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Phonon spectra in $CaFe_2As_2$ and $Ca_{0.6}Na_{0.4}Fe_2As_2$: Measurement of the pressure and temperature dependence and comparison with *ab initio* and shell model calculations

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We report the pressure and temperature dependence of the phonon density-of-states in superconducting $Ca_{0.6}Na_{0.4}Fe_2As_2$ ($T_c=21$ K) and the parent compound $CaFe_2As_2$ using inelastic neutron scattering. We observe no significant change in the phonon spectrum for $Ca_{0.6}Na_{0.4}Fe_2As_2$ at 295 K up to pressures of 5 kbar. The phonon spectrum for $CaFe_2As_2$ shows softening of the low-energy modes by about 1 meV when decreasing the temperature from 300 to 180 K. There is no appreciable change in the phonon density of states across the structural and antiferromagnetic phase transition at 172 K. These results, combined with our earlier temperature dependent phonon density of states measurements for $Ca_{0.6}Na_{0.4}Fe_2As_2$, indicate that the softening of low-energy phonon modes in these compounds may be due to the interaction of phonons with electron or short-range spin fluctuations in the normal state of the superconducting compound as well as in the parent compound. The phonon spectra are analyzed with *ab initio* and empirical potential calculations giving partial densities of states and dispersion relations.

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I. INTRODUCTION

MFe_2As_2 compounds are known to be stable with divalent M=Ba, Ca, Sr, and Eu atoms. At room temperature these compounds crystallize in the $ThCr_2Si_2$-type tetragonal ($I4/mmm$) structure. They are, in many aspects, similar to the family of ROFeAs (R=rare earth) compounds, which crystallize in the tetragonal ZrCuSiAs-type structure ($P4/nmm$). These compounds have recently attracted immense attention[1–19] in the scientific community. Both systems feature layers of FeAs. They undergo[9,10] a transition from tetragonal to orthorhombic symmetry below room temperature and order antiferromagnetically in the orthorhombic structure. Electron or hole doping into the parent compounds suppresses the structural and magnetic instabilities and induces superconductivity.[2] The magnetic order can be suppressed in the parent compound by the application of pressure.[4–6] Pressure can also induce superconductivity and $CaFe_2As_2$ is, in this context, the only compound that shows superconductivity[4] at a rather low pressure of 3.5 kbar. $CaFe_2As_2$ is thus an ideal candidate for the pressure-dependent investigation of structural and magnetic properties by neutron scattering. High-pressure neutron-diffraction measurements show[5,6] that $CaFe_2As_2$ undergoes a transition to a "collapsed tetragonal phase" under applied pressure below 50 K in which the c parameter is reduced by 10%. Band structure calculations show[5] that the collapse of the tetragonal phase is due to the loss of magnetism in the Fe system. This leads to further speculation that the loss of the iron magnetic moment may be important to stabilize the superconducting phase in iron-pnictide superconductors. Recent high-pressure inelastic neutron-scattering measurements[11] of $CaFe_2As_2$ showed that the antiferromagnetic spin fluctuations observed in the ambient pressure paramagnetic, tetragonal phase are strongly suppressed in the high-pressure collapsed tetragonal phase.

Superconductivity in FeAs compounds is believed to be mediated by antiferromagnetic spin fluctuations. Keeping this in mind inelastic neutron-scattering measurements have been carried out on polycrystalline[13] $Ba_{0.6}K_{0.4}Fe_2As_2$ as well as on single crystals[14] of $Ba(Fe_{0.92}Co_{0.08})_2As_2$ and $BaFe_{1.9}Ni_{0.10}As_2$, which indicate evidence of a resonant spin excitation. Phonon spectra have been shown to depend on the magnetic state[16] and a possible role in the pairing mechanism cannot be excluded. Earlier we have reported phonon dynamics for parent[17] $BaFe_2As_2$ as well as superconducting $Sr_{0.6}K_{0.4}Fe_2As_2$ and $Ca_{0.6}Na_{0.4}Fe_2As_2$ compounds[18] using the techniques of inelastic neutron-scattering and lattice dynamics calculations. In this paper, we report the measurements of phonon spectra at high pressure for $Ca_{0.6}Na_{0.4}Fe_2As_2$ and the temperature dependence for the parent $CaFe_2As_2$. Lattice dynamical calculations are also carried out for $CaFe_2As_2$ using the shell model and *ab initio* methods. The discussion given in this paper will be based on our earlier investigations of the $BaFe_2As_2$ and $Ca_{0.6}Na_{0.4}Fe_2As_2$ compounds. Section II gives an outline of the experimental technique, as adopted here.

