Pressure dependence of phonon modes across the tetragonal to collapsed-tetragonal phase transition in CaFe$_2$As$_2$

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The pressure dependence of a large number of phonon modes in CaFe$_2$As$_2$ with energies covering the full range of the phonon spectrum has been studied using inelastic x-ray and neutron scatterings. The pressure range was large enough to cover the first-order phase transition into the so-called collapsed phase where the c-axis contracts by about 6% whereas a and b axes expand by about 1.5%. Our main result is that pressure-induced phonon frequency shifts are well explained by the changes in relevant bond lengths throughout the pressure range, including those associated with the first-order phase transition. Specifically, the frequencies of phonons polarized in the ab plane as well as the Fe-As bond lengths change little across the phase transition. On the other hand, the transverse-acoustic phonons propagating along the c direction stiffen very significantly in response to the large contraction of the bonds along the c axis. Nonmagnetic density-functional calculations describe the frequencies in both the zero pressure and in the collapsed phase in a satisfactory way if based on the respective experimental crystal structures. This suggests that there is no need to invoke changes in magnetic moments on Fe atoms to explain the pressure-induced frequency shifts.

I. INTRODUCTION

The discovery of superconductivity in iron-arsenic compounds has triggered a large-scale research effort[1–13] to explore these materials and to understand the mechanism of superconductivity. Similar to many of 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 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 in the electron concentration by doping is essential for 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$_2$As$_2$, T_c is as high as 10 K at a moderate pressure of 3.5 kbar (Ref. 5) while for SrFe$_2$As$_2$ and BaFe$_2$As$_2$, superconductivity is achieved at about 28 K at 32 kbar and 45 kbar, respectively.[6]

Neutron powder-diffraction measurements have shown[4] that CaFe$_2$As$_2$ undergoes a structural phase transition at P =3.5 kbar at T=50 K. The new phase remains tetragonal but the lattice parameters change dramatically at the transition. For this reason, the new phase is generally called the collapsed phase: the structural transition causes a decrease in the c-axis lattice parameter by $\sim$6% and an increase in the a-axis parameter by $\sim$1.5%. This phase is not magnetically ordered and it was thought to be the primary candidate for the occurrence of superconductivity with $T_c \sim$ 10 K. However, recent magnetic-susceptibility experiments carried out under purely hydrostatic pressure conditions using He as the pressure medium indicate that superconductivity appears[11] in CaFe$_2$As$_2$ only under somewhat nonhydrostatic pressure conditions. Nevertheless, it seems that chemical doping is not indispensable for achieving superconductivity.

Density-functional theory (DFT) has been only partially successful[7,13] in predicting the structural, vibrational, and magnetic properties of the iron arsenides. It predicts several competing phases with nearly the same free energy. According to these calculations, the Fe-As bond strongly depends on the magnitude and the direction of the Fe-ordered magnetic moment. As a consequence, the Fe moment influences the optimized structure. A reasonable agreement of the optimized structure with the experimental low-temperature structure at ambient pressure can only be obtained when the calculated Fe moment is much larger than reported by neutron scattering.[13] This result led to the idea that Fe moments in
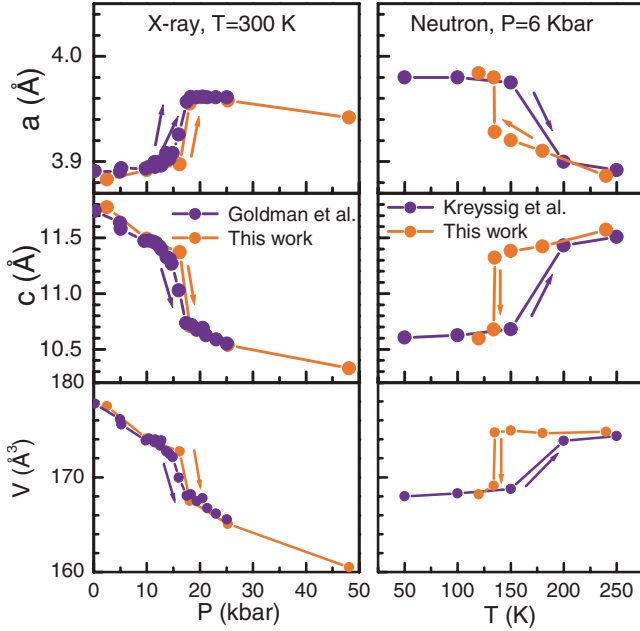
FIG. 1. (Color online) Temperature dependence of the *a*- and the *c*-axis lattice constants and unit-cell volume as measured by x-ray and neutron diffraction. For comparison, the data published by Goldman *et al.* Kreyssig *et al.* (Refs. 4 and 9) are shown, too. The Kreyssig *et al.* data were obtained on heating at a pressure of 6.3 kbar.

