Lattice and electronic anomalies of CaFe$_2$As$_2$ studied by Raman spectroscopy

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(Dated: October 13, 2008)

We report inelastic light scattering experiments on CaFe$_2$As$_2$ in a temperature range of 4 to 290 K. In in-plane polarizations two Raman-active phonon modes are observed at 189 and 211 cm$^{-1}$, displaying $\Lambda_{1g}$ and $B_{1g}$ symmetries, respectively. Upon heating through the tetragonal-to-orthorhombic transition at about $T_S = 173$ K, the $B_{1g}$ phonon undergoes a discontinuous drop of the frequency by 4 cm$^{-1}$ whereas the $\Lambda_{1g}$ phonon shows a suppression of the integrated intensity. Their linewidth increases strongly with increasing temperature and saturates above $T_S$. This suggests (i) a first-order structural phase transition and (ii) a drastic change of charge distribution within the FeAs plane through $T_S$.

PACS numbers: 74.70.Kn, 75.30.Gw,76.60.-k

Keywords:

The recently discovered iron-based superconductors R$_x$FeAsO$_{1-x}$F$_x$ ($R=$La,Nd,Ga,Sm) have triggered a burst of experimental and theoretical research activities because of the potential relevance to high-temperature superconductors. The Fe-based and cuprates superconductors have remarkable similarities in structural and magnetic aspects. The undoped compound has a two-dimensional electronic structure and a long range spin density wave (SDW) antiferromagnetic order at 134 K. Doping an undoped parent compound leads to a suppression of the magnetic order while inducing superconductivity.

More recently, the ternary A$_x$M$_{1-x}$Fe$_2$As$_2$ ($A=$K,Na; $M=$Ca,Sr,Ba) compounds have shown to share similar structural, magnetic, and superconducting properties with the R$_x$FeAsO$_{1-x}$F$_x$. Although the superconducting transition temperatures are a little lower, the ternary compounds have an advantage in addressing intrinsic superconducting properties owing to the lack of oxygen and the ease of growing sizable single crystals. Among the AFe$_2$As$_2$ family CaFe$_2$As$_2$ manifests the clearest first order SDW and structural phase transition, making it optimally suitable for investigating the interplay between lattice and spin degrees of freedom and superconductivity.

The undoped CaFe$_2$As$_2$ has the tetragonal ThCr$_2$Si$_2$-type crystal structure (space group I4/mmm) with lattice parameters $a = 3.912(68)$Å and $c = 11.667(45)$Å. Upon cooling, a structural phase transition takes place from the high temperature tetragonal to the low temperature orthorhombic phase (Fmmm) around $T_S \sim 173$ K. Drastic changes in resistivity, magnetic susceptibility, and lattice parameters as well as narrow hysteresis suggest that the structural phase transition is of first order. In contrast, the sister compounds SrFe$_2$As$_2$ and BaFe$_2$As$_2$ exhibit a gradual change in resistivity. This is ascribed to an extreme sensitivity of the structural instability to chemical, structural perturbations, and the presence of Sn-flux. The sharpness of the structural transition implies that CaFe$_2$As$_2$ is nearly free from such impurities. Concomitant with the structural transition, a magnetic transition to a commensurate antiferromagnetic ordering is accompanied with a saturated Fe moment of 0.8 $\mu_B$. $^{75}$As NMR measurements show a discontinuous formation of the energy gap associated with the SDW instability, giving evidence for a first order magnetic transition as well. Inelastic neutron scattering measurements unveiled anisotropic three dimensional magnetic behavior and a substantial spin gap.

In this brief report, we present Raman scattering measurements of CaFe$_2$As$_2$ single crystals. Raman-active phonon modes show an abrupt change in frequency and linewidth around $T_S$. This is consistent with a first order nature of the structural phase transition. Significantly, the 211 cm$^{-1}$ mode jumps by 4 cm$^{-1}$ through $T_S$. Since this mode involves the displacement of Fe atoms along c-axis, this is interpreted in terms of a sensitivity of the electronic change of the FeAs plane to the out-of-plane vibration. Furthermore, the strong decrease of their linewidth below $T_S$ evidences a drastic change of the electronic density of state at $E_F$ due to the SDW instability.

