



Beamline: ID28	Experiment title: Measurement of pressure dependence of phonon dispersion relation in CaFe_2As_2	Experiment number: HS-3872
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	Shifts: 18	Local contact(s): Alexei Bossak
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Report:

The discovery of superconductivity in iron arsenic compounds has triggered a large-scale research effort to explore [1-9] the physical properties of these materials. Similar to the high- T_c cuprates, the undoped compounds show [3] a structural phase transition from a high temperature tetragonal to a low temperature orthorhombic phase, followed by an antiferromagnetic spin-density-wave (SDW) transition. Electron or hole doping suppresses these phase transitions and induces superconductivity at lower temperatures. In contrast to the cuprates, these compounds are semimetals and therefore metallic even without doping. At present, it remains unclear whether the change of the electron concentration by doping is essential for achieving superconductivity or whether the suppression of the phase transition into a magnetically ordered state is the main effect. Indeed, it has been found that superconductivity can be induced without doping by applying pressure. For CaFe_2As_2 , T_c as high as 10 K has been found at a moderate pressure of 3.5 kbar [5], while for SrFe_2As_2 and BaFe_2As_2 , superconductivity is achieved [6] at about 28 K at 3.2 GPa and 4.5 GPa respectively.

Present-day density functional theory (DFT) is only partially successful in predicting the structural, vibrational and magnetic properties of the iron-arsenides. The calculations do say that there are several competing phases with nearly the same free energy but in the end, they fail to predict the correct phases as a function of pressure and temperature. In a previous investigation [8] we have shown that DFT gives a satisfactory account of the vibrational properties of CaFe_2As_2 if the calculations are based on the experimental structure. If, however, the calculations are based on the structure obtained from minimization of the free energy, there is very serious disagreement between experimental and calculated phonon frequencies. The disagreement can be traced to the fact that the optimized structure is rather far away from the experimentally observed one. Rather, it is close to a high pressure phase which has been term “collapsed phase” [4] because the volume shrinks considerably during the phase transition. In the present investigation, we used pressure to make the structure of CaFe_2As_2 close the optimized structure of DFT, and then studied lattice vibrations by inelastic x-ray scattering. With the available pressure cell, the experiments had to be performed at room

temperature, at which a fairly high pressure (about 17 kbar) is necessary to induce the phase transition into the collapsed phase. An even higher pressure (about 25 kbar) is necessary to make the c/a -ratio close to the value predicted by DFT for ambient pressure. The maximum pressure achieved in our experiments, i.e. 48 kbar, allowed us to explore also a pressure region far above the phase transition into the collapsed phase..

The inelastic x-ray measurements were carried out using the ID28 beam line at ESRF using Si (999) as monochromator and analyser which led to an energy resolution of 3 meV. The dimensions of the CaFe_2As_2 crystals were reduced to about 40-50 microns in diameter, and about 20 microns thick. The crystal was characterized before and after loading into a membrane diamond anvil cell. Neon was used as pressure transmitting medium in order to ensure hydrostatic conditions. The FWHM of crystal rocking curve was about 0.2° , which indicates good quality of the crystal, and found to remain almost the same during the entire experiment up to the highest pressure of 48 kbar.

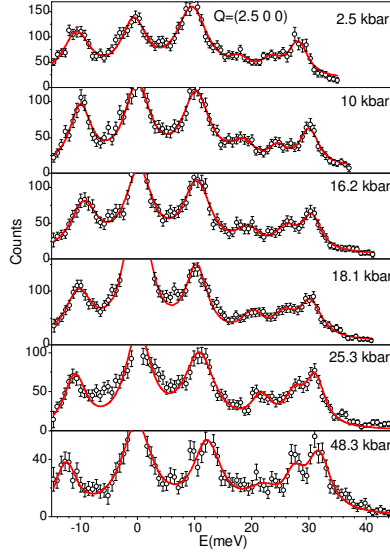


Fig. 1 Energy scans performed at $Q = (2.5 \ 0 \ 0)$. The open circles and full lines correspond to the experimental data and fit curves, respectively. The phase transition happened between 16.2 kbar and 18.1 kbar, leading to a rather large volume change ($\Delta V/V = 0.03$) in spite of the small increment in pressure.

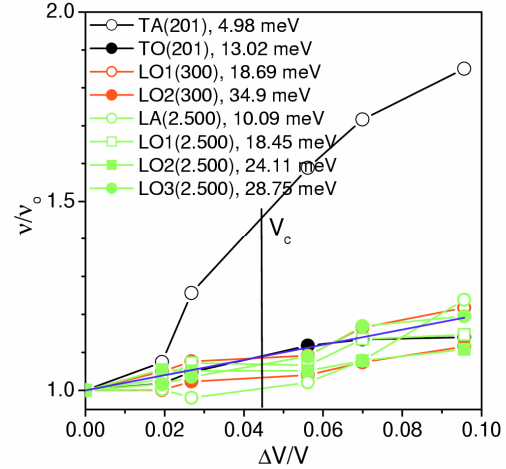


Fig. 2 The variation of phonon energies with volume. The numbers in the bracket after the mode assignment gives the Q values for the measurements, while numbers after the Q values gives the phonon energies at ambient pressure. The blue line is drawn assuming a mode Gruneisen parameter of 2 as expected for the normal behaviour of solid. V_C denotes the volume corresponding to the phase transition pressure of tetragonal to collapsed tetragonal phase of CaFe_2As_2 .

