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Influence of magnetism on phonons in $CaFe_2As_2$ as seen via inelastic x-ray scattering

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In the iron pnictides, the strong sensitivity of the iron magnetic moment to the arsenic position suggests a significant relationship between phonons and magnetism. We measured the phonon dispersion of several branches in the high-temperature tetragonal phase of $CaFe_2As_2$ using inelastic x-ray scattering on single-crystal samples. These measurements were compared to *ab initio* calculations of the phonons. Spin-polarized calculations imposing the antiferromagnetic order present in the low-temperature orthorhombic phase dramatically improve agreement between theory and experiment. This is discussed in terms of the strong antiferromagnetic correlations that are known to persist in the tetragonal phase.

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Iron-pnictide materials are currently the subject of enormous scientific activity. The discovery of superconductivity with T_c's up to 55 K and the ensuing efforts to understand the possible electronic, magnetic, and phononic mechanisms responsible have already revealed intriguing information.[1,2] For example, first-principles calculations using density functional theory for LaFeAsO strongly suggest that electron-phonon coupling is not sufficient to explain superconductivity.[3] Other calculations demonstrate the strong dependence of the iron magnetic moment on the As atomic position suggesting an interplay between certain phonons and magnetism.[4–6] Experiments and calculations of the crystal structure and magnetism of $CaFe_2As_2$ under pressure show the dramatic sensitivity of the magnetic moment to changes in the atomic positions.[7,8] The motivation for the present investigation was to study phonons in $CaFe_2As_2$ to ascertain any anomalies related to the structure and possible magnetic interactions.

We report measurements of the phonon dispersion in the paramagnetic high-temperature tetragonal phase of single-crystal $CaFe_2As_2$ using inelastic x-ray scattering. Several phonon branches consisting of c-axis polarized As modes are observed to have energies and intensities in poor agreement with nonspin-polarized (NSP) band-structure calculations of the phonon dispersion and structure factor. However, the imposition of antiferromagnetic (AFM) ordering in the tetragonal phase by spin-polarized (SP) calculations brings the dispersion into better agreement with the experimental data. Strong antiferromagnetic correlations have been observed by neutron scattering above the AFM ordering temperature[9] and extend above room temperature.[10] In addition, Wang *et al.*[11] measured a substantial linear increase in the magnetic susceptibility of $BaFe_2As_2$ up to 700 K. Such behavior may indicate spin fluctuations above the AFM ordering temperature.[12] Similar behavior has also been reported for $CaFe_2As_2$ up to at least 300 K.[13] Resistivity measurements also suggest spin fluctuations and spin scattering above the AFM transition temperature.[14] Given the known sensitivity of the Fe magnetic moment to the As z position in the crystal, measurements and calculations of the phonon structure factor indicate an important coupling between local magnetic order and interatomic force constants.

Samples of $CaFe_2As_2$ were prepared by two different research groups. The $CaFe_2As_2$ sample used for measurements along (110) was prepared by the Kanatzidis Group using a stoichiometric elemental mixture in Sn metal flux. Handling of all elements was carried out in a N_2-filled glove box and 0.2 g of Ca, Fe, and As and 4.0 g of Sn metal were used. The mixture was loaded into an alumina tube plugged with ceramic wool and sealed in a silica tube under vacuum. The mixture was heated to 1050 °C for 14 h and kept there for 8 h and then followed by cooling to 600 °C at a rate of 20 °C/h. The molten Sn flux was then filtered with a centrifuge. The resulting square plate crystals of $CaFe_2As_2$ were identified by x-ray powder diffraction.

All other measurements were performed on samples prepared by the Canfield Group out of Sn flux[8,13] using a conventional high-temperature solution growth technique. Small Ca chunks, Fe and As pieces, as well as Sn shots were loaded into an alumina crucible according to the ratio $Ca:Fe:As:Sn=2.13:3.74:4.28:89.84$. A second "catch" crucible containing quartz wool was placed on top of this "growth" crucible. Both crucibles were then sealed into a quartz tube under 1/3 atmosphere Ar gas. The sealed quartz tube was heated to 1150 °C, dwelled for 4 h, and then cooled to 600 °C for 50 h. Once the furnace reached 600 °C, the liquid was decanted from the platelike crystals.

