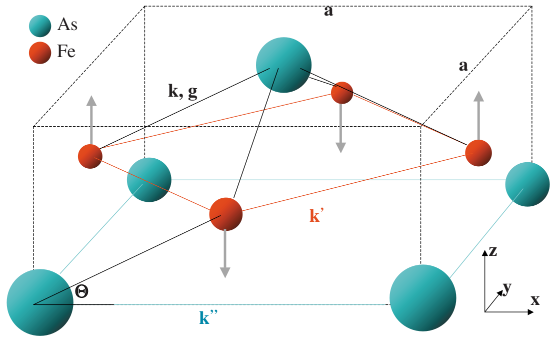

FIG. 4. (Color online) Schematic of the Fe-As plane with in-plane lattice parameter a. The harmonic interatomic couplings are k, k', and k'' and cubic coupling g as described in the text. Arrows indicate the Fe B_{1g} mode.

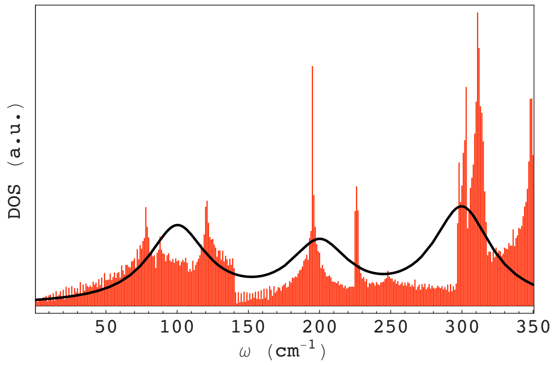

FIG. 5. (Color online) Phonon density of states of the isolated Fe-As plane calculated within the harmonic model discussed in the text and its approximation in terms of three Lorentzians (solid curve) that contain 4, 3, and 5 modes with increasing energy, respectively.

The expression is naturally understood as the scattering of the mode at ω 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 a temperature dependence close to the Klemens model $\Gamma(\omega)\sim[1+2n(\omega/2)]$.[18] Using the Kramers-Kronig relation $\Delta(\omega)=-\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\Gamma(\omega')}{\omega'-\omega}d\omega'$ gives

$$\Delta_0(\omega) = \frac{1}{2\hbar^2}V_0^2\sum_{i,j=1}^{3} m_i m_j\Bigg\{[1+n(\omega_i)+n(\omega_j)] \times\left[\frac{(\omega-\omega_i-\omega_j)}{(\omega-\omega_i-\omega_j)^2+4\gamma^2}-\frac{(\omega+\omega_i+\omega_j)}{(\omega+\omega_i+\omega_j)^2+4\gamma^2}\right] + [n(\omega_i)-n(\omega_j)] \times\left[\frac{(\omega+\omega_i-\omega_j)}{(\omega+\omega_i-\omega_j)^2+4\gamma^2}-\frac{(\omega-\omega_i+\omega_j)}{(\omega-\omega_i+\omega_j)^2+4\gamma^2}\right]\Bigg\}. \tag{7}$$

IV. DISCUSSION

Figure 6 shows the fit from Eq. (7) to the experimental values using $\omega=\omega_0+\Delta_0(\omega_{B_{1g}})$, with fitting parameters ω_0 and g ($\Delta_0\sim g^2$). For the Nd sample we find $\omega_0=221.7$ cm^{-1} and $g=103$ eV/Å^3 and for the Ce sample $\omega_0=221.0$ cm^{-1} and $g=116$ eV/Å^3, where ω_0 is close to the assumed harmonic value $\omega_{B_{1g}}=220$ cm^{-1}.[19] 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 can quite definitely be ruled out; the anharmonic contribution accounts to good accuracy for both the shift and linewidth variations of this mode.[20]

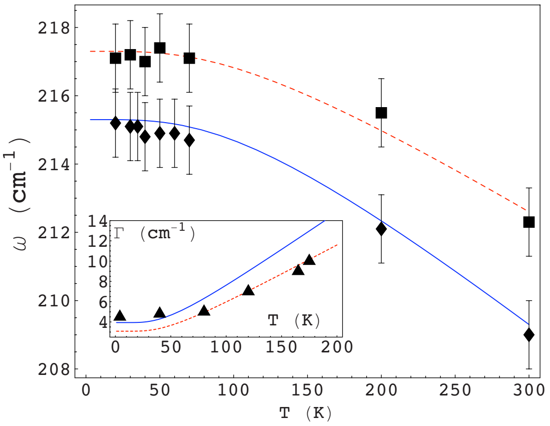

FIG. 6. (Color online) Fit of the model frequency shift (Δ_0) to data for NdFeAsO$_{0.88}$F$_{0.12}$ (boxes) and CeFeAsO$_{0.84}$F$_{0.16}$ (diamonds). Inset is the corresponding model lifetimes (Γ_0) together with linewidth data (triangles) on CaFe$_2$As$_2$ from Choi *et al.*[12]

