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Magnetism dependent phonon anomaly in LaFeAsO observed via inelastic x-ray scattering

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The phonon dispersion was measured at room temperature (above the Néel temperature $T_N$) along (0,0,L) in the tetragonal phase of LaFeAsO using inelastic x-ray scattering. Magnetostructural effects are well documented in the AFe$_2$As$_2$-based (A = Ca, Sr, Ba, Eu) systems. Only recently have single crystals of LaFeAsO become available. The experimentally observed splitting between two $A_{1g}$ phonon modes at 22 and 26 meV is only reproduced in spin-polarized calculations. Magnetostructural effects similar to those observed in the AFe$_2$As$_2$ materials are confirmed to be present in LaFeAsO. This is discussed in terms of the strong antiferromagnetic correlations that are known to persist above $T_N$ and into the tetragonal phase.

Despite rather convincing arguments that superconductivity in the AFe$_2$As$_2$ (A = Ca, Sr, Ba, Eu) and RFeAsO (R = La, Ce, Pr, Nd, Sm, Gd)-based compounds does not originate from conventional electron-phonon coupling, these systems do display significant sensitivity to the lattice geometry. While these magnetostructural effects are well documented in the AFe$_2$As$_2$-based systems, the difficulty of synthesizing RFeAsO in single-crystalline form allowed only for a limited quantitative confirmation of similar magnetostructural coupling across the AFe$_2$As$_2$ and RFeAsO systems.

LaFeAsO single crystals were synthesized in NaAs flux at ambient pressure as described elsewhere. Inelastic x-ray scattering measurements were performed on the HERIX instrument at sector 30-ID-C of the Advanced Photon Source at Argonne National Laboratory. Scattering is described in terms of the tetragonal $P4/nmm$ unit cell. In order to understand the features of the phonon dispersion, the experimental measurements were compared to ab initio calculations of the phonons using Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT). The experimental lattice parameters at room temperature in the tetragonal phase ($a = 4.03533 \text{ Å}$ and $c = 8.74090 \text{ Å}$) were used for all calculations. The calculated relaxed positions, where all forces were zero, were used for the internal $z$-parameters determining the position of lanthanum and arsenic atoms. Structural parameters used for the nonmagnetic and spin-polarized calculations as well as experimental results are given in Table I. The pseudopotentials chosen used the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional. Additional experimental and computational details are given elsewhere.

Figure 1 shows a scan consisting of several phonon excitations at $Q = (0,0,8.4)$ at room temperature. Experimental data are given by green dots and pseudo-Voigt fit by a solid black line. The peak positions for this and other scans were used to construct the dispersion of phonon branches along different directions, as shown in Fig. 2. The intensity of the phonon modes multiplied by the energy is also represented in Fig. 2 by the diameter of the circles. At $(0,0,8.4)$, the acoustic mode and a nearby optical mode are present at 7 and 11 meV, along with three other modes at 22, 26, and 34 meV, respectively. Over the entire range measured, the Lorentz fraction $\eta$ varies between 0.48 and 1.0 and the full width at half maximum $\Gamma$ varies between 1.85 and 3.96.

Fig. 3 shows several calculations of the dynamical structure factor at $Q = (0,0,8.4)$, which can be directly compared to Fig. 1. The red dotted line is a nonmagnetic calculation. Frequencies for the acoustic and lowest optical modes are in reasonable agreement with the experiment, but the calculated intensity of the optical mode is too high. The phonon excitation near 24 meV consists of two modes separated by less than 1 meV. These two $A_{1g}$ modes consist of As and La motion polarized along the $c$-axis. This result from the nonmagnetic calculation is inconsistent with the measurements, where these two modes are clearly split by 4 meV at $(0,0,8.4)$. At this value of $Q$, the 32 meV feature consists of both Fe and As motion, but the intensity is extremely weak.

In the spin-polarized calculation corresponding to the observed spin density wave (SDW) structure, the effect of the Fe magnetization is to strongly split the two 24 meV branches at $(0,0,8.4)$ with the 21 meV excitation, containing As motion, lowering its energy by approximately 7.8%. The ratio of intensities between the acoustic and the nearby optical mode moves in the same direction as...
in the experiment. In order to better understand the importance of the specific magnetic order and the size of the Fe moment on the lattice dynamics, two additional calculations were performed for hypothetical magnetic structures. First is the “checkerboard” magnetic structure. It is a tetragonal space group, where Fe neighbors have opposite spins. Second is the CeFeAsO structure, also referred to as “striped.” It is an orthorhombic space group with ferromagnetic coupling of Fe moments along the \( c \)-axis. The dynamical structure factor for this material is shown with black dashes in Fig. 3.