Inelastic x-ray scattering measurements were performed at Sector-3-ID-C of the Advanced Photon Source at Argonne National Laboratory. The incident energy was set to 21.66 keV with an energy resolution of 2.379 meV full width at half maximum. Measurements were performed on a single crystal of $CaFe_2As_2$ measuring approximately 2×2 mm with a thickness of 100 μm. The sample was mounted in both the $(H0L)$ and (HHL) tetragonal planes in a closed-cycle Helium refrigerator and most measurements were performed at room temperature, although some scans were also performed at lower temperatures.

Phonons were measured using constant-Q energy scans along the tetragonal $(0,0,5+\xi)$, $(1,0,3+\xi)$, $(1+\xi,0,3)$, and $(\xi,\xi,4)$ directions at room temperature. The energy transfer scale for each scan was calibrated for monochromator and analyzer temperature drifts. The scans were fit to several peaks using a pseudo-Voigt line profile. The normalized pseudo-Voigt function is given in Eq. (1), where $f_G(x;\Gamma)$ and $f_L(x;\Gamma)$ are normalized Gaussian and Lorentzian functions, respectively. The mixing parameter η=0.393 and resolution full width at half maximum (FWHM) Γ=2.379 meV was determined from fits to the elastic scattering width of Plexiglas,

$$f_{pV}=(1-\eta)f_G(x;\Gamma)+\eta f_L(x;\Gamma). \tag{1}$$

Figures 1(a) and 1(b) show line scans consisting of several phonon excitations at $Q=(0,0,5.75)$ and $Q=(1.5,0,3)$, respectively, along with fits to the data. The peak positions for these and other scans were obtained from the fits and used to construct the dispersion of phonon branches along the different scan directions.

In order to understand the features of the phonon dispersion, the experimental measurements were compared to *ab initio* calculations of the phonons. The phonon dispersion was calculated using density functional perturbation theory (DFPT).[15] There is not yet a consensus on the proper lattice parameters to use for these calculations. In nonmagnetic calculations, relaxing the lattice parameters results in a large contraction of the c axis. In spin-polarized calculations, the lattice distorts into an orthorhombic structure. With these difficulties in mind, experimental lattice parameters were used.[7] In addition, there is controversy over the appropriate internal As parameter to use. We chose relaxed positions so that all forces were zero. For nonmagnetic and spin-polarized calculations, the relaxed As z position is z_{As}=0.3575 and z_{As}=0.3679, respectively. Mittal *et al.*[5] used the experimental value of z_{As}=0.372(1). The pseudopotentials chosen used the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional.[16,17] Settings of an $8\times8\times8$ k-mesh and 24 and 400 eV energy cutoffs for the wave functions and charge density were chosen to ensure that the precision of the calculated phonon dispersion was better than 1.0 meV. Due to the paramagnetic state of $CaFe_2As_2$ at room temperature, nonmagnetic calculations were first performed. Phonon frequencies were calculated on a $2\times2\times2$ q-mesh and then interpolated along several symmetry directions. The resulting phonon frequencies and eigenvectors were used to calculate the dynamical structure factor along the selected scan directions. The dynamical structure factor, which is proportional to the x-ray scattering intensity, is given in Eq. (2).[18] The Debye-Waller factor, $W_d(\mathbf{Q})$, was set equal to zero, and the scattering length is proportional to Z_d, the atomic number of the corresponding atom. $\sigma^j_{\mathbf{d}}(\mathbf{q})$ is the eigenvector corresponding to the normalized motion of atom d in the jth phonon branch.