The details about the lattice dynamics calculations are given in Sec. III, followed by the results and discussion, and conclusions in Secs. IV and V, respectively.

II. EXPERIMENTAL

The polycrystalline samples of $CaFe_2As_2$ and $Ca_{0.6}Na_{0.4}Fe_2As_2$ ($T_c = 21$ K) were prepared by heating stoichiometric mixtures of the corresponding purified elements. Structural analysis from x-ray powder diffraction indicates that the $CaFe_2As_2$ sample contains about 2.5% of FeAs as an impurity phase. For the high-pressure inelastic measurements on $Ca_{0.6}Na_{0.4}Fe_2As_2$ we have used the same sample as was used in our previous measurements[18] of the temperature dependence of the phonon density of states. The details about the characterization of superconducting $Ca_{0.6}Na_{0.4}Fe_2As_2$ are given in our previous publication.[18] The inelastic neutron-scattering experiments were carried out using the IN4C and IN6 time-of-flight spectrometers at the Institut Laue Langevin (ILL), France. Both the spectrometers are based on the time-of-flight technique and are equipped with a large detector bank covering a wide range of about $10° - 115°$ of scattering angle. A polycrystalline sample of 10 g of $CaFe_2As_2$ was placed inside a sealed aluminum container in the form of a thin slab, which was mounted in a cryostat, at 45° to the incident neutron beam for temperature-dependent measurements. For high-pressure measurements we have used about 8 g of $Ca_{0.6}Na_{0.4}Fe_2As_2$ sample.

An incident neutron wavelength of 1.2 Å (58.8 meV) was chosen for the IN4C measurements, which allowed the data collection in the neutron-energy loss mode. The measurements for $CaFe_2As_2$ were performed at 2, 140, and 190 K. The high-resolution measurements for $CaFe_2As_2$ at 300 and 180 K at ambient pressure and high-pressure measurements at 295 K for superconducting $Ca_{0.6}Na_{0.4}Fe_2As_2$ were performed on IN6. For these measurements we have used an incident neutron wavelength of 5.1 Å (3.12 meV) in neutron-energy gain mode. The elastic energy resolution was about 80 μeV. The high-pressure measurements for $Ca_{0.6}Na_{0.4}Fe_2As_2$ at ambient pressure, 0.3, 2.8, and 5 kbar at 295 K were performed using a gas pressure cell with argon as the pressure transmitting medium. The incoherent approximation[20] has been used for extracting neutron weighted phonon density of states from the measured scattering function $S(Q,E)$. The weighting factors $\frac{4\pi b_k^2}{m_k}$ for various atoms in the units of barns/amu are Ca: 0.071; Fe: 0.208, and As: 0.073. The experimental one-phonon spectrum is obtained by subtracting the multiphonon contribution from the experimental data. In the case of the IN6 data multiphonon contributions were obtained via a self-consistent formalism, while Sjolander[21] formalism has been used for obtaining the multiphonon contributions for the IN4C data.

III. LATTICE DYNAMICAL CALCULATIONS

The phonon frequencies as a function of wave vectors in the entire Brillouin zone have been calculated for $CaFe_2As_2$ using quantum-mechanical *ab initio* methods and semiempirical interatomic potentials as in Ref. 18. The parameters of the interatomic potential satisfy the conditions of static and dynamic equilibria.[22,23] The shell model calculations have been carried out using the current version of the code DISPR (Ref. 24) developed at Trombay.

