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Anomalous phonons in CaFe$_2$As$_2$ explored by inelastic neutron scattering

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Abstract. Extensive inelastic neutron scattering measurements of phonons on a single crystal of CaFe$_2$As$_2$ allowed us to establish a fairly complete picture of phonon dispersions in the main symmetry directions. The phonon spectra were also calculated by density functional theory (DFT) in the local density approximation (LDA). There are serious discrepancies between calculations done for the optimized structure and experiment, because the optimised structure is not the ambient pressure structure but is very close to the “collapsed” structure reached at $p = 3.5$ kbar. However, if the experimental crystal structure is used the calculation gives correct frequencies of most phonons. The most important new result is that linewidths/frequencies of certain modes are larger/softer than predicted by DFT-LDA. We also observed strong temperature dependence of some phonons near the structural phase transition near 172 K. This behavior may indicate anomalously strong electron phonon coupling and/or anharmonicity, which may be important to the mechanism of superconductivity.

1. Introduction

The discovery of superconductivity at temperatures exceeding 50 K in iron arsenide compounds with general compositions RFeAsO (R = rare earth) and MFe$_2$As$_2$ (M = alkaline earth metal) and MFeAsF has attracted great interest [1-15] in these materials. At present, it is hotly debated whether these compounds are unconventional metals similar to the cuprate superconductors or can be understood within the same theoretical framework as conventional intermetallic compounds like the borocarbides or MgB$_2$. Superconductivity in these compounds appears either at a critical doping level of the parent compound, or by application of pressure above a critical value. The role of the phonons for the mechanism of superconductivity is not known at present. DFT calculations predict weak electron-
phonon coupling [9] with a negligible contribution to the superconductivity mechanism. Inelastic x-ray scattering investigation [10] of the phonon density of states in LaFeAsO$_1$F$_x$ and NdFeAsO, as well as measurements of a few phonon branches [10(a),11] on single crystals of BaFe$_2$As$_2$ and PrFeAsO$_{1+y}$ showed that DFT is only moderately [10(a),12] successful in predicting phonon frequencies in these compounds. The phonon density of states in BaFe$_2$As$_2$, Sr$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ and Ca$_{0.6}$Na$_{0.4}$Fe$_2$As$_2$ was investigated on polycrystalline samples using inelastic neutron scattering [13,14]. Empirical models used to analyze the data again had limited success.

2. Experiment and phonon calculations

Single crystals of CaFe$_2$As$_2$ (15 mm × 10 mm × 0.4 mm) were grown from a high temperature solution using Sn as flux [15]. The details of crystal characterization are given in Ref. [15]. The neutron measurements were performed on the 1T1 triple-axis spectrometer at the Laboratoire Léon Brillouin, Saclay. Measurements were done with pyrolytic graphite (PG002) as a monochromator and analyzer. Most measurements were carried out at 300K with open collimations and double focusing on both the analyzer and the monochromator. Selected phonons were studied as a function of temperature down to $T = 100$ K, which is well below the magnetic/structural phase transition at 172 K.

The calculations were carried out within the framework of the LDA and GGA using a mixed basis pseudopotential method [16]. A density functional perturbation approach was used for calculating the phonon frequencies and phonon eigenvectors [17]. We employed norm-conserving pseudopotentials and a plane-wave cutoff of 22 Ryd, augmented by local functions at the Ca and Fe sites. Brillouin zone (BZ) summations were done with a Gaussian broadening technique using a broadening of 0.2 eV and 40 wavevector points in the irreducible part of the BZ.

3. Results and discussion

![Comparison of experimentally determined phonon frequencies (solid circles) in the (100), (001) and (110) directions at T = 300 K with results of density functional theory (solid lines). The calculations were based on the experimental crystal structure. The 15 phonon modes along the $\Delta(100)$, $\Lambda(001)$ and $\Sigma(110)$ directions can be classified as $\Delta : 5\Delta_1 + 2\Delta_2 + 5\Delta_3 + 3\Delta_4$; $\Lambda : 4\Lambda_1 + 4\Lambda_2 + 5\Lambda_3$; $\Sigma : 4\Sigma_1 + 2\Sigma_2 + 4\Sigma_3 + 5\Sigma_4$.](image)

Fig. 1 Comparison of experimentally determined [21] phonon frequencies (solid circles) in the (100), (001) and (110) directions at T = 300 K with results of density functional theory (solid lines). The calculations were based on the experimental crystal structure. The 15 phonon modes along the $\Delta(100)$, $\Lambda(001)$ and $\Sigma(110)$ directions can be classified as $\Delta : 5\Delta_1 + 2\Delta_2 + 5\Delta_3 + 3\Delta_4$; $\Lambda : 4\Lambda_1 + 4\Lambda_2 + 5\Lambda_3$; $\Sigma : 4\Sigma_1 + 2\Sigma_2 + 4\Sigma_3 + 5\Sigma_4$.

The optimized structure was initially used for the phonon dispersion calculation. However, as reported previously [18,19], we soon realized that the optimized structure is relatively far away from the experimental one. Figure 1 shows that DFT in the LDA is quite successful in predicting the phonon frequencies in CaFe$_2$As$_2$ if, instead of the relaxed structure, the experimental one is used. It is important to emphasize here that one must impose a nearly perfect tetrahedral environment of the Fe atoms as observed in experiment in order to obtain best agreement between calculated and experimental phonon frequencies. However, even in this case it is worse than in many other
compounds, including conventional superconductors with high $T_c$ like MgB$_2$ [20]. This finding is similar to the previous observations on the Ba122 compounds by inelastic x-ray scattering [10(a)].

