Charge order and phonon renormalizations: Possible implications for cobaltates.

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Several experimental and theoretical studies in cobaltates suggest the proximity of the system to charge ordering (CO). We show, qualitatively, in the frame of a $t-V$ model coupled to phonons that optical phonon modes at the $K$ and $M$ points of the Brillouin zone, which involves only $O$-ions displacement around a Co-ion, are good candidates to display anomalies due to the CO proximity. If by increasing of $H_2O$ content the system is pushed closer to CO, the mentioned phonon modes should show softening and broadening.

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The discovery of superconductivity in $Na_2CoO_2.yH_2O$ for $x = 0.35$ and $y = 1.3$ (Ref.[1]) has motivated a large interest in the solid state physics community due, in part, to the similarities between this compound and high-$T_c$ cuprates. Cobaltates are 3$d$-electron systems having a quasi-two-dimensional structure, $CoO_2$, where the Co-atoms are in a triangular lattice. Recently, for describing superconductivity in these materials, some authors proposed the interplay between electronic correlations and the proximity to a charge density wave (CDW) instability\textsuperscript{2,4}. These papers focus on a two-dimensional $t-V$ model on a triangular lattice where the nearest neighbors Coulomb interaction $V$ is the relevant parameter for bringing the system to the CDW instability which occurs for $V > V_c$ at the momentum $q = (4\pi/3,0)$. This CDW phase is called $\sqrt{3} \times \sqrt{3}$-CDW\textsuperscript{2,4}. Although some experimental reports in hydrated\textsuperscript{5-8} and unhydrated samples\textsuperscript{7,8} suggest a possible interpretation in favor of the CO proximity, this scenario is still controversial\textsuperscript{8,9}. Therefore, it is relevant to solve the CO controversy. In this paper we propose that if the system is close to the CO, signatures of it in the phonon subsystem can be expected. Hence, theoretical and experimental studies on phonon anomalies may be important for testing the CO hypothesis. Those phonons which couple more directly with charge fluctuations are candidates to show anomalies and are discussed in this paper.

Since the $\sqrt{3} \times \sqrt{3}$-CDW order takes place in the $CoO_2$ planes, we have performed for simplicity a 2$D$ lattice dynamics calculation\textsuperscript{10} in order to understand qualitatively which phonon modes are more sensitive to the proximity of CO. For this purpose, we have studied the phonon eigenvectors. For $q = 0$ we have obtained a double degenerated optical phonon, where only the $O$-ions move, associated with the Raman-active-in-plane $E_{1g}$ mode\textsuperscript{12} of frequency $\omega \sim 480$ cm$^{-1}$ and also listed in table I of Ref.[13]. Increasing $q$ along this branch the degeneracy is removed. At the $K$-point of the Brillouin zone $[q = (4\pi/3,0)]$ we have obtained two phonon modes, $A$ and $B$, with complex eigenvectors which lead to the displacements of the $O$-ions shown in Fig[1a]. At the $M$-point $[q = (\pi,\pi/\sqrt{3})]$ there are two modes, $C$ and $D$, with real eigenvectors with $O$-ions displacements presented in Fig[1b]. Interestingly, in the modes $A$ and $C$ the average distance to the $Co$-ion of the six $O$-ions changes with time leading to the possibility for the coupling of these modes to the density at the $Co$ site. For $B$ and $D$ modes the average distance remains almost constant. The displacements of the $O$-ions in the mode $A$ have a breathing-like pattern of displacements.

FIG. 1: a) $O$-ions pattern of displacements of the two optical phonon modes at $K$-point discussed in the text. b) The same for the $M$-point. Big (small full) circles represent the $Co$ ($O$) ions. The crosses are the equilibrium positions of the $O$'s. The arrows indicate the displacements of the $O$-ions. In the modes $A$ and $C$ the average distance to the $Co$-ion of the six $O$-ions changes with time leading to the possibility for the coupling of these modes to the density at the $Co$ site. For $B$ and $D$ modes the average distance remains almost constant. As it is sketched in Fig[1b] the displacements of the $O$-ions in the mode $A$ have a breathing-like pattern of displacements around $Co$-ions and therefore, an adequate symmetry to couple with the charge fluctuations at the $Co$-site when the system approaches the $\sqrt{3} \times \sqrt{3}$-CDW phase. In addition, this mode has the same $q = K$ vector than the CO.