The x-ray measurements could not be started at zero pressure, because the cell had to be loaded first with a certain gas pressure which depends on the final pressure to be reached in this experiment. However, the pressure actually chosen ($p = 2.5$ kbar) was low enough to allow an easy comparison with the zero pressure neutron data. Indeed, we found little difference between the data taken at zero pressure by neutrons and at $p = 2.5$ kbar taken by x-rays. The pressure was then increased in two steps to $p = 16.5$ kbar, i.e. a pressure slightly below that inducing the phase transition into the collapsed phase. The next pressure was chosen as $p = 18.3$ kbar, i.e. slightly above the phase transition. We conclude from our determination of the lattice constants that the phase transition happened indeed in this pressure interval as expected from ref. [4,9]. Thereafter, we increased the pressure in two steps up to the maximum pressure achievable with this set-up, i.e. $p = 48$ kbar. At each pressure, several energy scans were performed at $Q = (2.5 \ 0 \ 0)$, (201) and (300). At 25 kbar and 48 kbar we have carried out additional scans at $Q = (2.25 \ 0 \ 0)$ and $(2.75 \ 0 \ 0)$. Typical scans taken at $Q = (2.5 \ 0 \ 0)$ as a function of pressure are shown in Fig. 1. The scans were fitted to several peaks using a Lorentzian profile. The peak positions, normalized to that observed at the lowest pressure, are plotted in Fig. 2. versus the relative volume. Obviously, the relative volume seems to be the most important parameter determining the frequency changes, because the phase transition does not stand out in the diagram. Further, it appears that most of the phonon modes do not respond very strongly to the pressure induced volume

reduction. The TA001 frequencies are an exception, because they stiffen very much. From our DFT calculations using different structures as input we know that the very strong increase of the TA frequencies is linked not so much to the volume reduction rather than to the shrinkage of the c-axis lattice constant. The comparison between the experimental data and density functional calculations is shown in Fig. 3. In this figure, we have chosen to plot the 25 kbar data because the structure observed at 25 kbar is closest to the optimized structure of DFT. Obviously, the agreement between theory and experiment is far from being perfect, but still satisfactory. This confirms our conjecture that DFT describes the vibrational properties of CaFe_2As_2 in a satisfactory way if based on the respective crystal structure.

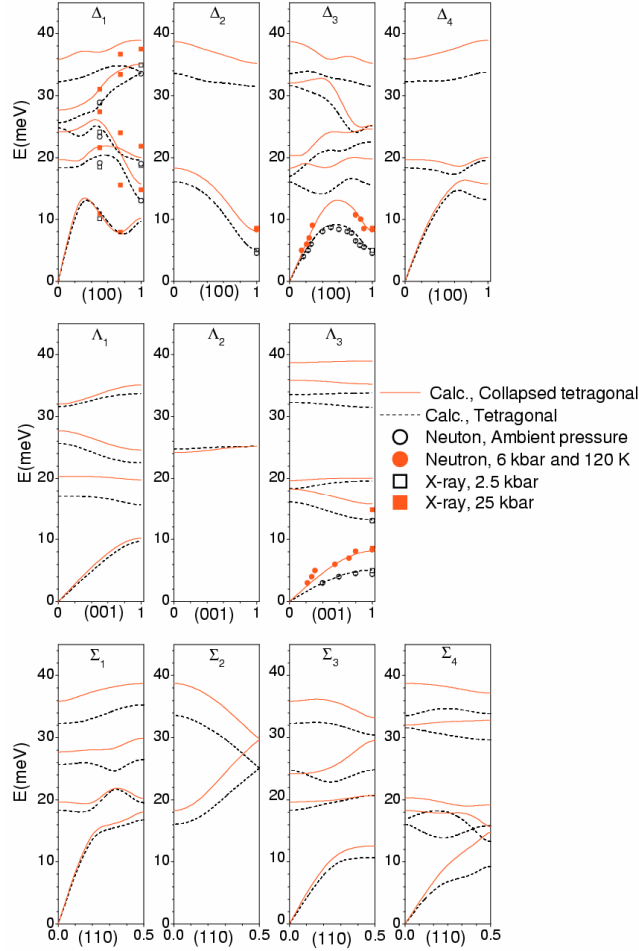


Fig. 3 Comparison between the experimental and calculated phonon dispersion relation in ambient pressure and high pressure collapsed tetragonal phase of CaFe_2As_2 . Results obtained from high pressure neutron inelastic measurements carried out at 6 kbar and 120 K are shown as well.

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