Fig. 2 compiles all of the experimental data and calculations of the nonmagnetic and SDW magnetic structure by showing several contour plots of the dynamical structure factor along \((0,0,L)\). Values range from no intensity (blue) to high intensity (red), and have been multiplied by the energy to improve visibility of the optical modes. The white dots show the experimentally determined energies, as described in the text, with the intensity (also multiplied by the energy) shown by the size of the dot. (a) Nonmagnetic calculation and (b) calculation with SDW magnetic order.

alignment, and in better agreement with the experiment compared to the nonmagnetic calculations. This behavior can be interpreted as a consequence of Fe moments still being present above \( T_N \), albeit without long-range order.\(^{13-15}\) Compared to nonmagnetic calculations, imposing an antiferromagnetic (AFM) ordering better describes phonons in LaFeAsO. Consequently, it is likely that the presence of Fe moments, ordered or not, affects the force constants. On-site Fe and As force constants show significant softening compared to

**TABLE I.** Theoretically relaxed and experimentally observed \( z \)-position for La and As atoms at room temperature, and the associated magnetic moment per Fe atom observed below \( T_N \) and total energy. In each case, the room temperature experimental lattice parameters of \((a = 4.03533 \text{ Å} \text{ and } c = 8.74090 \text{ Å})\) were used.\(^{7,8}\)

<table>
<thead>
<tr>
<th></th>
<th>NM</th>
<th>SDW</th>
<th>Striped</th>
<th>Checkerboard</th>
<th>Exp.(^{7,8})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( z_{\text{La}} )</td>
<td>0.13993</td>
<td>0.13875</td>
<td>0.13883</td>
<td>0.13887</td>
<td>0.14154</td>
</tr>
<tr>
<td>( z_{\text{As}} )</td>
<td>0.63829</td>
<td>0.64820</td>
<td>0.64770</td>
<td>0.64401</td>
<td>0.6512</td>
</tr>
<tr>
<td>( \mu_{\text{Fe}} )</td>
<td>0.0</td>
<td>2.32</td>
<td>2.30</td>
<td>1.91</td>
<td>0.36-0.78</td>
</tr>
<tr>
<td>( E ) (Ry)</td>
<td>0.0</td>
<td>-0.032</td>
<td>-0.033</td>
<td>-0.009</td>
<td></td>
</tr>
</tbody>
</table>

**FIG. 1.** Energy scan at constant-Q at \( Q = (0, 0, 8.4) \) measured at room temperature on LaFeAsO. Experimental data are given by solid green dots. The black line is a fit using a pseudo-Voigt function.

**FIG. 2.** Contour plots of the calculated dynamical structure factor along \((0,0,L)\). Values range from no intensity (blue) to high intensity (red), and have been multiplied by the energy to improve visibility of the optical modes. The white dots show the experimentally determined energies, as described in the text, with the intensity (also multiplied by the energy) shown by the size of the dot. (a) Nonmagnetic calculation and (b) calculation with SDW magnetic order.

**FIG. 3.** Dynamical structure factor calculation of constant-Q line scan at \( Q = (0, 0, 8.4) \). The dotted red line corresponds to nonmagnetic calculations of the dynamical structure factor. The solid green line corresponds to spin-polarized calculations imposing the SDW AFM ordering observed at lower temperatures. The black dashed line and blue dashed-dotted lines correspond to spin-polarized calculations with a striped (ferromagnetic along \( c \)) and checkerboard ordering, respectively. The experimentally observed frequencies in Fig. 1 are shown with vertical grey lines. The inset zooms in on the anomalous modes near 24 meV.
nonmagnetic calculations; however, an investigation of the real-space force constants associates the magnetoelastic coupling with a complex renormalization instead of softening of a specific pairwise force.

In summary, we have measured the phonon dispersion along (0,0,L) in the tetragonal phase of LaFeAsO at room temperature, well above the magnetic ordering temperature of 138 K. Nonmagnetic calculations fail to reproduce the observed splitting between two \( A_{1g} \) phonon modes at 22 and 26 meV. Spin-polarized first-principles calculations imposing a number of hypothetical antiferromagnetic orders are qualitatively similar and in better agreement with the experimental results than non-spin-polarized calculations. The presence of Fe-spins is necessary to predict the observed spectrum above \( T_N \); however, the renormalization of the force constants is quite complex and cannot be reduced to a single pair-wise force constant.

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9We used the pseudopotentials La.pbe-nsp-van.UPF, Fe.pbe-paw_kj.UPF, As.pbe-n-van.UPF, and O.pbe-van_ak.UPF from http://www.quantum-espresso.org distribution.