Ab initio calculations were performed using the projector-augmented wave (PAW) formalism[25] of the Kohn-Sham density-functional theory (DFT) (Refs. 26 and 27) at the generalized gradient approximation level (GGA), implemented in the Vienna *ab initio* simulation package (VASP).[28,29] The GGA was formulated by the Perdew-Burke-Ernzerhof (PBE) (Refs. 30 and 31) density functional. The Gaussian broadening technique was adopted and all results are well converged with respect to *k* mesh and energy cutoff for the plane-wave expansion. Experimentally refined crystallographic data in the low- and high-temperature ranges corresponding to the orthorhombic and tetragonal phases, respectively, have been considered. These structures were used to calculate the generalized density of states (GDOS) and dispersion relations for the orthorhombic phase under the *Fmmm* space group (number 69) having the local point-group symmetry D_{23}^{2h} and for the tetragonal phase under the $I4/mmm$ space group (number 139) having the local point-group symmetry D_{17}^{4h}. In the *ab initio* lattice dynamics calculations, in order to determine all interatomic force constants, the supercell approach has been adopted.[32] Therefore for both phases, the single cell was used to construct a (2^*a, 2^*b, c) supercell containing 16 formula units (80 atoms) and (3^*a, 3^*b, c) supercell containing 18 formula units (90 atoms) for the orthorhombic and tetragonal phases, respectively (a and b being the shorter cell axes). Total energies and interatomic forces were calculated for the 18 and 16 structures resulting from individual displacements of the three symmetry inequivalent atoms along the three Cartesian directions ($\pm x$, $\pm y$, and $\pm z$). The 15 phonon branches corresponding to the five atoms in the primitive cell were extracted in subsequent calculations using the PHONON software.[33] While initial structures used for phonon calculations include, where relevant, the observed magnetic ordering, the interatomic force constants, calculated in this way, do not include magnetic interactions.

IV. RESULTS AND DISCUSSION

A. High-pressure inelastic neutron-scattering measurements on $Ca_{0.6}Na_{0.4}Fe_2As_2$

Recently we have reported an experimental phonon study[18] of the $Sr_{0.6}K_{0.4}Fe_2As_2$ and $Ca_{0.6}Na_{0.4}Fe_2As_2$ superconducting compounds using inelastic neutron scattering. In both compounds the low-energy phonon modes soften with temperature. In general phonon modes are expected to shift toward higher energies with a decrease of the unit-cell volume induced by a decrease in temperature. We speculated that the softening of low-energy phonons might be due to electron-phonon coupling effects. To separate effects of temperature and cell volume, we have carried out high-pressure inelastic neutron-scattering experiments for superconducting $Ca_{0.6}Na_{0.4}Fe_2As_2$. The measured phonon spectra at ambient pressure, 0.3, 2.9, and 5 kbar are shown in Fig. 1. The large contributions to the measured spectra from the pressure cell do not allow us to obtain the experimental phonon spectra

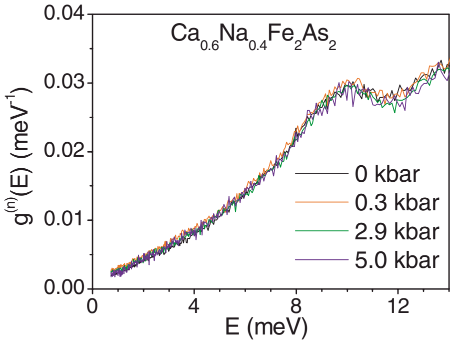

FIG. 1. (Color online) The experimental phonon spectra for $Ca_{0.6}Na_{0.4}Fe_2As_2$ as a function of pressure at a fixed temperature of 295 K.

beyond 14 meV. Our results indicate that the compression of the unit-cell volume has no effect on the phonon spectrum within the explored range.

High-pressure studies of $Ca_{0.6}Na_{0.4}Fe_2As_2$ have not been reported. However, the calculated variation of volume with pressure for $CaFe_2As_2$ using *ab initio* methods[12] gives bulk modulus values of 56.2 and 81.6 GPa, respectively, for the tetragonal and collapsed tetragonal states of $CaFe_2As_2$. Using the above tetragonal phase value of the bulk modulus we estimate a reduction in unit-cell volume of about 0.88% on compression from ambient pressure to 5 kbar. The change in volume on compression[10] is roughly the same as that found (~0.7%) for $CaFe_2As_2$ on lowering the temperature from 300 to 140 K. We assume that thermal-expansion behavior is nearly the same in both parent and superconducting Ca compounds. The change in phonon energies with temperature is due to "implicit" as well as "explicit" anharmonicities. The implicit anharmonicity of phonons is due to the change of the unit-cell volume and/or concomitant changes of structural parameters. The explicit anharmonicity includes changes in phonon frequencies due to thermal effects. A possible explicit effect is the thermal smearing of electronic states. This smearing implies that the influence of electron-phonon interactions on the phonon frequencies changes as a function of temperature. The Grüneisen parameter of the modes has not yet been determined from other optical spectroscopic measurements. The elastic energy resolution of the IN6 spectrometer for 3.12 meV incident energy is about 80 μeV. Our measurements show that change in frequency of modes up to 14 meV on compression of the unit-cell volume of $Ca_{0.6}Na_{0.4}Fe_2As_2$ to 5 kbar is within the noise of the measurements.

