Raman scattering studies on the collapsed phase of $CaCo_2As_2$*

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In this work, Raman scattering measurements have been performed on the collapsed phase $CaCo_2As_2$ crystals. At least 8 Raman modes were observed at room temperature though $CaCo_2As_2$ is structurally similar to other 122 compounds like $BaFe_2As_2$. Two Raman modes are assigned to the intrinsic A_{1g} and B_{1g} of this material system respectively. The other ones are considered to originate from the local vibrations relevant to cobalt vacancies. Careful polarized measurements allow us to clearly resolve the four-fold symmetry of the B_{1g} mode, which put strong constraints on possible point group symmetries of the system with Co vacancies. The temperature-dependent measurements demonstrate that the anomalies in both frequency and width of the B_{1g} mode occur around Neel temperature T_N. The anomalies are considered to be related to the gap opening near the magnetic transition. The study may shed light on the structural and magnetic changes and their correlations with superconductivity in 122 systems.

Keywords: iron-based superconductivity, Raman scattering, collapsed phase

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1. Introduction

The $ThCr_2Si_2$-type compounds have attracted a tremendous amount of attention since the discovery of iron-based superconductors in 2008.[1,2] Besides iron pnictides, many other 122 systems have also been extensively studied. Superconductivity was found in $CaPd_2As_2$ (Tc $\sim$ 1.27 K) and $SrPd_2As_2$ ($T_c \sim 0.92$ K) single crystals.[3] A checkerboard antiferromagnetic (AF) structure was observed in insulating $BaMn_2As_2$ and relevant compounds.[4,5] Itinerant antiferromagnetism was reported in $BaCr_2As_2$.[6,7]

Cobalt-based 122 compounds are closely similar to 122 iron pnictides in many aspects. However, no superconductivity was measured in the doped $SrCo_2As_2$.[8] However, a clear negative thermal expansion was observed in the compound.[9] $CaCo_2As_2$ has received particular interest among the cobalt-based 122 compounds. It has a typical $ThCr_2As_2$ structure (space group $I4/mmm$) and a small ratio of $c/a \sim 2.59$ under ambient pressure, suggesting a collapsed phase,[10,11] just as was found in $CaFe_2As_2$. A range of external pressures can reduce its c axis by a factor of $\sim 9.5\%$ and drive a collapsed phase transition[12,13] with no magnetic[12–15] or superconducting[16] transition. Similar to the AF transition at $\sim$ 170 K in $CaFe_2As_2$, A-type AF ordering in $CaCo_2As_2$ was also observed by different research groups. The reported T_N ranges from 70 K to 76 K.[17,18] It increases to 90 K with 10% Sr doping.[17] Interestingly, a spin flop transition was observed in all the above measurements.[17,18] However, if Sn instead of CoAs is used as flux, the crystals have a T_N of only $\sim$ 52 K and 7% Co vacancies.[19,20] It is unclear if the reduction of T_N is related to Co vacancies and the issue remains an open question so far. As one of the fundamental techniques sensitive to crystal microstructures, Raman scattering has been proved to be an effective way to probe vacancies and their ordering.[21]

Raman scattering measurements on $CaCo_2As_2$ were carried out in this work. At least 8 modes were observed, which is much more than the number of symmetry-allowed Raman modes. Polarized Raman measurements indicate that three of the modes have a four-fold symmetry and one has a full-symmetry. The temperature-dependent Raman spectra reveal that the strongest peak shows clear anomalies in both frequency and width near the AF transition. This is similar to the cases of 122 and 11 iron pnictides and provides the important information on vacancies in the material. The present study may provide insight into superconductivity, magnetism and collapsed phase because of the close similarity between $CaCo_2As_2$ and other 122 systems including the superconducting ones.

2. Experiments and methods

The $CaCo_2As_2$ crystals used in the work were grown through the self-flux method that has been described in detail elsewhere.[13,22] Structural and thermodynamic characteriza-

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tions can be found in Ref. [20]. Raman measurements were performed using a Jobin Yvon HR800 single-grating system equipped with a liquid-nitrogen cooled CCD detector and a He–Ne laser source of 632.8 nm (Melles Griot). A backscattering configuration was adopted in all the measurements. The laser power was controlled at the level of ~ 1 mW and the laser spot was ~ 5 μm in diameter. The cleaved surface was parallel to the ab-plane and the incident light is perpendicular to the surface or parallel to the c axis. $X'X'$ denotes that the polarizations of both incident and scattering light are parallel to the diagonals between a and b axes, while $X'Y'$ means that their polarizations are orthogonal. Polarized Raman measurements were made at room temperature by fixing the perpendicular polarizations between incident and scattering light and rotating crystal at a step of 15°. The space and point groups of $CaCo_2As_2$ are $I4/mmm$ and D_{4h} respectively, which allows 4 Raman-active modes including one A_{1g} mode, one B_{1g} mode, and doubly degenerate E_g mode (see the inset of Fig. 1).

