Phonon dispersion in Sr$_2$RuO$_4$ studied by a first-principles cumulative force-constant approach

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The phonon frequencies along several high symmetry lines for Sr$_2$RuO$_4$ were calculated using the real-space cumulative force-constant approach. Except for the highest $\Delta_1$ ($q(00)$ and $\Sigma_1$ ($q(\xi\delta)$) dispersions, all other 54 branches were quantitatively described very well, including the anomalous softening of the RuO$_6$ octahedra rotational mode which was the lowest $\Sigma_1$ dispersion along the ($\xi\delta$) direction. We did not see any imaginary phonon modes for Sr$_2$RuO$_4$ and demonstrated that the softening of the rotational mode of the RuO$_6$ octahedra was not due to the anharmonic effects.

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The study of lattice dynamics for copper oxide high-temperature superconductors has been a focus of interest ever since their discovery in 1986,1 attempting to understand the role of electron-phonon interactions2 on their superconductivity.3–8 As pointed out by the recent review by Kresin and Wolf,2 there has been growing evidence, mainly from various experimental studies, that electron-phonon interactions could play important role in high $T_c$ superconductivity of the cuprates. However, accurate first-principles calculations of the phonon frequencies of their parent compound La$_2$CuO$_4$ have been stymied by the strong correlation from various experimental studies, that electron-phonon interactions could play important role in high $T_c$ superconductors has been a focus of interest.

In principle, anharmonic effects18 can be accounted for within the finite difference approach to lattice dynamics, in which the force constants between the atoms are calculated by moving an atom by a small displacement from its equilibrium position. In comparison, density-functional-perturbation theory19 for lattice dynamics assumes that the electrons linearly respond to the change in lattice geometry without actually moving an atom. For this reason, the information of anharmonic effects might be lost in the calculated force constants by density-functional-perturbation theory. Accordingly, both the finite difference approach and the density-functional-perturbation theory as implemented in VASP 5.2 are adopted in calculating the real-space cumulative force constants in this work. These are performed with an energy cutoff of 500 eV as well as with various $k$ meshes and supercell sizes to examine the parameter effects on the calculated phonon frequencies.

The phonon frequencies were obtained14 by solving the dynamic matrix of

$$\tilde{D}_{\alpha\beta}(q) = \frac{1}{\sqrt{\mu_{j}\mu_k}} \sum_{p=0}^{N} \phi_{\alpha\beta}(0,P) \exp[iq \cdot (R(P))] = \frac{1}{\sqrt{\mu_{j}\mu_k}} \sum_{p=0}^{N} \phi_{\alpha\beta}(0,P) \exp[iq \cdot (R(P))],$$

where $\phi_{\alpha\beta}(0,P)$ is the cumulative force constants the between atom $j$ in the primitive cell $M$ and atom $k$ in the primitive cell $P$ calculated using the conventional supercell method, $q$ the wave vector, $\alpha$ and $\beta$ the Cartesian axes, $N$ the number of primitive unit cells in the supercell, $\mu_j$ is the atomic mass of the $j$th atom in the primitive unit cell, and $R(P)$ the position of the $P$th primitive unit cell in the supercell.

In using the finite difference approach or supercell approach, inaccuracies are thought to arise from the truncation of the force constants.19,20 This is not completely true as demonstrated by our recent works for the calculations of phonon properties for polar materials14 of $\alpha$-Al$_2$O$_3$, MgO, c-SiC, and $h$-BN, and the calculations of the phonon dispersions for Mott-Hubbard insulators13 of NiO and MnO. At this point, we want to clarify some important aspects of the cumulative force-constant approach. Since we employ the supercell method, the calculated $\phi_{\alpha\beta}(0,P)$ is, in fact, the cumulative contributions of the atom indexed by $k$ and $P$ in the supercell and all its images by translational transformation of the supercell in the whole space. Let $L_i$ ($i=1,2,3$) represent the lattice vectors of the supercell, then

$$\phi_{\alpha\beta}(0,P) = \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty} \varphi_{\alpha\beta}(0,P+n_1L_1+n_2L_2+n_3L_3),$$

where $\varphi_{\alpha\beta}(0,P)$ represents the true two-atom interaction force constant only between the atom $j$ in the referenced supercell and atom $k$ in the supercell positioned at $P+n_1L_1+n_2L_2+n_3L_3$. Since the exact wave vectors $q_{\alpha\beta\gamma}$ satisfies

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FIG. 1. (Color online) Calculated phonon dispersions (solid curves) of Sr$_2$RuO$_4$ using a $2a \times 2a \times 2c$ supercell and the finite difference approach. The symbols are the measured data by Braden et al. (Ref. 22) with, from left to right, $\bigodot$: $\Delta_1$, $\bigodot$: $\Delta_2$, $\bigtriangleup$: $\Delta_3$, and $\Delta$: $\Delta_4$ representing $\Gamma$-Z ($\xi 00$) dispersions; $\bigodot$: $\Sigma_1$, $\bigodot$: $\Sigma_2$, $\bigtriangleup$: $\Sigma_3$, and $\Delta$: $\Sigma_4$ for Z-X ($\eta 00$) dispersions.

