Inelastic neutron scattering and lattice-dynamical calculations of $BaFe_2As_2$

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We report here extensive measurements of the temperature dependence of phonon density of states of $BaFe_2As_2$, the parent compound of the FeAs-based superconductors, using inelastic neutron scattering. The experiments were carried out on the thermal time-of-flight neutron spectrometer IN4 at the Institut Laue Langevin on a polycrystalline sample. There is no appreciable change in the spectra between $T=10$ and 200 K, although the sample undergoes a magnetic as well as a tetragonal-to-orthorhombic structural phase transition at 140 K. This indicates a rather harmonic phonon system. Shell-model lattice-dynamical calculations based on interatomic potentials are carried out to characterize the phonon data. The calculations predict a shift of the Ba phonons to higher energies at 4 GPa. The average energy of the phonons of the Ba sublattice is also predicted to increase on partial substitution of Ba by K to $Ba_{0.6}K_{0.4}$. The calculations show good agreement with the experimental phonon spectra and also with the specific-heat data from the literature.

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The discovery of high transition temperature (T_c) superconductivity in fluorine-doped RFeAsO (R=rare earth) and K-doped $BaFe_2As_2$ has attracted immense attention[1–25] in the scientific community. It is important to note that these compounds have high superconducting transition temperatures without requiring the presence of copper oxide layers. The application of hydrostatic pressure in F-doped LaFeAsO results[4] in an increase in T_c from 25 to 43 K. Similarly the substitution of rare-earth atoms equally results[5] in an increase in T_c of 43 K at ambient pressure in $Sm_{1-x}F_xFeAsO$. A T_c of 38 K has been reported[7] in bilayer compound $Ba_{0.60}K_{0.40}Fe_2As_2$. Pressure-induced superconductivity has been reported[12,13] in MFe_2As_2 (M=Ba, Ca, and Sr). These measurements indicate that a T_c of 12, 27, and 29 K can be achieved at high pressures in the parent compounds $CaFe_2As_2$, $SrFe_2As_2$, and $BaFe_2As_2$, respectively. Anomalies in the specific heat, electrical resistance, and magnetic susceptibility indicate[7] structural and magnetic phase transitions in $BaFe_2As_2$ at 140 K. X-ray diffraction measurements indicate that an orthorhombic (space group $Fmmm$) to tetragonal ($I4/mmm$) structural phase transition takes place at 140 K.[7] The magnetic ordering in this compound has been confirmed by neutron diffraction on both powder[19] and single-crystal samples.[18] Theoretical electronic structure calculations[8,9,20,25] have been reported for LaFeAsO and $BaFe_2As_2$. These calculations show that in LaFeAsO electronic bands around the Fermi level are formed mainly by Fe-As layers, whereas the bands of La-O layers are far from the Fermi level. Therefore superconductivity in these compounds is believed to be mainly due to the structural and electronic states of the Fe-As layers. Structural, electronic, and magnetic properties of $BaFe_2As_2$ and LaFeAsO are remarkably similar, which makes $BaFe_2As_2$ a parent compound for oxygen-free superconductors.

Concerning the dynamics Raman[10] and infrared data[21] have been reported in LaFeAsO, while Raman modes have been experimentally measured[14] in $SrFe_2As_2$. Phonon density of states in $LaFeAsO_{1-x}F_x$ has been measured[16,23] using inelastic neutron scattering. *Ab initio* calculation of the phonon spectra has been reported in LaFeAsO.[15] The zone-center phonon modes have been calculated[14] for $SrFe_2As_2$ using shell-model lattice dynamics. A strong electron-phonon coupling of in-plane Fe breathing modes has been suggested for the $LaO_{1-x}F_xFeAs$ superconductor.[17] Meanwhile, a magnetic instability due to either magnetic ordering of a localized iron magnetic moment or spin-density waves in a more itinerant picture has been experimentally realized in the parent compounds.[2] This raises possibility that superconductivity in iron pinictides might also be mediated by spin fluctuations, in a case similar to cuprates. Indeed, very recent inelastic neutron-scattering work[22] on superconducting $Ba_{0.6}K_{0.4}Fe_2As_2$ has found indication for the existence of spin fluctuations. The mechanism of superconductivity, and in particular the role of lattice dynamics in superconducting pair formation in these materials that superconduct with relatively high T_c, although not as high as that found in cuprates, is still to be settled. Meanwhile it is necessary to study phonon dynamics carefully in these materials. This has motivated us to carry out measurements of the temperature dependence of the phonon density of states in $BaFe_2As_2$. The phonons spectra as well as some thermodynamic properties have equally been calculated.