3. Results and discussions

Figure 1 shows polarized Raman spectra at room temperature. There are 8 peaks under two configurations. Four of them appear in the parallel channel ($X'X'$) and the other four in the cross channel ($X'Y'$). On the other hand, only A_{1g} (As) and B_{1g} (Co) are symmetry-allowed under the present configuration. This means that six of the observed modes are unexpected. One may argue that the extra modes come from the intensity leakage of E modes if the crystal surface is a little tilted. However, the scenario seems incompatible with the observations since the leakage intensity is usually very small and there are only four modes totally even if all the symmetry-allowed modes are counted. Local vibrations induced by impurities also seem unlikely since no signal of impurities is seen in the structural measurements.[18] Another possibility is that the extra modes are contributed by the local modes which are induced by Co vacancies. As mentioned above, powder x-ray diffraction and elastic neutron scattering[19,20] indicate that $\sim 7\%$ Co vacancies exist in the crystals with Sn as flux. Most of the observed peaks are very broadened with a full width at half maximum (FWHM) of more than 20 cm^{-1}. This coincides with the local modes, and implies that Co vacancies exist not only in the crystals grown with Sn flux but also in the crystals with CoAs as flux. It is likely that the vacancies cause a relaxation of selection rules and introduce some non-Raman active or non-Gamma modes into the Raman channel. The strong and narrow P_4 peak in Fig. 4 can be reasonably assigned to the intrinsic mode of bulk crystals.

We further made polarized Raman measurements by rotating crystals to resolve mode symmetries. The spectra are shown in Figs. 2(a) and 2(b). P_4 exhibits periodic modulations in intensity and P_6 remains almost unchanged in the parallel configuration, while P_6 disappears and the intensities of P_1, P_4, and P_5 change with rotating crystals. The rotation-angle dependence is illustrated in Figs. 2(c) and 2(d) respectively. Under parallel polarization configuration, the intensities of P_4 are proportional to $\sin 4\theta$, indicating a four-fold rotation symmetry, while P_1, P_4, and P_5 exhibit the four-fold symmetry in cross polarization configuration and have a phase difference of 45°. These results allow to attribute P_4 and P_6 to B_{1g} and A_{1g} modes respectively. P_5 is a B_{1g}-like mode which may originate from local vibrations as discussed above. The vibration patterns of B_{1g} and A_{1g} modes are exactly similar to those in $BaFe_2As_2$ and illustrated in the inset of Fig. 1.

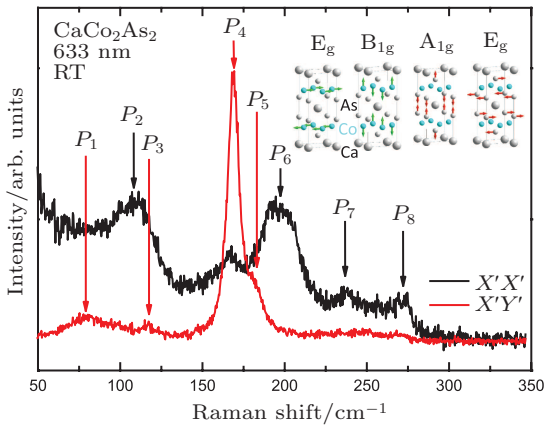


Fig. 1. (color online) Polarized Raman spectra collected at room temperature. The inset shows the vibration patterns of four Raman-active modes in 122 system.

The temperature-dependent Raman spectra are shown in Fig. 3. All the observed modes become softening and broadening with increasing temperatures. We made careful Lorentz fitting for the strongest P_4 peaks and the fitting results are summarized in Fig. 4. The evolution of Raman frequency with temperature coincides with the inharmonic phonon decay model.[23] This suggests that $CaCo_2As_2$ has a normal positive thermal expansion which is opposite to the clear negative thermal expansion observed in $SrCo_2As_2$.[9] The contrast difference may stem from the absence of a collapsed phase in $SrCo_2As_2$.[24] The anomalies in mode width are observed around Neel temperature $T_N \sim 74$ K. In fact, the reversal of temperature evolution of mode widths starts even at ~ 150 K, far beyond T_N. This is considered as a precursor effect of AF transition. In the parent compound $BaFe_2As_2$ of 122 Fe-based superconductors, phonon anomalies have been reported near spin-density-wave (SDW) transition and are attributed to phonon self-energy renormalization induced by the SDW gap opening.[25–27] Just like $BaFe_2As_2$, $CaCo_2As_2$ is also an AF metal and its magnetic transition can similarly lead to phonon anomalies around transition temperature through some form of spin-phonon interaction.