Although the calculations based on the experimental structure appear to be more accurate, some important differences with experiment remain. The main one is for the phonons of $\Delta_3$ symmetry between $q=(0.5 \ 0 \ 0)$ and $(1 \ 0 \ 0)$. Some appear around 19 meV but predicted at 22 meV and others are observed around 16 meV but predicted 2 meV lower. One must also keep in mind that the good agreement for other phonons may be somewhat misleading in the sense that the predicted eigenvectors may differ from the experimental ones even where the phonon frequencies agree. In experiment, phonon eigenvectors determine observed phonon intensities. When phonons are nearly degenerate as in CaFe$_2$As$_2$ near 20 meV, different phonon branches may hybridize. In this case small differences between calculated and experimental frequencies result in large differences in the eigenvectors and the comparison between predicted and calculated phonon intensities is not very meaningful. However, in the case of the $\Sigma_3$-frequencies observed at the zone boundary, the situation is clear-cut: because of the high symmetry of the zone boundary point, the $\Sigma_3$-phonons decompose into sub-groups. The mode observed at $E \approx 18$ meV with very high intensity at $(2.5,1.5,0)$ is single and hence, its eigenvector is completely determined by symmetry. It therefore can be unambiguously assigned to a mode calculated at 23 meV by theory. On these grounds, the disagreement between calculated and observed frequencies of $\Sigma_3$-symmetry at the $q=(0.5,0.5,0)$ zone boundary is stronger than one might guess from inspection of Fig. 1 when considering the eigenvectors, the data points shown at 18 meV and 23 meV correspond to calculated frequencies at 23 meV and 20 meV, respectively, i.e. the phonon frequencies are "flipped".

![Fig. 2](image.png)

**Fig. 2** Energy scans [21] taken at $Q = (2.5,1.5,0)$ at room temperature and at a temperature far below the structural phase transformation. The calculated phonon structure factors for non-magnetic and spin-polarized are shown in left and right panels respectively. For better visibility the calculated profiles (dashed lines) in the lower and upper panels are shifted down by 200 counts. The insert in the left panel shows the $q$-dependence of the phonon line widths of the branch around 18 meV (red dots) and around 24 meV (blue dots).

We also found substantial line broadenings for a number of phonons. For instance, an energy scan at a wavevector $Q = (2.5,1.5,0)$ and $T = 300$ K shows a pronounced broadening for a mode at 18 meV (Fig. 2, left), which, based on its intensity, can be unambiguously assigned to Fe vibrations. The line broadening of this branch is maximum at the zone boundary, which becomes a reciprocal lattice point in the low temperature orthorhombic phase. As already mentioned above, its frequency is considerably lower than 23 meV calculated by DFT. There is very little change of this mode on cooling from 300 K to 190 K but its linewidth shrinks considerably below the tetragonal-to-orthorhombic phase transition at 172 K (Fig. 2, right). These observations indicate a close relationship between the line broadening and the structural instability. However, there is no direct relationship between the elongation patterns of the 18 meV mode and the displacements during the phase transition.
We have also carried out spin-polarized DFT-GGA calculations in the orthorhombic phase of CaFe$_2$As$_2$. The calculated phonon spectra for non-magnetic/spin-polarized structures are shown as dashed lines Fig. 2 left/right respectively. It appears that the calculated line widths of phonon modes are larger in the orthorhombic phase because the orthorhombic distortion leads to a splitting of modes. The agreement between our experimental results and the calculation is poor, which further suggest anomalous phonons in CaFe$_2$As$_2$. Unlike the case of BaFe$_2$As$_2$ [11], including magnetism does not improve agreement with experiment (Fig. 2 right).

Simple anharmonicity is unlikely to account for the observed line widths. Strong coupling of phonons to electron-hole excitations is another possibility. However, we calculated the electron-phonon coupling induced phonon line widths using density functional perturbation theory and found that the calculated line widths are much smaller than observed. Also, no strong broadenings appear in BaFe$_2$As$_2$ [3], which has similar electronic and crystal structure, and also orders magnetically below 170 K. Since the main difference between BaFe$_2$As$_2$ and CaFe$_2$As$_2$ that the former is not close to the “collapsed” high pressure phase, this points to the proximity to the “collapsed” high pressure phase as the most probable explanation of the phonon anomalies in CaFe$_2$As$_2$. A mechanism for this behavior, which accounts for the difference between CaFe$_2$As$_2$ and BaFe$_2$As$_2$, has been proposed in [18]. On the other hand, our observation that the broadening of the 18 meV mode becomes much smaller in the magnetic phase leads to the conclusion that the proximity to the magnetic phase is important.

4. Conclusions
More work is necessary to understand the effects we report here. In any case, our findings indicate that the interplay between magnetism and the lattice vibrations is in some way responsible for the anomalous phonons in CaFe$_2$As$_2$. That is to say, the coupling of the vibrational and the electronic degrees of freedom is stronger than calculated by DFT, and hence phonons might play an important role in superconductivity in the doped compounds.