The polycrystalline sample of $BaFe_2As_2$ was prepared and characterized as reported elsewhere.[7] Both x-ray and neutron powder-diffraction refinements show that the sample con-

tains less than 5% of impurity phases. The inelastic neutron-scattering experiments were performed on a polycrystalline sample of $BaFe_2As_2$ using the thermal time-of-flight neutron spectrometer IN4 at the Institut Laue Langevin (ILL), France. The incident neutron wavelength of 1.18 Å was chosen which allowed the spectra to be obtained in the neutron energy-loss mode (Stoke side) up to 45 meV. The detector bank covered scattering angles up to 120°. About 1.6 g of polycrystalline $BaFe_2As_2$ sample were placed inside a thin aluminum foil. The temperature dependent data were taken at 10, 100, and 200 K. The data were processed in order to obtain the dynamical structure factor $S(Q,E)$ and the neutron-weighted "generalized" phonon density of states $g^{(n)}(E)$. The so-called "incoherent approximation" is used to derive $g^{(n)}(E)$ which implies averaging the spectra over the whole scattering angle.[26] In the energy-loss mode, the neutron-weighted phonon density of states are obtained[27] from the measured scattering function $S(Q,E)$ via

$$g^{(n)}(E) = A\left\langle \frac{e^{2w_k(Q)}}{Q^2}\frac{E}{n(E,T)+1}S(Q,E)\right\rangle, \quad (1)$$

$$g^{n}(E) = B\sum_k \left\{\frac{4\pi b_k^2}{m_k}\right\} g_k(E), \quad (2)$$

where $n(E,T)=[\exp(E/k_BT)-1]^{-1}$, A and B are normalization constants, and b_k, m_k, and $g_k(E)$ are, respectively, the neutron-scattering length, mass, and partial density of states of the kth atom in the unit cell. The quantity within $\langle$----$\rangle$ represents the proper average over all Q values at a given energy. $2W(Q)$ is the Debye-Waller factor.

The present lattice-dynamical calculations are carried out using a shell model. Each ion consists of a core and an adiabatic, i.e., massless shell of charge, which are connected by a harmonic spring constant. The shell can displace itself from the core causing a dipole, leading to a proper description of the crystal dielectric behavior. The form of the potentials used[28,29] for the calculations is

$$V(r) = \left\{\frac{e^2}{4\pi\varepsilon_o}\right\}\left\{\frac{Z(k)Z(k')}{r}\right\} + a\exp\left\{\frac{-br}{R(k)+R(k')}\right\}, \quad (3)$$

where r is the separation between the atoms of type k and k', $Z(k)$ and $R(k)$ are empirical charge and radius parameters of the atom of type k, $1/(4\pi\varepsilon_o)=9\times10^9$ $Nm^2/Coul^2$, $a=1822$ eV, and $b=12.364$.

The covalent nature of Fe-As bond is described by the following potential:

$$V(r) = -D\exp[-n(r-r_o)^2/(2r)]. \quad (4)$$

The radii parameters used in our calculations are $R(\mathrm{Ba})=2.20$ Å, $R(\mathrm{Fe})=0.30$ Å, and $R(\mathrm{As})=2.48$ Å. Partial charges of $Z(\mathrm{Ba})=1.50$, $Z(\mathrm{Fe})=0.75$, and $Z(\mathrm{As})=-1.50$ are used in the calculations. The parameters of the stretching potential are $D=2.4$ eV, $n=7$ $Å^{-1}$, and $r_o=2.392$ Å. The shell charge Y(As) and shell-core force-constant K(As) for As atoms are -1.0 and 140 $eV/Å^2$. The parameters of the potential are determined from the static and dynamic equilibrium conditions of the crystal lattice. The lattice-dynamical calculations are carried out using DISPR (Ref. 30) software package developed at Trombay.