For a qualitative study of those phonons which couple more directly with density fluctuations at $Co$ site ($A$ and $C$) we proposed the following Hamiltonian\textsuperscript{2}:

$$H = H_0 + \Delta H$$
\[ H = -t \sum_{<ij>} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + h.c.) + V \sum_{<ij>} n_i n_j + \sum_i \omega_0 (a_i^\dagger a_i + \frac{1}{2}) + g \sum_i (a_i^\dagger + a_i) n_i \]  \tag{1}

The highest commensurate doping and destruction operators for holes, respectively, under phon coupling and states (DOS). We will present results for the interpretation in terms of the proximity of the Zang-Rice singlet energy. This view was also used in Ref.[13] for studying the anomalous softening and broadening for the half-breathing mode in cuprates.

Theoretical calculations in Ref.[14] show that a one-band \( t - J \) model plus phonons can be derived, from the three-band Hubbard model plus phonons, for studying cases where the \( O \)-ions displacements lead to a modulation of the Zang-Rice singlet energy. The phonon frequency shifting and phonon linewidth are \( \Delta \omega \) and \( \Gamma \), respectively. These parameters the instability to the CDW order. From \( E_k \) we obtain for the dressed electronic DOS \( N^*(0) \sim 0.631/t \) while the bare DOS is \( N(0) = x/2N^*(0) \sim 0.11/t \). For the present parameters the instability to the \( \sqrt{3} \times \sqrt{3} \)-CDW order takes place for \( V > V_c = 1.12 \).

The phonon frequency shifting and phonon linewidth are \( \Delta \omega = R e \Pi(\mathbf{q}, \omega_0 + i\eta) \) and \( \Gamma = I m \Pi(\mathbf{q}, \omega_0 + i\eta) \) respectively. In Fig 3 we show \( \Delta \omega / \lambda_0 \) and \( \Gamma / \lambda_0 \) as a function of \( V \) for the phonons at \( \mathbf{q} = K \) and \( \mathbf{q} = M \). The frequency is \( \omega_0 = t/2.5 \); being \( t \sim 150 \text{ meV} \), \( \omega_0 \sim 480 \text{ cm}^{-1} \) which is close to the frequency of the two optical A and C phonon modes. With increasing \( V \), approaching the \( \sqrt{3} \times \sqrt{3} \)-CDW phase, the two phonons become soft.
the $\sqrt{3} \times \sqrt{3}$-CDW instability occurs at $q = K$, softening and broadening of the $q = K$ phonons are larger than for the $q = M$ mode.

The origin of the softening and broadening near the charge instability is understood as follows. The role played by charge densities is clearly evident by looking at eq.(3): As stated in Refs.23, $D_{RR}$ is proportional to the charge-charge correlation function $\chi''(q, \omega) = -N(\pi/2)^2 D_{RR}(q, \omega)$ showing that charge fluctuations have a direct influence on the renormalized e-ph interaction. In Fig.3 are presented results for the density response, $Im\chi''(q = K, \omega)$, for different $V$. The momentum was fixed at $K$ where the $\sqrt{3} \times \sqrt{3}$-CDW phase takes place. For $V = 0$, it is clearly seen a collective peak at $\omega \sim 4.2t$ at the top of the particle-hole continuum. With increasing $V$ the collective peak softens and for $V = 1$ is still well defined at high energy of the order $\sim 3t$. But it has transferred spectral weight to a broad structure at low energies with a maximum at $\omega \sim t/2$. When the instability takes place, at $V = V_c = 1.1$, this broad structure reaches $\omega = 0$ and the static charge susceptibility diverges. As result of this charge dynamics, the e-ph vertex is renormalized leading to the effects shown in Fig.4. Since the instability is of static character, the effect will be stronger for low energy phonons than for large energy phonons. Contrary to the case for quarter filling on the square lattice20, the charge instability at $x \sim 1/3$ can not be seen strictly as the softening of a collective charge mode, but a redistribution of spectral weight takes place. The reason for this behavior can be found in the form of the particle-hole continuum which starts at $\omega = 0$ (inset in Fig.3) and then, the collective peak never merges from the bottom of the continuum. Finally, it is important to notice that the static CO was not experimentally confirmed (see Ref.10), however the effects discussed in present paper need only a dynamical CO proximity in which the electronic system remains homogeneous.