The phonon spectrum of these compounds reacts, as known from our calculations, very sensitively (Sec. IV D) to the structural parameters. It would thus be possible that the softening observed as a function of temperature could be solely described by the changes in lattice parameters and/or concomitant adjustment of the As structural parameter. However, the combination of our present high-pressure results with our earlier temperature dependent measurements[18] of the phonon spectra for $Ca_{0.6}Na_{0.4}Fe_2As_2$ shows that a simple contraction of the unit cell with its concomitant structural changes at room temperatures does not produce softening. Therefore, the softening of the low-energy phonon modes on lowering of the temperature is due to explicit effects, which may be due to interaction of phonons with electron or short-range spin fluctuations in the normal state of superconducting sample.

B. Temperature dependence of phonon spectra for $CaFe_2As_2$

We have also measured the temperature dependence of the phonon spectra [Fig. 2(a)] for the parent compound $CaFe_2As_2$. Previous measurements on $Ca_{0.6}Na_{0.4}Fe_2As_2$ revealed[18] the softening of the low-energy modes on cooling from 300 to 140 K, while no effect was observed on heating

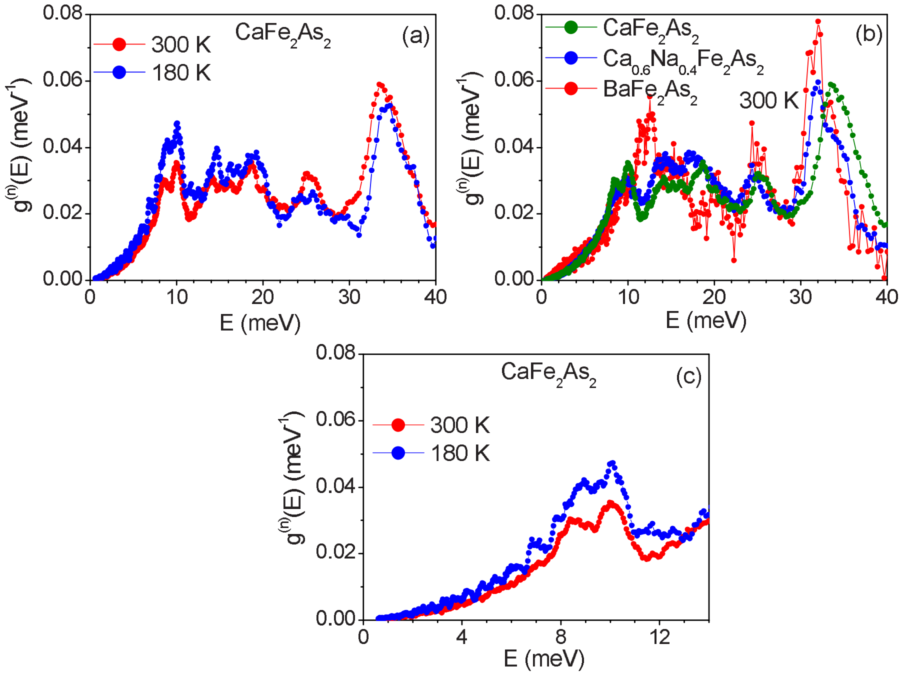

FIG. 2. (Color online) (a) The temperature dependence of the phonon spectra of $CaFe_2As_2$. (b) The comparison of the experimental phonon spectra for $CaFe_2As_2$, $Ca_{0.6}Na_{0.4}Fe_2As_2$, and $BaFe_2As_2$. The phonon spectra are measured with an incident neutron wavelength of 5.12 Å using the IN6 spectrometer at the ILL. The experimental phonon data for $BaFe_2As_2$ and $Ca_{0.6}Na_{0.4}Fe_2As_2$ are taken from Refs. 16 and 18, respectively. All the phonon spectra are normalized to unity. (c) Zoom of the low-energy part of the temperature dependence of the phonon spectra of $CaFe_2As_2$.