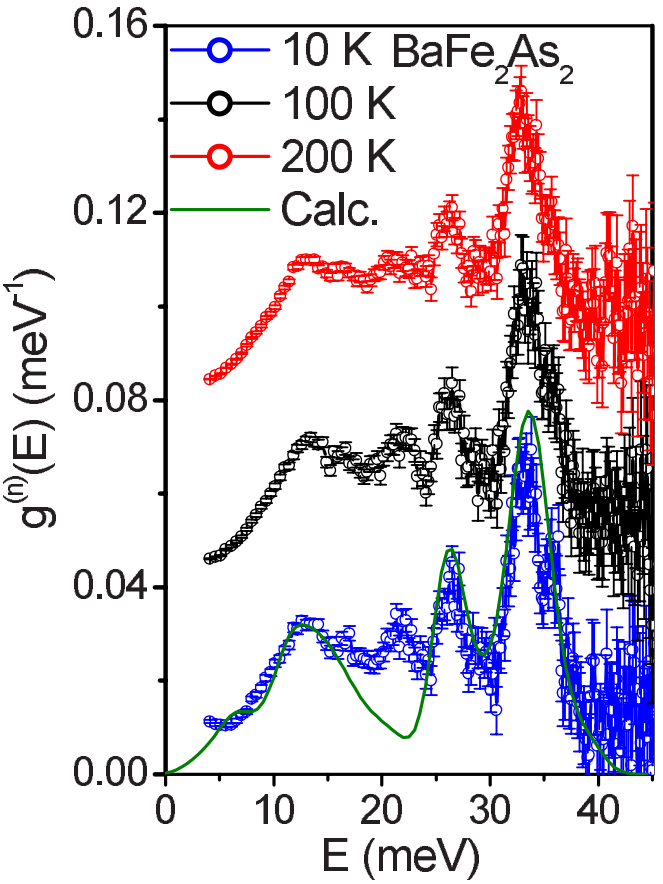

FIG. 1. (Color online) Comparison between the calculated and experimental phonon spectra of $BaFe_2As_2$. For better visibility the experimental phonon spectra at 100 and 200 K are shifted along the y axis by 0.04 and 0.08 meV^{-1}, respectively. The calculated spectra have been convoluted with a Gaussian of full width at half maximum (FWHM) of 3 meV in order to describe the effect of energy resolution in the experiment.

The phonon spectra collected for $BaFe_2As_2$ at 10, 100, and 200 K are shown in Fig. 1. $BaFe_2As_2$ has an orthorhombic-to-tetragonal structural and magnetic phase transition at 140 K when increasing the temperature. The orthorhombic distortion is rather small. The experimental phonon spectrum at 200 K in the tetragonal phase is quite similar to those in the orthorhombic phase at 10 and 100 K. The experimental $S(Q,E)$ plots (Fig. 2) at 10, 100, and 200 K show no immediately recognizable signs of magnetic excitations in $BaFe_2As_2$ in our measurements between 5 and 45 meV. Our present interatomic potential produces a stable tetragonal structure. The calculations are compared (Fig. 1) with the experimental phonon data at 10 K. The calculations compare very well with the experimental data except for a peak at about 21.5 meV, which is not reproduced by the calculations. Recent work[23] on LaFeAsO shows that the three-peak structure between 20 to 50 meV in the experimental phonon density of states could not be reproduced by *ab initio* calculations, which show only one peak. Shell model