the pnictides have a large fluctuating component, which makes them unobservable by elastic neutron scattering.[13–15]

If, however, the Fe moment is fixed to zero (a nonmagnetic calculation), the resulting optimized structure of $CaFe_2As_2$ is quite close to that of the collapsed phase. This result led to the suggestion that Fe moments disappear in the collapsed phase.[13,16] Indeed, recent inelastic neutron-scattering experiments on $CaFe_2As_2$ under applied pressure revealed that antiferromagnetic spin fluctuations are strongly suppressed in the collapsed phase.[17]

Comparison of experimental and calculated phonon frequencies offers an independent way to investigate bonding in the pnictides. In a previous investigation, we have shown[8] that DFT gives a satisfactory account of the vibrational properties of $CaFe_2As_2$ if the calculations are based on the experimentally determined structure. A further check of DFT results can be made either by studying the magnetic low-temperature phase or by studying the collapsed phase by applying pressure. The latter was done in the present study. It allowed us to compare the calculated and predicted frequency changes associated with the very large pressure-induced structural changes. Moreover, it allowed us to see whether the observed frequency changes can be explained from the change in the structure alone. If the fluctuating Fe moment is indeed reduced at high pressure, one may expect that some phonons would stiffen more than expected just from the change in bond lengths.

The x-ray experiments were performed at room temperature. In this case, 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 was considerably higher, i.e., 48 kbar. This allowed us to study the pressure-induced frequency changes also in a pressure range where $CaFe_2As_2$ is expected to show the normal behavior of a solid, i.e., not influenced by a nearby phase transition.

The pressure cell used in the neutron measurements could be cooled to low temperatures. Therefore, a much lower pressure was sufficient to bring the sample into the collapsed phase. The structure finally reached at $P=6$ kbar and $T=120$ K was not much different from that at $P=25$ kbar and room temperature in the x-ray measurements. We will show that the phonon frequencies measured by x rays or neutrons in the different phases correspond quite well to those predicted by DFT when the calculations are based on the respective crystal structures.

II. EXPERIMENTAL

Platelike single crystals of $CaFe_2As_2$, which crystallize in the $ThCr_2Si_2$ tetragonal structure (space group $I4/mmm$), were grown from a Sn flux.[12] The inelastic x-ray experiments were carried out using the ID28 beamline at ESRF, Grenoble (France). For our measurements, we have chosen an energy resolution of 3 meV, corresponding to an incident photon energy of 17 794 eV using the Si (999) setup. The dimension of the $CaFe_2As_2$ crystal was 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 pressure was determined using the ruby fluorescence line. The full width at half maximum 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.

For the inelastic neutron-scattering measurements, we have used the same sample as in our previous measurements[8] for the study of the phonon-dispersion relation at room temperature. It had dimensions of 15 mm × 10 mm × 0.4 mm. The experiments were carried out on the 1T1 triple-axis spectrometer at the Laboratoire Leon Brillouin, Saclay, which is equipped with vertically and horizontally focusing monochromators and analyzers resulting in high neutron intensity. For the high-pressure measurements, the sample was mounted in a gas pressure cell with helium gas as the pressure-transmitting medium. The cell was loaded with a pressure of $P=6$ kbar and then slowly cooled down to 120 K.