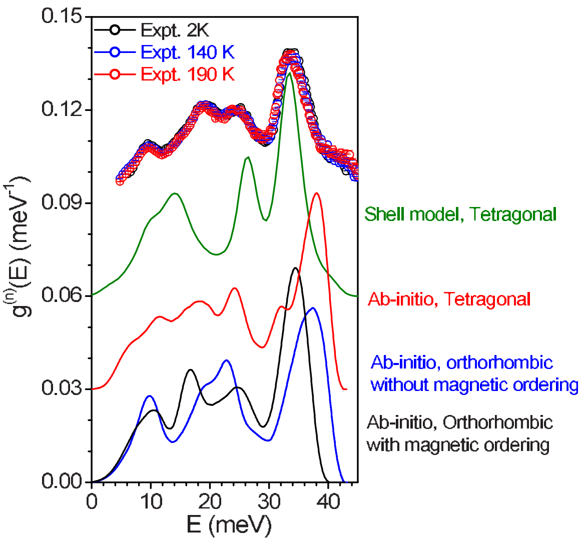

FIG. 3. (Color online) Comparison between the calculated and experimental phonon spectra of $CaFe_2As_2$. The measurements are carried out with incident neutron wavelength of 1.2 Å using the IN4C spectrometer at the ILL. For better visibility the phonon spectra are shifted along the y axis by 0.03 meV^{-1}. The calculated spectra have been convoluted with a Gaussian of full width at half maximum (FWHM) of 3 meV in order to describe the effect of energy resolution in the experiment.

from 2 to 50 K across the superconducting transition temperature of 21 K. $CaFe_2As_2$ has an orthorhombic-to-tetragonal structural and antiferromagnetic phase transition at 172 K on heating. Now in order to investigate whether phonon softening is related to the structural and magnetic phase transitions or due to paramagnetic fluctuations above 172 K, we have measured high-resolution phonon spectra using IN6 spectra at 300 and 180 K.

Measurements on IN6 performed with small incident neutron energy of 3.12 meV in the neutron-energy gain mode do not give enough intensity at low temperatures. Therefore measurements using IN4C spectrometer are carried out at 2, 140, and 190 K. The high-resolution measurements using IN6 spectrometer clearly show (Fig. 2) that low-energy phonon modes soften by about 1 meV while cooling from 300 to 180 K, while spectra obtained from IN4C show (Fig. 3) no temperature dependence when heating from 2 to 190 K. It seems therefore that the orthorhombic to tetragonal phase transition[10] at 172 K has no effect on the phonon spectra. As discussed above, the phonon softening observed in our temperature dependent DOS measurements may be due to short-range spin fluctuations in the paramagnetic state of $CaFe_2As_2$.

Recent measurements[19] of the temperature dependence of phonon-dispersion relations in $CaFe_2As_2$ show that the zone boundary, transverse-acoustic mode of energy about 10.5 meV, with polarization (1–10) along (110), shows softening on approaching the phase-transition temperature (172 K) from higher temperature. However, below the phase-transition temperature of 172 K the energy of the transverse acoustic mode again shifts backs to about 10.5 meV. In our density of states measurements we observe that modes around 10 meV are most affected by the temperature. It should be noted that the density of states measurements integrate over the whole Brillouin zone. Our measurements on the polycrystalline sample are consistent with the single-crystal measurements in that they are unlikely to detect the small changes in specific dispersion branches measured for the single crystal.