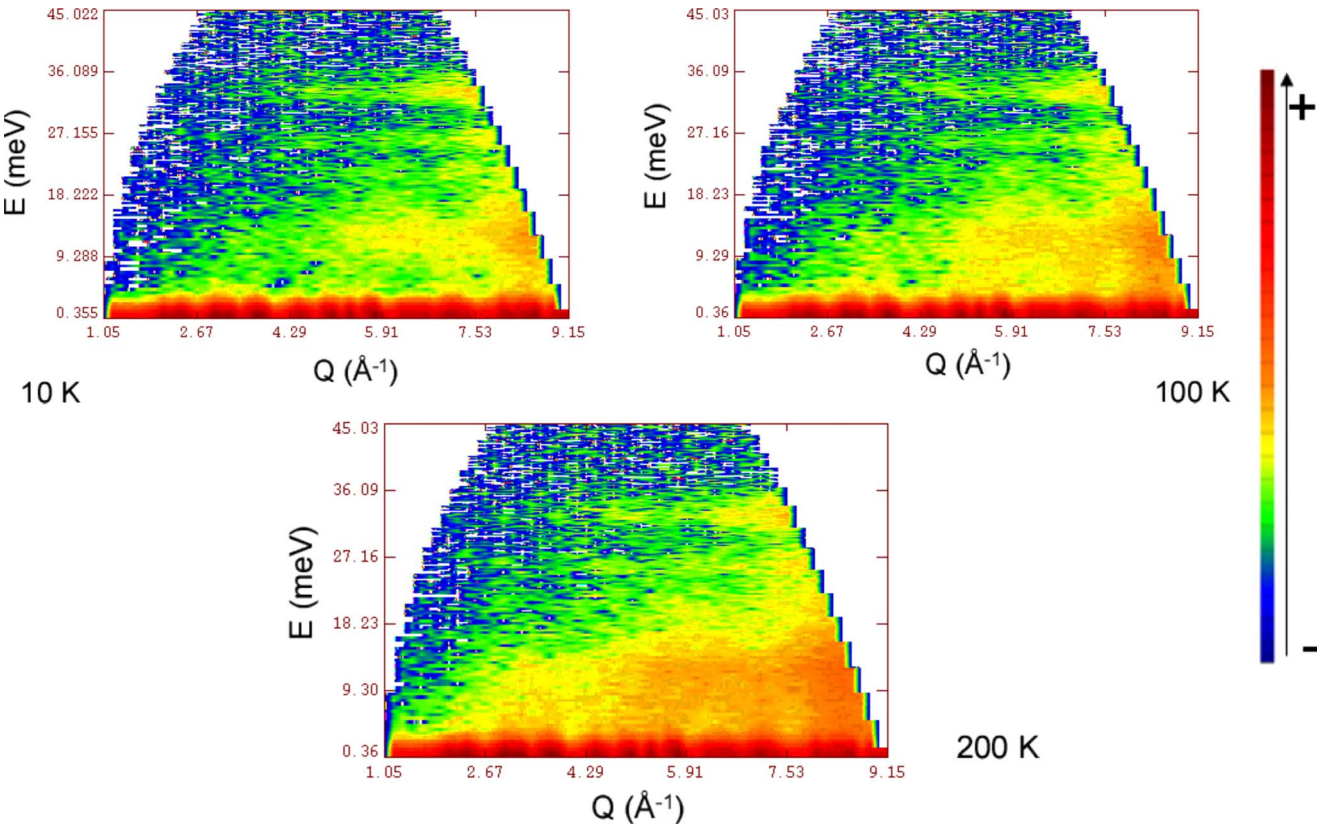

FIG. 2. (Color online) The experimental $S(Q,E)$ plots for $BaFe_2As_2$ at 10, 100, and 200 K.

may be able to fit the peak at 21.5 meV if we introduce additional force constants as adjustable parameters. The intensity of the peak at 21.5 meV is observed to scale with the Bose factor at all the temperatures. The shape of this peak shows an identifiable temperature variation between 10 and 200 K. The experimental $S(Q,E)$ (Fig. 2) plots show that this peak does not arise from intensity at low Q. This suggests that the origin of this peak is not magnetic. There are expected small changes in data with temperature due to anharmonocity. These do not reflect major changes in the one-phonon density of states. At present we may only speculate on the origin of 21.5 meV peak. Electronic structure calculations[25] give an evidence of Fermi-surface nesting in LaFeAsO. Fermi-surface nesting can lead to phonon anomalies.[31,32] An in-plane Fe breathing mode of 20 meV has been found[17] to be relevant for $LaO_{1-x}F_xFeAs$ in this respect. Same physical argument should also hold for $BaFe_2As_2$. Our lattice dynamics calculations are carried out using an atomistic approach, wherein the effects arising from Fermi-surface nesting have not been incorporated. Recently $S(Q,E)$ has been measured[22] for superconducting $Ba_{0.6}K_{0.4}Fe_2As_2$ at 7–50 K. The measurements are carried out in the energy, and momentum transfer ranges up to 25 meV and 2.5 $Å^{-1}$, respectively. These measurements indicate neutron-scattering evidence of a resonant spin excitation at 15 meV in $Ba_{0.6}K_{0.4}Fe_2As_2$. However our measurements on parent $BaFe_2As_2$ show no sign of any magnetic excitations as described above.

In order to understand the contribution of various atomic motions to the phonon spectra we have calculated the partial densities of states (Fig. 3). The Ba atoms mainly contribute in the 0–20 meV range, while the Fe and As atoms contribute in the entire 0–40 meV ranges, respectively. Above 30 meV the contributions are mainly due to Fe-As stretching modes.