The measurements at ESRF as well as at LLB were carried out in the *a-c* scattering plane. The *ab initio* calculation of one-phonon structure factors was used to select the most appropriate Bragg points for the detection of particular phonons.

III. COMPUTATIONAL DETAILS

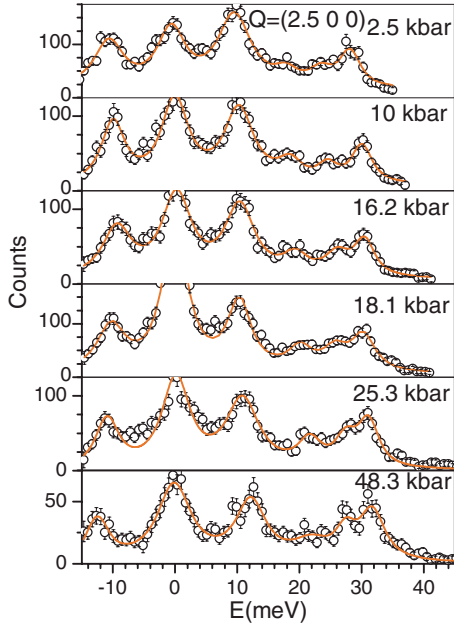Calculations in the framework of density-functional theory were carried out using the mixed-basis pseudopoten-

FIG. 2. (Color online) Energy scans performed at $Q=(2.5\ 0\ 0)$ in the inelastic x-ray scattering experiments. The open circles and full lines correspond to the experimental data and fit curves, respectively. The phase transition happened between 16.2 and 18.1 kbar, leading to a rather large volume change ($\Delta V/V = -0.03$) in spite of the small increment in pressure.

tial method.[18] We employed norm-conserving pseudopotentials and a plane-wave cutoff of 22 Ry, augmented by local functions at the Ca and Fe sites. Brillouin-zone summations were done with a Gaussian broadening of 0.2 eV and 40 k points in the irreducible part of the Brillouin zone (IBZ). In this study, we only used the generalized gradient approximation as given by Perdew, Becke, and Ernzerhof.[19] The linear-response technique was employed for the phonon calculations.[20] Dynamical matrices were calculated on a simple tetragonal $4\times4\times2$ grid (15 q points in the IBZ) from which phonon dispersions were obtained by standard Fourier interpolation.[21,22] We note that all the calculations for the present study were nonspin-polarized because all the phases investigated in this study are not magnetically ordered.