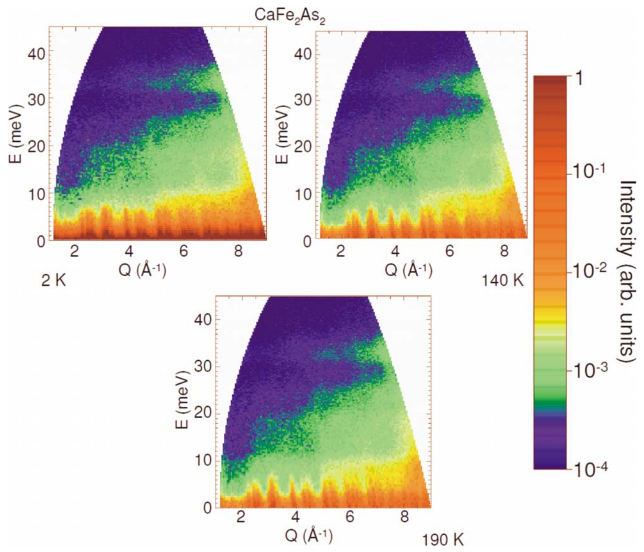

FIG. 4. (Color online) The experimental Bose factor corrected $S(Q,E)$ plots for $CaFe_2As_2$ at 2, 140, and 190 K measured using the IN4C spectrometer at the ILL with an incident neutron wavelength of 1.2 Å. The values of $S(Q,E)$ are normalized to the mass of sample in the beam. For clarity, a logarithmic representation is used for the intensities.

For $CaFe_2As_2$, the high-frequency bands around 34 meV are found to be narrower at 180 K and shifted to higher energies as expected on compression of the unit-cell volume by a decrease of the temperature from 300 to 180 K. The temperature dependence of the phonon spectra for $Ca_{0.6}Na_{0.4}Fe_2As_2$ showed a similar behavior.

$CaFe_2As_2$ orders antiferromagnetically[10] in the orthorhombic structure below 172 K. The experimental Bose factor corrected $S(Q,E)$ plots for $CaFe_2As_2$ at 2, 140, and 190 K measured using IN4C spectrometer are shown in Fig. 4. The experimental data show no signs of magnetic excitations in the attainable (Q,E) range of IN4C. However recent measurements carried out on powder samples[15] of $BaFe_2As_2$, using the MERLIN spectrometer at ISIS, show evidence of spin excitations in the antiferromagnetically ordered state of $BaFe_2As_2$.This may be due to the fact that the (Q,E) range attainable at IN4C is different from that of MERLIN at low Q values. Further investigations might be necessary before drawing any final conclusions concerning $CaFe_2As_2$.

C. Comparison of phonon spectra for $CaFe_2As_2$, $Ca_{0.6}Na_{0.4}Fe_2As_2$, and $BaFe_2As_2$

Now we compare the high-resolution phonon densities of states measured for the Ca, CaNa, and Ba compounds using IN6 at 300 K. On partial doping of Na at the Ca site, the modes up to 12 meV show no change, while those above 12 meV soften by about 1 meV. Both the Ca and CaNa com-

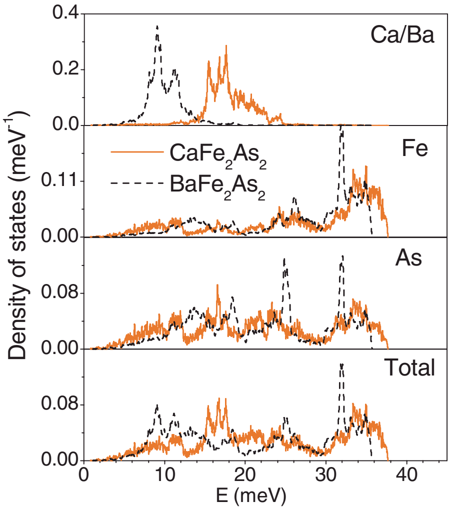

FIG. 5. (Color online) The calculated partial density of states for the various atoms in $CaFe_2As_2$ (red lines) and $BaFe_2As_2$ (black lines) from *ab initio* calculations. The calculations are carried out for the orthorhombic phases with magnetic ordering. The partial density of states of various atoms and the total density of states are normalized to unity.

pounds have nearly the same value of the lattice parameter *a* (~3.89 Å), while the lattice parameter *c* in $CaFe_2As_2$ and $Ca_{0.6}Na_{0.4}Fe_2As_2$ is 11.758 and 12.066 Å, respectively. The doped compound has slightly longer *M*-As and Fe-As bond lengths that would result in a softening of the phonon modes, as reported above.

The phonon spectra [Fig. 2(b)] of the parent $BaFe_2As_2$ and $CaFe_2As_2$ compounds below 25 meV differ significantly. Both compounds have nearly the same lattice parameter *a*, while the lattice parameter *c* in the Ca compound (11.758 Å) is about 10% smaller than that of the Ba compound (13.04 Å). Similarly the mass of Ba ($m=137.34$ amu) is large in comparison to Ca ($m=40.08$ amu). We expect that both the mass effect and the contraction of unit cell should result in shifting the phonon modes to higher energies but we find that in the Ca compound the low-energy modes up to 22 meV is shifted toward lower energies.