Application of hydrostatic pressure up to 4 GPa in F-doped LaFeAsO results[4] in an increase in T_c from 25 to 43 K. Similarly pressure induced superconductivity has been

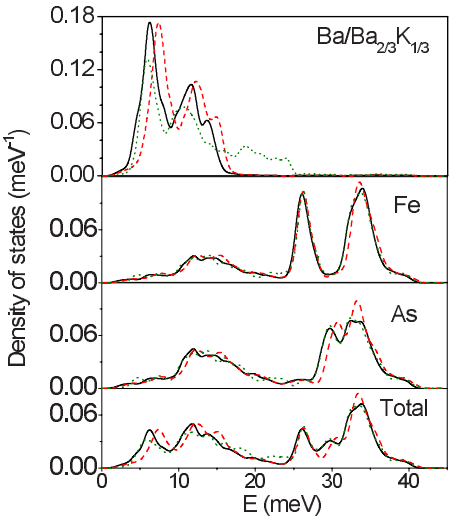

FIG. 3. (Color online) The calculated partial density of states of the various atoms in $BaFe_2As_2$ and $Ba_{2/3}K_{1/3}Fe_2As_2$. Solid line, dashed line, and dotted line correspond to the calculated partial density of states of various atoms in $BaFe_2As_2$ (0 GPa), $BaFe_2As_2$ (4 GPa), and $Ba_{2/3}K_{1/3}Fe_2As_2$ (0 GPa), respectively.

found in $CaFe_2As_2$ (Refs. 12 and 24) and $BaFe_2As_2$ (Ref. 13) at 0.5 and 3.8 GPa, respectively. Phase transition to a collapsed tetragonal phase and superconductivity seem to be related[12,24] in these compounds. $BaFe_2As_2$ shows superconductivity at 3.8 GPa, so in order to understand the role of phonon in increasing T_c, we have calculated phonon spectra at 4 GPa. We find that the effect of pressure is largest on the barium modes (Fig. 3) at pressure corresponding to the onset of superconductivity. At ambient pressure $BaFe_2As_2$ shows superconductivity if we partially substitute Ba with K. Pressure generates nearly the same effect as the partial substitution of Ba by K atoms. In order to understand this we have carried out supercell calculations $(3\times3\times3)$ for $Ba_{2/3}K_{1/3}Fe_2As_2$. The calculated phonon spectra for $Ba_{2/3}K_{1/3}Fe_2As_2$ are also shown in Fig. 3. The atomic mass of K (39.10 amu) is smaller in comparison to Ba (137.34 amu). This results in an increase in the average phonon energy of $Ba_{2/3}K_{1/3}$ site atoms only. Experimental measurements of Raman modes[14] in $SrFe_2As_2$ also show that substitution of K for Sr has little effect on the frequencies of modes involving As and Fe atoms. Modes involving Sr or $Sr_{0.6}K_{0.4}$ could not be measured by Raman spectroscopy since these A_{2u} or E_u modes are only sensitive to the infrared technique.

The calculated one-phonon density of states $g(E)$ is shown in Fig. 3 and is used to compute the specific heat $C_V(T)$ as a function of temperature. The difference $C_P-C_V=\alpha_V^2 BVT$, where α_V is the volume thermal expansion and B is the bulk modulus. For comparison with the experimental specific heat of $BaFe_2As_2$ the experimental electronic specific-heat coefficient[11] $\gamma(=37\ \mathrm{mJ/mol\,K^4})$ is added to the calculated phonon contribution. The calculated $C_P(T)$ is compared with the experimental data[11] in Fig. 4. The average phonon frequency for the experimental and calculated neutron-weighted phonon spectra are 24 and 25 meV, respectively. This is consistent with the slight excess in the observed specific heat. For $BaFe_2As_2$ the calculated value of bulk modulus is 69 GPa. Experimental data is not available for comparison.

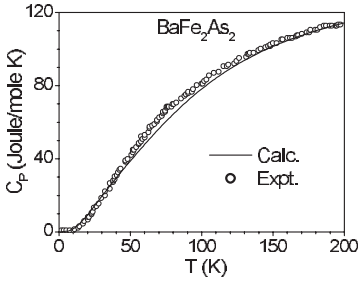

FIG. 4. Comparison between the calculated and experimental specific heats (Ref. 11).

In conclusion, we have measured the temperature dependence of the phonon density of states in the parent compound $BaFe_2As_2$. We find no indications for strong anharmonic effects. Lattice-dynamical calculations are carried out for microscopic understanding of the phonon spectra. The comparison between our experimental phonon data and shell model is very good apart from one peak in the experimental spectra that could not be reproduced by the calculations. The peak at 21.5 meV is not reproduced by conventional phonon calculations and might be due to electronic effects such as Fermi-surface nesting. This unusual feature needs more detailed study using single-crystal phonon spectroscopy. We have shown that the effect of pressure on the phonon vibrations is the strongest for the barium modes and so also is the effect of a partial substitution of Ba by K atoms on the modes of the Ba-K sublattice.

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