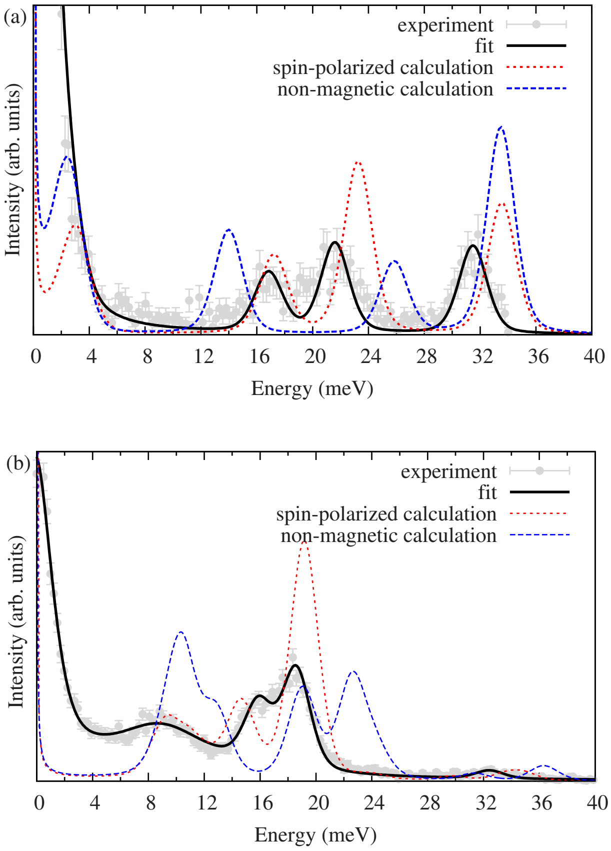

FIG. 1. (Color online) (a) Constant-Q line scan at $Q=(0,0,5.75)$. (b) Constant-Q line scan at $Q=(1.5,0,3.0)$. Experimental data are given by points and pseudo-Voigt fits by the solid line. The dotted (red) and dashed (blue) lines correspond to calculations of the phonon structure factor for spin-polarized and nonmagnetic calculations, respectively.

$$S_j(\mathbf{q},\omega)=\frac{|H^j_{\mathbf{q}}(\mathbf{Q})|^2}{2\omega_j(\mathbf{q})}[1+n_j(\mathbf{q})]\delta[\omega-\omega(\mathbf{q})], \tag{2}$$

$$H^j_{\mathbf{q}}(\mathbf{Q})=\sum_d \frac{Z_d}{\sqrt{M_d}}\exp[-W_d(\mathbf{Q})+i\mathbf{Q}\cdot\mathbf{d}][\mathbf{Q}\cdot\sigma^{\mathbf{j}}_{\mathbf{d}}(\mathbf{q})]. \tag{3}$$

For comparison with experiment, the delta functions were broadened with a pseudo-Voigt function whose parameters were chosen to match the experimental resolution. Figure 1 shows the comparison of the calculated structure factor to the data for two scans. For the scans shown, the nonmagnetic calculations show poor agreement with the phonons observed near ~17 and 20 meV. Figures 2(a) and 3(a) show several observed phonons (white dots) along $(00L)$ and $(H03)$ compared to the nonmagnetic calculated phonon

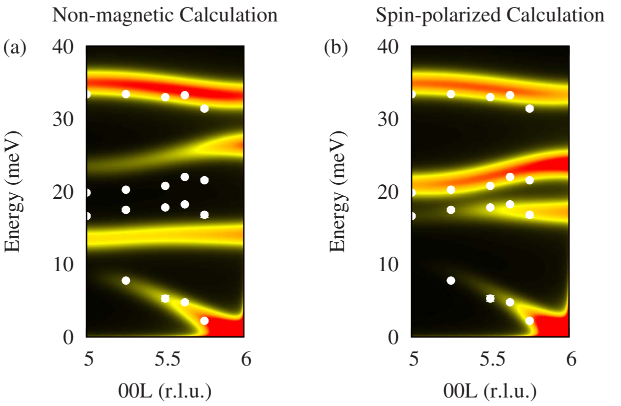

FIG. 2. (Color online) Phonon dispersion weighted by the structure factor along (00L) (a) without and (b) with antiferromagnetic order. The white dots are experimental data points.