Single crystals of CaFe$_2$As$_2$ were grown out of Sn flux using high temperature solution growth technique. The high quality of the studied crystals is confirmed by an extensive characterization by means of X-ray, neutron diffraction, thermodynamic and transport technique. For Raman measurements, a plate-like single crystal with
In the in-plane scattering geometry, methods and compared to the experimental results of the asymmetry of the Γ-point phonons are calculated by ab initio. The sharpness of the observed phonon modes simultaneously. Thus, by referring to the comparative study in SrFe$_2$As$_2$, we are able to identify the symmetry of the two peaks. The 189 and 211 cm$^{-1}$ peaks are assigned to the A$_{1g}$ and B$_{1g}$ mode, respectively.

Here we note that the sample has a plate-like shape whose plane is perpendicular to the crystallographic c-axis. The observed Raman scattering intensity is extremely low and the sample thickness is of the order of the laser spot size. This restricts the scattering configuration to the plane. Furthermore, we collect the Raman spectra in the (xu) polarization because it gives a stronger intensity than the (xx) polarization and enables us to study the A$_{1g}$ and B$_{1g}$ modes simultaneously.

In Fig. 2 Raman spectra at three different laser lines are compared at 4 K. All laser lines show commonly the two sharp phonon peaks at 189 and 211 cm$^{-1}$. For the blue and green laser lines, the intensity of the 189 cm$^{-1}$ mode is weaker than that of the 211 cm$^{-1}$ mode. The scattering intensity of both modes becomes comparable for the red laser line. Overall, the blue and green laser lines give stronger Raman intensity than the red one. Thus, detailed temperature dependence was measured using $\lambda = 488$ and 532 nm.

Before proceeding, we will discuss Raman scattering on electronic excitations. In simple metals light scattering by electrons is hardly observable at low energy because variations of the charge density are screened by itinerant electrons, and electrons will be collectively excited at a plasma frequency of several eV. In contrast, correlated electron systems show distinct electronic excitations and collective modes in the optical phonon energy range. For examples, the cuprate and hydrated cobal-
tate Na$_x$CoO$_2$·yH$_2$O superconductors show similar flat, broad electronic continua in a certain doping range. The studied system exhibits no appreciable electronic excitations at least in the energy range of 40 – 800 cm$^{-1}$ within the resolution and sensitivity of our spectrometer. The absence of an electronic continuum might suggest that correlation effects are not as strong as the cuprate and cobaltate superconductors. In addition, the phonon modes remain sharp and have a typical Lorentz shape rather than a Fano line shape. This implies that coupling of the phonons to other excitations is small. According to a first principle calculation, electron-phonon coupling is evenly distributed among all of the phonon branches and the electron-phonon matrix elements are extremely small due to the strongly delocalized character of the Fe-$d$ states around the Fermi level, $E_F$.

Figure 3 displays the temperature dependence of Raman spectra. The dashed vertical bar indicates the position of the 211 cm$^{-1}$ mode at T=4 K. With increasing temperature the intensity of the A$_{1g}$ modes remain sharp and have a typical Lorentz shape. Next, we consider the change of interionic distances. The 211 cm$^{-1}$ phonon frequency jumps by 2 % around $T_S$ and the 189 cm$^{-1}$ A$_{1g}$ modes soften by about 3 cm$^{-1}$ with increasing temperature. In the narrow temperature interval around $T_S$ the 211 cm$^{-1}$ mode shows an abrupt, large jump by 4 cm$^{-1}$ and then undergoes a tiny softening by 1 cm$^{-1}$ between $T_S$ and room temperature. Its linewidth ($\Gamma$) also shows a distinct change at about $T_S$; for the 211 cm$^{-1}$ mode it increases strongly with increasing temperature and saturates above about 173 K. Below 173 K the 189 cm$^{-1}$ mode also shows a strong broadening but the saturation cannot be identified due to a suppression of the scattering intensity. The discontinuous change of the phonon frequency and linewidth at $T_S$ demonstrates a first-order nature of the structural transition as consistent with other transport, thermodynamic, and magnetic studies.