IV. RESULTS

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. 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. After the first increase, the pressure was $P=16.5$ 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 determin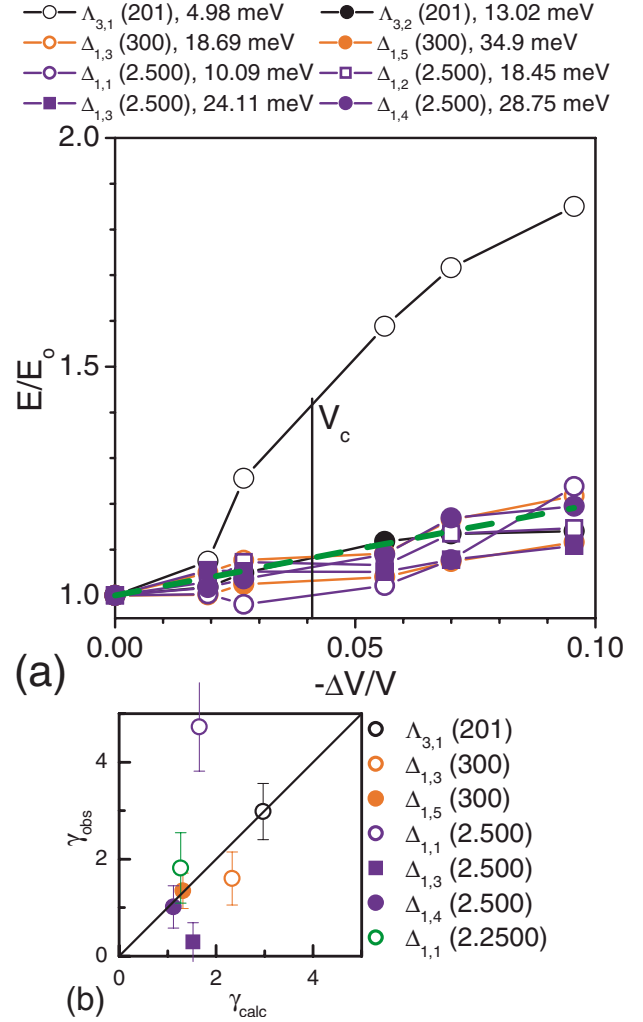ation of the lattice constants that the phase transition happened indeed in this pressure interval as expected from Refs. 4 and 9 (see Fig. 1). Thereafter, we increased the pressure in two steps up to the maximum pressure achievable with this setup, i.e., $P=48$ kbar. At each pressure, several energy scans were performed at $Q=(2.5\ 0\ 0)$, (201) and (300). At 25 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. 2. The scans were fitted to several peaks using a Lorentzian

FIG. 3. (Color online) (a) The variation in phonon energies with volume. (b) Observed mode Grüeneisen parameters γ_{obs} versus calculated mode Grüeneisen parameters γ_{calc} in the pressure range above 25 kbar. $\Delta_{i,j}$ and $\Lambda_{i,j}$ represent the jth phonon mode in the group theoretical representations Δ_i (along [100]) and Λ_i (along [001]), respectively. The $\Lambda_{3,1}$ and $\Lambda_{3,2}$ represent the TA001 and the first transverse-optic phonon branch along [001] (TO001), respectively. The branches labeled as $\Lambda_{3,1}$, $\Lambda_{2,1}$, and $\Delta_{3,1}$ all meet at their zone boundaries. So also the branch $\Lambda_{3,2}$ meets $\Delta_{1,2}$ at the zone boundary. 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 dashed green line is drawn assuming a mode Grüeneisen parameter of 2 as expected for typical normal behavior of solid. V_C denotes the average of the volume before and after the transition from tetragonal to collapsed-tetragonal phase of $CaFe_2As_2$.
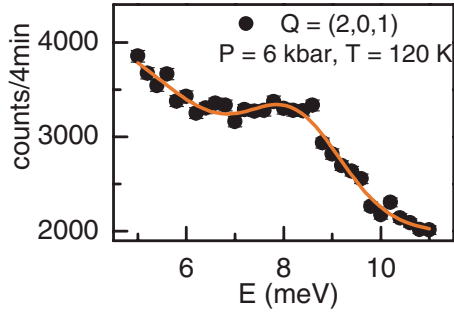
FIG. 4. (Color online) The energy scans obtained from the neutron inelastic experiments in the collapsed phase of $CaFe_2As_2$.

profile. The peak positions, normalized to those observed at the lowest pressure, are plotted in Fig. 3 versus the relative volume.

The neutron measurements suffered from a very large background generated by the walls of the pressure cell. The background increased with energy reflecting the phonon density of states of aluminum, i.e., the material of which the pressure cell was made. Moreover, as aluminum is a coherent scatterer, this background showed structure in momentum transfer Q. In the end, only scans searching for transverse-acoustic phonon branches propagating along a (TA100) and c (TA001) in the low-energy region up to about 10 meV could be evaluated with confidence. A typical energy scan of that sort is depicted in Fig. 4. The bulk of the measurements were carried out at $P = 6$ kbar and $T = 120$ K. A few further scans were taken during the slow cooling procedure. The results of these scans are included in Fig. 5. The other neutron results are depicted in Fig. 6 together with the high-pressure x-ray results.