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 $\langle 0|\delta r|0\rangle=\frac{\hbar g}{4(m*)^{1/2}k^{3/2}}$ 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 → ^{54}Fe gives an expansion of the in-plane lattice parameter $\Delta a=5.1\times10^{-4}$ Å and Fe-As distance $\Delta d_{\text{Fe-As}}=2.5\times10^{-4}$ Å, which compared to $a\approx 4$ Å and $d_{\text{Fe-As}}\approx 2.5$ Å (Ref. 5) gives a relative expansion $\lesssim 2\times10^{-4}$.

What is the possible effect of a small lattice expansion on T_c and T_{SDW}? There is a direct effect on the electronic hopping integrals t, and theories of an isotope effect based on this have been suggested for the cuprates and C$_{60}$ as well the pnictides.[10,11,21] Assuming $t=t_0e^{-q(r/r_0-1)}$ with $q\sim 1$ (Ref. 22) and where $\vec{r}=r_0\hat{r}+\vec{\delta}$ with small displacement $\vec{\delta}$, we find $\frac{\delta t}{t_0}=-q\frac{\delta_r}{r_0}-\frac{q}{2}\frac{\delta_\perp^2}{r_0^2}+\frac{q^2}{2}\frac{\delta_r^2}{r_0^2}$, where $\delta_r=\vec{\delta}\cdot\hat{r}$ and $\delta_\perp=\vec{\delta}\times\hat{r}$. 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 δ^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 $\frac{k}{2}\delta r^2\approx\epsilon_0/4$ ($k=8.7$ eV/Å^2), giving the difference $\delta_r^2\approx\Delta\epsilon_0/(2k)\approx 2.3\times10^{-5}$ Å^2 and for the transverse fluctuations $\delta_\perp^2\approx 2\delta_r^2\approx 4.6\times10^{-5}$ Å^2.[23] The contribution to the shift of the hopping integrals is partially canceled by the different signs and in total smaller by 1 order of magnitude compared to the anharmonic contribution.

B. Isotope effect

Consider a weak-coupling (nonphonon mediated) SC or SDW transition with $T_c \sim \Omega e^{-1/N(0)V}$, where Ω is the relevant energy cutoff, which may be the magnon energy for spin-fluctuation mediated pairing, V is the effective interaction, and $N(0)$ is the relevant electronic DOS at the Fermi energy. Focusing on the contribution from the DOS, $N(0) \sim 1/t$ gives the isotope exponent $\alpha = -\frac{d \ln T_c}{d \ln m} \approx -\frac{1}{N(0)V} \frac{d \ln N(0)}{d \ln m} \approx \frac{0.5 \times 10^{-2}}{N(0)V} \approx 10^{-2}$. [Assuming $N(0)V \approx 0.5$, it cannot be much smaller to get a high T_c.] The interaction strength and Ω 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 interorbital and intraorbital hopping integrals and interactions that only depend indirectly on the lattice parameters.

Alternatively, we may relate the change in lattice parameter to a corresponding pressure of $dP = \frac{3\Delta a}{a} / \beta \approx 0.4$ kbar through the compressibility $\beta = -\frac{d \ln V}{dP} \approx 1.0 \times 10^{-3}/\text{kbar}$ (Ref. 24). (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_c of around 0.2 K/kbar has been reported in several materials at different dopings, although close to optimal doping it appears that the effect is generally significantly smaller.[25] 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. 9. Encouraging perhaps is the sign from the naive weak-coupling analysis based on a change in the electronic DOS that does agree with experiments and would naturally imply a similar exponent for both SC and SDW.[26]

V. SUMMARY

In summary, we find that the temperature-dependent shift and width of a Raman active phonon are well represented by the anharmonic contribution, consistent with weak electron-phonon interactions. At the same time, we estimate the change in electronic hopping integrals due to Fe isotope substitution and find that these are too small to generate an isotope effect on T_c or T_{SDW} of the magnitude reported in Ref. 9 without an explicit phonon contribution. These apparently contradictory results present a significant challenge for any theory of superconductivity in the iron-pnictides.

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 $\sim 1 \times 10^{-3}$ Å, which is greater than the change $\Delta a \approx 5 \times 10^{-4}$ Å calculated here. There also appeared a report of a negative Fe isotope effect with $\alpha = -0.18$.[27] Again, XRD data find the same in-plane lattice parameter within experimental error of $\sim 1 \times 10^{-3}$ Å.[28]

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