We now discuss possible origins of the observed phonon anomalies. They cannot be ascribed to the change of optical parameters since the intensity of the 211 cm$^{-1}$ mode is largely temperature-independent (not shown here) although the 189 cm$^{-1}$ mode is strongly suppressed above $T_S$. Next, we consider the change of interionic distances. The 211 cm$^{-1}$ phonon frequency jumps by 2 % around $T_S$. The phonon frequency relies on a bond length, $\omega^2 \sim l^3$. Between room temperature and $T_S$ the c-lattice parameter changes by 0.4 %. Thus, the lattice parameter change cannot fully explain the observed large jump of the phonon frequency. Although in-plane lattice parameters jumps by $\sim 1\%$, it will not directly couple to the B$_{1g}$ mode, which involves the out-of-plane displacements of the Fe ions. Rather, it might be related...
to the change of a charge distribution in the FeAs planes through $T_S$. This explains well the temperature dependence of the linewidth.

In a phonon-phonon interaction mechanism, the broadening of a phonon mode is given by the decay of the optical phonon into acoustic modes. Since anharmonic effects are described by Boltzmann functions, the temperature dependence of a phonon linewidth does not saturate in contrast to our case. Thus, electron-phonon interactions should be taken into account. In this mechanism, the ratio $\Gamma/\omega_0$ is given by

$$\Gamma/\omega_0 = \pi N(0) / \hbar \omega_0 \lambda,$$

where $N(0)$ is the electronic density of states at $E_F$, $\omega_0$ is the frequency of the specific mode, and $\lambda$ is the electron-phonon coupling parameter. As discussed above, the electron-phonon interactions are not strong due to the strong delocalization of the electronic density of state at $E_F$. However, the structural phase transition can modify the electronic state and accordingly the strength of electron-phonon interactions can vary. Since electron-phonon interactions scale with the temperature dependence of the electronic density of state $E_F$, the strong reduction of the linewidth below $T_S$ can be attributed to an opening of a gap due to the SDW instability. We find that an activated function $exp(-\Delta/k_B T)$ with $\Delta = 168 - 202 K$ provides a reasonable description to the temperature dependence of the linewidth (see the solid line of Fig. 4). However, this value should not be taken literally because we cannot separate this effect from the contribution of anharmonicity to the phonon broadening. Here we mention that recent NMR measurements show a jump of an electric field gradient in the $c$ direction and an abrupt change of spin-lattice relaxation at $T_S$. This is interpreted in terms of the dramatic change of an on-site charge distribution in the As orbitals.

To summarize, we present Raman scattering measurements of CaFe$_2$As$_2$. The frequency and linewidth of Raman-active phonon modes show a discontinuous change around $T_S$. This confirms a first order nature of the structural phase transition. Significantly, the large shift of the 211 cm$^{-1}$ mode by 4 cm$^{-1}$ at $T_S$ and the strong decrease of the linewidth below $T_S$ give evidence for (i) a strong change of the electronic density of state at $E_F$ and (ii) a sensitivity of the electronic and magnetic change of the FeAs plane to the out-of-plane structure.

Acknowledgments

This work was supported by DFG and ESF-HFM. One of us (K.Y.C.) acknowledges financial support from the Alexander-von-Humboldt Foundation. Work at the Ames Laboratory was supported by the Department of Energy, Basic Energy Sciences under Contract No. DE-AC02-07CH11358.

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