V. DISCUSSION

Two conclusions can be directly drawn from inspection of Fig. 3: (i) the frequency changes in the phonons propagating in the ab plane are much smaller than those of the (TA001). (ii) The phase transition does not stand out in the diagram. The latter point tells us that the relative volume seems to be
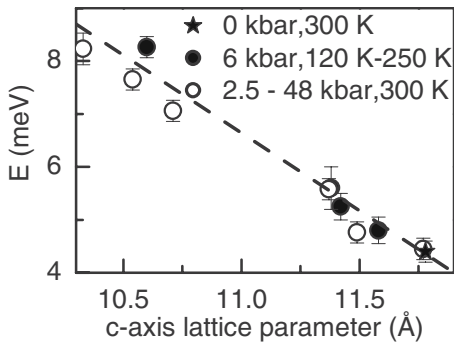

FIG. 5. Frequency of the zone-boundary TA001 phonon versus c-axis lattice parameter as observed under various conditions in pressure and temperature. Full and open symbols refer to neutron and x-ray data, respectively. The broken line is a guide to the eyes only.
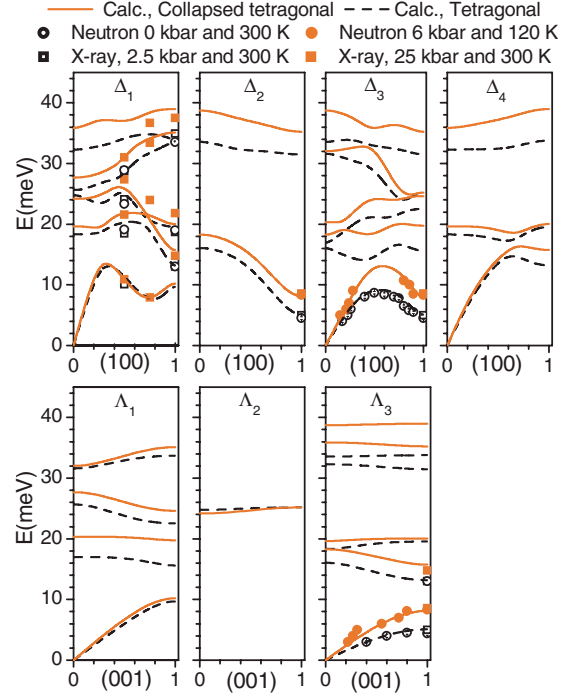

FIG. 6. (Color online) Comparison between the experimental and calculated phonon-dispersion relation in ambient-pressure and high-pressure collapsed-tetragonal phase of $CaFe_2As_2$. Results obtained from high-pressure neutron inelastic measurements carried out at 6 kbar and 120 K are shown as well. The 15 phonon modes along $\Delta(100)$ and $\Lambda(001)$ directions can be classified as $\Delta: 5\Delta_1 + 2\Delta_2 + 5\Delta_3 + 3\Delta_4$; $\Lambda: 4\Lambda_1 + \Lambda_2 + 5\Lambda_3$ (Λ_3 are doubly degenerate).

the most important parameter determining the frequency changes, and that the phase transition itself does not entail particular changes in the bonding properties. It follows that either the Fe moment does not change across the phase transition—which is unlikely in view of the results reported in Ref. 17—or it has no effect on the stiffness of the Fe-As bonds if it does change.

The relatively weak response of most phonon modes to the pressure-induced structural changes can be qualitatively understood by a near cancellation of the stiffening due to shrinkage of the c axis and the softening due to an expansion in the a-b plane. The TA001 frequencies are an exception because they seem to be sensitive to the c-axis lattice parameter only (see Fig. 5, which shows a compilation of both neutron and x-ray data).