To our knowledge the exact value of the e-ph coupling is not known for cobaltates, however recent experiments suggest that this is nonnegligible20. In Refs.21,22, for estimations of $T_c$, we have proposed for the total e-ph coupling $\lambda = 0.4$ which is close to the order of other recent estimates23,24. In the context of superconductivity, this value must be related with $\lambda = \sum \lambda_{\nu}$ where $\nu$ runs over the number of phonon branches and $\lambda_{\nu}$ is the coupling for each branch. Considering for instance $\lambda_0 = 0.04$, which is one tenth of $\lambda$, we have found, for $V \sim 0.9$, a phonon frequency shifting $\Delta \omega \sim 50$ cm$^{-1}$ (15 cm$^{-1}$) for the $K$ ($M$) phonon with respect to the situation for $V \ll V_c$. A similar estimate can be done for $\Gamma$ showing a broadening of the order of $\Gamma \sim 25$ cm$^{-1}$ (6 cm$^{-1}$) for the $K$ ($M$) phonon mode with respect to weakly or unhydrated samples. In spite of the crudeness of the estimate, it shows that the effect is large enough as to be observed.

It is important to make one remark. For $q = 0$, in the $E_{1g}$ mode $O$-ions move parallel to the planes compressing the Co-atoms. However, from eq.(2) we expect phonon anomalies to be weaker for $q \sim 0$ modes than for large $q$ ones. Therefore, if $q \sim 0$ phonons probe the charge fluctuations due to the proximity to CO, it is through inter-band transitions while, for large $q$ phonons, intra-band transitions are directly involved and we expect the effect to be larger.

Let us discuss how the presented results may be verified experimentally. When studying superconductivity, we obtain an increment of $T_c$ when $V$ increases to $V_c$. Based on the experimental results showing that $T_c$ increases with the water content23, we suggest a positive correlation between $V$ and $y$. On the other hand, and in spite of a microscopic relation between $V$ and $q$ is lacking, experiments24 and theory24 show that hydration causes the electronic structure to become more two dimensional and then, one may argue that the Coulomb interaction between nearest-neighbors is less screened. Then, if hydration pushes the system closer to CO, we

![FIG. 3: a) Phonon shifting $\Delta \omega/\lambda_0$ as a function of $V$ for the phonon modes at $q = K$ and $q = M$. The phonon frequency is $\omega_0 = t/2.5$. b) Phonon broadening $\Gamma/\lambda_0$ as a function of V. With increasing V the system approaches the CO and the two phonons soften and broaden.](image)

![FIG. 4: Imaginary part of the density response $\chi''(q = K, \omega)$ for $x = 1/3$, at $K = (4\pi/3, 0)$, for different $V$, approaching $V_c$ showing the redistribution of the spectral weight. For $V$ near $V_c$, low energy charge fluctuations renormalize the e-ph interaction and cause the phonon renormalizations shown in Fig.3. Inset: particle-hole continuum.](image)
expect larger phonon anomalies for samples with large $y$. Since the predictions in the present paper are for large $q$ optical phonons, they are in general accessible to neutron scattering experiments and, more recently, to inelastic x-rays scattering. Since hydration expands the lattice, mainly in the $c$-direction, one could expect that phonon dispersions also change due to this effect, making hard the detection of the predictions of the present paper. However, as the phonons modes discussed here are mainly of two dimensional character and perpendicular to the $c$-axis, we expect our result to be dominant.

In summary, we have studied the influence of charge fluctuations, near the CO instability, on optical phonons modes at $K$ and $M$ points of Brillouin zone. We have discussed two in-plane optical phonons where only O-ions move compressing the Co-atoms. These phonons were predicted to be soft and broad when the systems is pushed near the charge instability. Softening and broadening were found to be larger for $K$ than for $M$ phonon because the former has the correct $q$ and symmetry to couple with the $\sqrt{3} \times \sqrt{3}$-CDW phase.

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