In order to understand this difference, we have calculated the partial density of states (Fig. 5) of various atoms (Sec. IV D) in $BaFe_2As_2$ and $CaFe_2As_2$. We find that the vibrational modes due to Ca atoms in $CaFe_2As_2$ scale approximately with the Ba vibrations in $BaFe_2As_2$ in the ratio expected from the masses of the Ca and Ba atoms. These modes thus behave as expected. Further we notice that there is a substantial difference in the vibrations of Fe and As atoms in both these compounds. The calculated Fe and As vibrations are found to soften in the range below 22 meV by about 2 meV in the Ca compound in comparison to the Ba compound. This is contrary to our expectation. We would naively guess that the shorter Ca-As and Fe-As bond lengths result in a hardening of all the Fe and As vibrations. We find this trend only for the peak at 32 meV, which indeed moves to higher energies. The unexpected softenings of the rest of the Fe and As vibrations are found to be responsible for the softening of the entire phonon spectra [Fig. 2(b)] below 22 meV as seen in $CaFe_2As_2$.

D. Phonon calculations in $CaFe_2As_2$

The calculated phonon spectra using the shell model are shown in Fig. 3. The calculated spectra compare reasonably well with the experimental data. However there are discrepancies between the calculated and experimental phonon spectra at energies around 20 meV. We have also calculated the phonon spectra for $CaFe_2As_2$ using *ab initio* methods for both the orthorhombic (low-*T*) and tetragonal (high-*T*) phases. For the tetragonal phase the calculated spectral profile is good (Fig. 3). However the Fe-As stretching frequency is overestimated since the cell optimization prior to the force-constant calculation results in a significant shortening[5] (collapse) of the *c* axis and, accordingly, the Fe-As bond. Imposing the experimental value of the *c* axis shifts the highest frequency vibration to the position as observed in the experiment.

The density of states in the orthorhombic phase was calculated with and without the observed magnetic ordering (Fig. 3). All the observed features are well reproduced computationally. Without magnetic ordering, as for the tetragonal phase, there is a significant structural perturbation in the *c* direction and the Fe-As stretching vibration frequency is overestimated. The calculated orthorhombic distortion is found to be strongest for the observed magnetic structure and matches the experimental value. In this case, the magnetic coupling between the Fe-As planes helps to reproduce the measured value of the *c* axis and the As *z* coordinate. Accordingly the spectral frequencies and intensities match better the experimental data at 2 K.

The *ab initio* results for the orthorhombic structure with observed magnetic ordering are in better agreement (Fig. 3) with the inelastic neutron-scattering data compared to the empirical shell model calculations and the published *ab initio* calculations[16] for the Ba compound. In order to understand this improved result and in the context of the foregoing discussion of the effect of cation mass and cell parameters (Sec. IV C), it is essential to consider the partial density of states (pDOS) for each atomic species (Fig. 5). For Ca, which is the lightest atom in the $CaFe_2As_2$ compound, the pDOS is localized in the frequency range from 15 to 24 meV. This limited frequency range is indicative of the dominantly ionic nature of the Ca interaction with the Fe-As layers. Covalent bonding would result in the pDos of the light Ca atom covering the same frequency range as the Fe and As atoms. The Ba pDOS is localized at lower frequency in the range from 8 to 12 meV since it is the heaviest atomic species in the $BaFe_2As_2$ compound. Ba has a mass 3.5 times greater than Ca which approximately accounts for the frequency shift, again suggesting ionic interactions between the cations and the Fe-As layers that are not significantly modified on changing the cation.