To explain pressure-induced phonon energy shifts, DFT calculations were performed for three different structures, all of tetragonal symmetry (space group $I4/mmm$): (i) the fully optimized structure with $a = 3.988$ Å and $c = 10.608$ Å, (ii) a compressed structure with $a = 3.942$ Å and $c = 10.33$ Å, and (iii) the experimental structure observed at ambient conditions with $a = 3.885$ Å and $c = 11.78$ Å. In the cases (i) and (ii), the internal structural parameter was fully relaxed whereas in (iii), the experimental value of the internal parameter was used. As mentioned above, the optimized structure is quite close to that of the collapsed phase obtained at $P = 6$ kbar and $T = 120$ K or at $P = 25$ kbar and room temperature and therefore was used for comparison with the corre-

sponding phonon data. (We just note that the compressed structure corresponds to that observed at $P=48$ kbar in the x-ray experiments.) The experimental structure at ambient conditions was used for comparison. From a previous investigation,[8] we know that DFT calculations give a good account of the phonon dispersion at ambient conditions when they are based on the experimental structure.

As is shown in Fig. 6, the calculated frequencies for the optimized structure agree indeed quite well with the 25 kbar/300 K and the 6 kbar/120 K data. Clearly, the agreement is not perfect but nevertheless, the calculations capture the general trends when going from the ambient-pressure phase to the collapsed phase. To facilitate the assessment, we have included some zero-pressure data for a direct comparison. Inspection of Fig. 6 shows that the exceptionally strong stiffening of the transverse-acoustic modes in the 100 and the 001direction is quantitatively reproduced by the calculations.

The pressure-induced structural changes are very large for pressures up to the phase transition and slightly above. For even higher pressures, $CaFe_2As_2$ is approaching the normal behavior of slightly anharmonic solids. At room temperature, this is the case for pressures higher than 25 kbar. For such high pressures, DFT predicts indeed mode Grüeneisen parameters $\gamma=-(\Delta\nu/\nu)/(\Delta V/V)$ (where ν is the frequency and V is the volume) which lie mostly between 1 and 2, i.e., values found in most other metallic solids. We tried to check the theoretical result by comparing the experimentally determined frequency shifts between 25 and 48 kbar with those predicted by theory. Unfortunately, these frequency shifts are quite small which hampers a rigorous check of the theory. The few shifts which could be evaluated with confidence are in fair agreement with the predictions [Fig. 3(b)]. In particular, the relatively large Grüneisen parameter calculated for

the zone-boundary TA001 mode was confirmed by experiment. It reflects the fact that even for pressures above 25 kbar, the reduction in the lattice parameters is anisotropic, with the c axis being more compressed than the a axis.

The results presented in this paper indicate that the vibrational properties of $CaFe_2As_2$ are governed mostly by the crystal structure, leaving for the Fe moment only a secondary role. Indeed, the spin-polarized calculations of the phonon spectrum in $CaFe_2As_2$ (Ref. 8) did not improve the agreement with experiments, quite unlike what was found in case of $BaFe_2As_2$.[15]

VI. CONCLUSIONS

The structure of $CaFe_2As_2$ responds much more to pressure than most other metallic solids. In particular, the c/a ratio changes enormously on applying a few tens of kilobar. However, the vibrational properties change surprisingly little at the same time, except for a few modes, which are very sensitive to the c-axis lattice parameter. It shows that the dynamical couplings are very similar for the different structures of $CaFe_2As_2$. The observed changes in the lattice dynamics as a function of the crystal structure are reasonably well described by nonmagnetic DFT calculations with the structure constrained to the experimental structure. From this finding, we conclude that this type of theory reliably captures the bonding properties of this compound. Specifically, the changes in the Fe moment across the structural phase transition reported in Ref. 17 do not seem to have a major influence on the phonon properties. Thus, our results for $CaFe_2As_2$ do not support the widely held view that the phonons in the pnictides are strongly coupled to the spins.

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