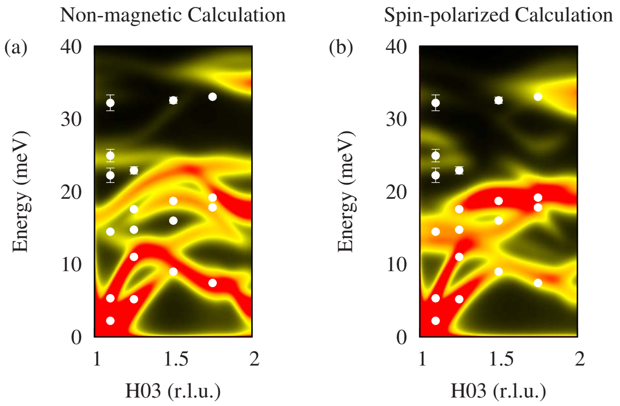

FIG. 3. (Color online) Phonon dispersion weighted by the structure factor along (H03) (a) without and (b) with antiferromagnetic order. The white dots are experimental data points.

dispersion weighted by the structure factor.

The agreement between calculations and the data dramatically improved when spin-polarized calculations were performed using a $4\times4\times4$ k mesh in a supercell using the observed antiferromagnetic structure of orthorhombic $CaFe_2As_2$. PBE overestimates the magnetic moment, with a value of $2.39\mu_B/\mathrm{Fe}$ versus $0.80(5)\mu_B/\mathrm{Fe}$ observed experimentally.[19] Similar discrepancies between the calculated and observed magnetic moment were discussed in phonon studies of $BaFe_2As_2$.[20] Software limitations prevented constraint of the magnetic moments while performing phonon calculations. Figure 1 shows that the spin-polarized calculations not only provide better agreement with the phonon energies but even the phonon intensities (eigenvectors) show marked improvement. Along (00L) in Fig. 2(b), the agreement of the middle two branches at 17 and 20 meV is dramatically improved by including the AF ordering, which reduces the energy splitting of these two branches. Examination of the eigenvectors of these modes shows that they have Λ_1 symmetry and consist of longitudinally polarized Ca and As modes. SP calculations also show marked improvement for phonon branches in the same energy range along the (100) direction, which connect to the two Λ_1 branches at the zone boundary. Figure 1(b) shows a scan at (1.5,0,3) where SP calculations dramatically improve agreement with the two Δ_3 phonon branches consisting of c-axis polarized transverse Ca and As modes in the 14–20 meV range. Figure 3(b) also shows improved agreement of the SP calculations of select phonon branches along (H03) to the measured dispersion. Measurements of other phonon branches along (110) and (10L) also show better agreement with the SP calculations (not shown).

Along both (00L) and (H00), the upper branch that softens with the introduction of AF order is associated with c-axis polarized As vibrations. Such modes have been predicted to have a strong influence on magnetism due to the sensitivity of the Fe moment on the As z position.[6] Surprisingly, the lower branches starting at 17 meV are primarily c-axis polarized Ca modes in the NSP calculations. However, the spin polarization introduces a strong mixing of these two branches of identical symmetry. Such mixing leads to the increased frequency and changes in intensity between SP and NSP calculations shown in Figs. 2 and 3.

The improved agreement of the spin-polarized calculations in the paramagnetic phase may seem surprising; however, resistivity and magnetic susceptibility measurements suggest spin fluctuations and spin scattering above the AFM transition temperature.[8] Inelastic neutron-scattering experiments indicate substantial antiferromagnetic correlations that persist above $T_N=172$ K (Ref. 9) and up to at least 300 K.[10] These correlations are observed up to high energies (>60 meV) with correlation lengths up to 20 Å, which indicates that strong AF correlations exist between sizable Fe moments even above T_N. Magnetism must be accounted for when considering the chemical binding and the interatomic forces. Cooling of the sample into the AF ordered orthorhombic phase at 140 K appears to have little influence on the position or linewidth of the phonons along (00L).

In summary, we have measured the phonon dispersion along several high-symmetry directions for the paramagnetic high-temperature tetragonal phase of $CaFe_2As_2$. Spin-polarized first-principles calculations are in better agreement with the experimental results than nonspin-polarized calculations. The effects of large theoretical magnetic moments and the details of the spin fluctuations at room temperature are issues still under investigation.

Recently, Mittal *et al.*[5] posted data from inelastic neutron-scattering experiments and nonspin-polarized band-structure calculations for $CaFe_2As_2$. This measurement is in excellent agreement with their published dispersion curves. Considerations of magnetic effects on the phonon force constants and density of states were posted by Mazin and Johannes[4] and Yildirim.[6]

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