The shift of the cation pDOS to higher frequency results in changes of the Fe and As pDOS in precisely the frequency range of the Ca pDOS. In the Ba case there are prominent peaks at 14 and 18 meV, whereas in the Ca system there is a

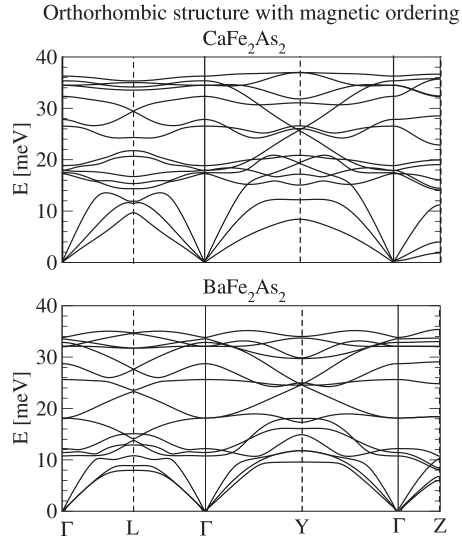

FIG. 6. The calculated phonon-dispersion relations for $CaFe_2As_2$ (upper) and $BaFe_2As_2$ (lower) in the orthorhombic phases with magnetic ordering. The Bradley-Cracknell notation is used for the high-symmetry points along which the dispersion relations are obtained: $L=(1/2,0,0)$, $Y=(1/2,0,1/2)$, and $Z=(1/2,1/2,0)$.

single broad spectral peak centered at 16 meV. The high-frequency tail of the Ca signal also corresponds to increased intensity in the Fe and As pDOS at 22 meV, the frequency at which a peak is measured[16] for $BaFe_2As_2$ but not calculated.

Above 24 meV, there are two notable differences between the Ca and Ba cases. First, the Ba system is characterized by sharper features in the pDOS for Fe and As and, second, the high-frequency cutoff for Ba is lower than that of the Ca system, as in the experimental data [Fig. 2(b)]. The sharp features in the pDOS can be understood from the phonon-dispersion relations (Fig. 6). Close inspection and comparison of the two sets of dispersion relations reveals broad similarities, but the Ba case is characterized by dispersion branches that are flatter over wide ranges of reciprocal space. The branches involving the Ca cation occur at higher frequency than those of Ba, which appears to perturb all higher frequency branches. Accordingly there is only one gap in the GDOS of $CaFe_2As_2$ at 30 meV, whereas the $BaFe_2As_2$ also has a calculated gap at 20 meV, which is not observed experimentally.

From a computational point of view, this analysis leads us to tentatively conclude that the Ca cation couples dynamically more strongly to the Fe-As layers, whereas the Ba cation is chemically harder (its iconicity is higher) and more decoupled due in part to the significantly lower frequency of the Ba pDOS. The extent of this decoupling is overestimated in our calculations[16] as evidenced by the fact that we do not reproduce the measured peak at 21 meV in $BaFe_2As_2$.

Very recent calculations[34] that include magnetic interactions in the interatomic force constants give a redistribution of intensity in the phonon density of states, which tends to reproduce the peak at 21 meV in $BaFe_2As_2$ but also leads to a significant loss in intensity at 16 meV. We will investigate this approach in future work on the series of compounds $M Fe_2As_2$ ($M=$Ca, Sr Ba) to determine whether including magnetic interactions in the interatomic force constants gives a general improvement in the calculated phonon density of states.

V. CONCLUSIONS

We have reported measurements of the pressure as well as the temperature dependence of phonon spectra for $Ca_{0.6}Na_{0.4}Fe_2As_2$ superconducting and parent $CaFe_2As_2$ compounds, respectively. Our measurements as a function of temperature show that the structural phase transition at 172 K appears to be irrelevant for the phonon softening in the parent $CaFe_2As_2$, observed between 180 and 300 K. The tetragonal to orthorhombic phase transition is suppressed in the superconducting $Ca_{0.6}Na_{0.4}Fe_2As_2$ compound. Phonon softening in $Ca_{0.6}Na_{0.4}Fe_2As_2$ and $CaFe_2As_2$ is found only above 180 K, corresponding to the paramagnetic state of $CaFe_2As_2$. The combined study of pressure as well as temperature dependence of the phonon spectra thus indicates that the softening of low-energy phonon modes in these compounds may be due to the interaction of phonons with the short-range spin fluctuations in the paramagnetic state of $CaFe_2As_2$ or due to electron-phonon coupling in the superconducting $Ca_{0.6}Na_{0.4}Fe_2As_2$. The comparison of phonon spectra for Ba and Ca compounds shows strong renormalization effects in the phonon spectra of these compounds, which cannot be simply explained by the lattice contraction and mass effect.

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