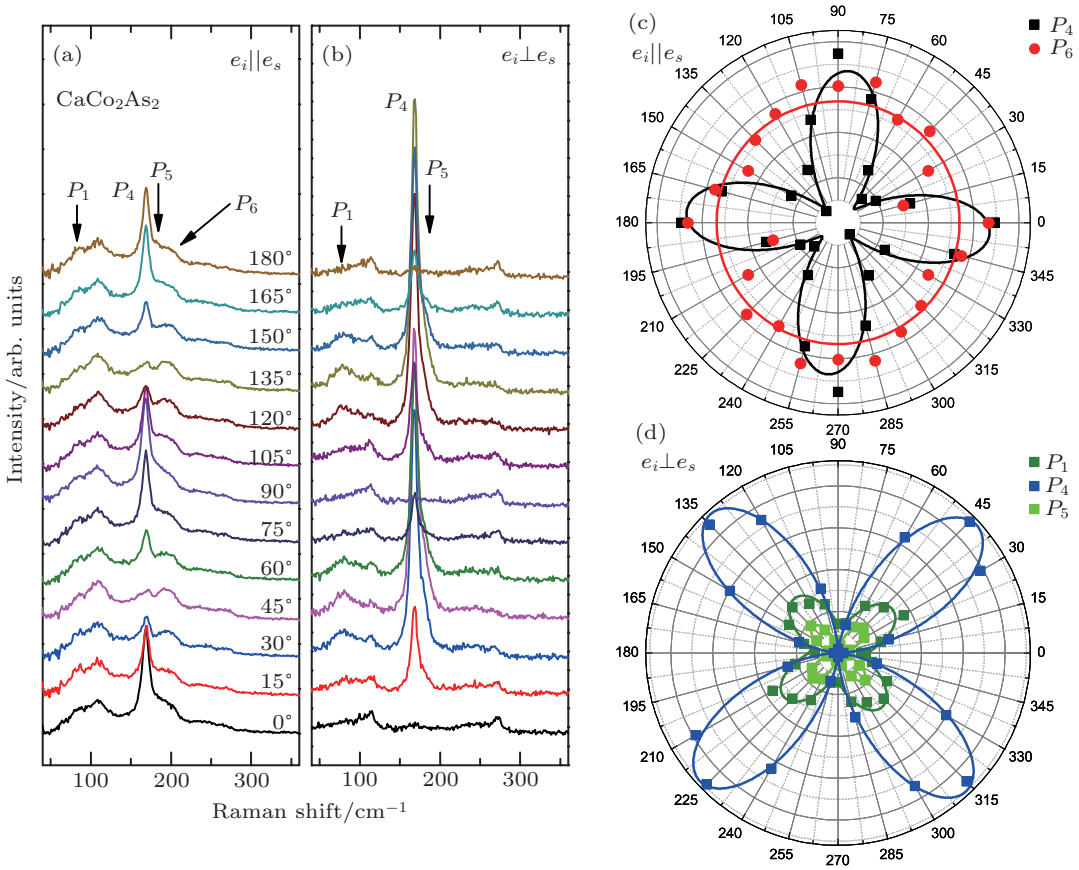


Fig. 2. (color online) Rotation-angle dependence of Raman spectra in $CaCo_2As_2$. (a) and (b) Raman spectra collected under parallel and cross polarization configurations respectively. (c) and (d) Intensity modulations with rotation angles in two configuration channels. The angles are the ones between *a* axis and polarization of incident light.

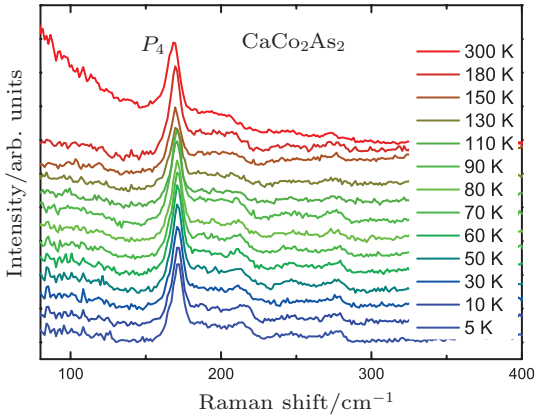


Fig. 3. (color online) Temperature-dependent Raman spectra of $CaCo_2As_2$.

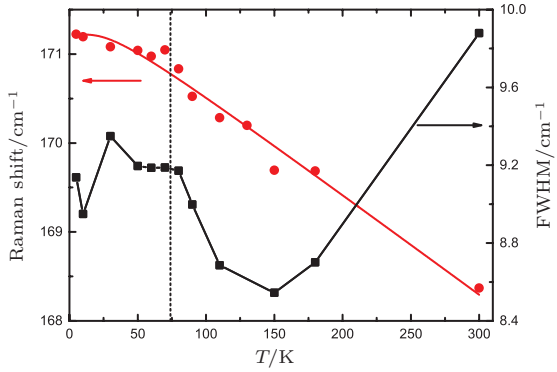


Fig. 4. (color online) Temperature dependence of P_4 phonon's frequencies and widths. The red line is the fitting curve using inharmonic phonon decay model.

4. Summary

In summary, Raman scattering studies of collapsed phase $CaCo_2As_2$ have been made in this work and at least 8 peaks are observed. Two of them are assigned as intrinsic A_{1g} and B_{1g} modes, and the other ones are considered to come from the local vibrations induced by Co vacancies. Polarized Raman measurements determine the four-fold symmetry of the system, which put strong constraints on the possible patterns of Co vacancies. Further temperature-dependent experiments reveal that the anomalies of B_{1g} mode in width are related to the AF transition through a spin-phonon coupling.

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