The lowest $\Sigma_3$ ($\xi 00$) dispersion possesses a rather soft frequency, as seen in the dip when approaching to the X point (0.5, 0.5, 0), due to the rotational mode of the RuO$_6$ octahedron around the c axis. Braden et al. (note that the X point labeled in this work was labeled as M point in Ref. 22) have suggested this soft mode is related to the structural phase transition observed in Ca$_{2-x}$Sr$_x$RuO$_4$. However, this is not the case, as shown by a calculation plotted in Fig. 3 using the 112-atom $2\sqrt{2}a \times 2\sqrt{2}a \times c$ supercell, $2 \times 2 \times 2$ $\Gamma$-centered $k$ mesh, and the finite difference approach at the experimental equilibrium geometry. The results are shown in Fig. 2. What we find is that the disagreement between the calculation and the experiment remains the same.

For the highest $\Delta_1$ ($\xi 00$) dispersion, our calculations predict a rather high bump in the middle of this branch, marking the largest disagreement between the present calculation and the experiment by Braden et al. The second disagreement between the present calculation and the experiment by Braden et al. is shown by the highest $\Sigma_3$ ($\xi 00$) dispersion as assigned by Braden et al. These two dispersions are very interesting. For La$_{1.8}$Sr$_{0.2}$CuO$_4$, the corresponding experimental $\Delta_1$ ($\xi 00$) dispersion shows a rather deep dip in the middle and the $\Sigma_3$ ($\xi 00$) dispersion shows very steep downward behavior.

To find out if the above-mentioned disagreements between the present calculation and the experiment is due to the effect of the adopted supercell shape by the present calculation, we performed a calculation using the 112-atom $2\sqrt{2}a \times 2\sqrt{2}a \times c$ supercell, $2 \times 2 \times 2$ $\Gamma$-centered $k$ mesh, and the finite difference approach at the experimental equilibrium geometry. The results are shown in Fig. 2. What we find is that the disagreement between the calculation and the experiment remains the same.

In Fig. 1, we show the calculated phonon dispersions for Sr$_2$RuO$_4$ using the 112-atom $2a \times 2a \times 2c$ supercell, $4 \times 4 \times 4$ Monkhorst $k$-mesh and the finite difference approach at the experimental equilibrium geometry reported by Maeno et al. of $a = 3.87$ Å and $c = 12.74$ Å (the internal atomic positions have been theoretically optimized) together with the recently measured phonon frequencies from inelastic neutron scattering by Braden et al. In general, the measured data are predicted rather well by the present work, except for the highest $\Delta_1$ dispersion along the $\Gamma$-Z ($\xi 00$) direction and the $\Sigma_3$ dispersion (the second highest curve) along the $\Gamma$-X ($\xi 00$) direction.

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The lowest $\Sigma_3$ ($\xi 00$) dispersion possesses a rather soft frequency, as seen in the dip when approaching to the X point (0.5, 0.5, 0), due to the rotational mode of the RuO$_6$ octahedron around the c axis. Braden et al. (note that the X point labeled in this work was labeled as M point in Ref. 22) have suggested this soft mode is related to the structural phase transition observed in Ca$_{2-x}$Sr$_x$RuO$_4$, due to the close connection between the static octahedron rotation and the electronic and magnetic properties. Braden et al. also tried to attribute the behavior of the rotational mode to electron-phonon interactions. At first glance, the theoretical success for the current prediction of the lowest phonon branch along the $\Gamma$-X direction appears due to the use of the finite difference method. However, this is not the case, as shown by a calculation plotted in Fig. 3 using the 112-atom $2\sqrt{2}a \times 2\sqrt{2}a \times c$ supercell, $4 \times 4 \times 4$ Monkhorst $k$ mesh, and density-functional-perturbation theory at the experimental equilibrium geometry. Comparing Figs. 2 and 3, one finds the theoretical phonon frequencies predicted by the finite difference approach and the density-functional-perturbation theory are rather similar. Considering the difference in supercell shape, $k$ mesh, and methods in calculating the force con-
ear response approach. The symbols are the measured data by Braden et al. (Ref. 22) with the same meaning as Fig. 1.

stants, we demonstrate that the softening of the rotational mode is not due to anharmonic effects.

For the above mentioned $\Sigma_3 (\xi \xi 0)$ soft phonon mode, we see no anomaly or imaginary phonon frequencies along the $\Gamma$-X direction from the present calculation. Even the downward behavior of the rotational mode observed in the experiment is well predicted. This is in contrast to the \textit{ab initio} tight-binding rigid ion model calculation made by Bauer and Falter\textsuperscript{23} who predict a rather steep imaginary phonon dispersion for the above-mentioned rotational mode near the X point.

In the present calculation, the largest disagreement with experiments are found in the highest $\Delta_1$ dispersion [half-breathing mode at $q=(0.5,0,0)$] and the highest $\Sigma_3$ dispersion, showing that the electron-phonon effects are not properly included in the standard density-functional theory. The half-breathing mode anomaly is common in high-temperature superconductors. For the insulating state, when calculated using the local density approximation (or GGA), the energy of this mode is much lower than the experimental value and it can be improved by using the LDA+U method [e.g., Zhang et al.\textsuperscript{25}]. In general, the role of $U$ (Ref. 26) is to enhance the on-site force constant for Cu or Ru. For metallic Sr$_2$RuO$_4$, Bauer and Falter\textsuperscript{23} demonstrated that the frequencies of these modes increase with $U$, which improves the agreement with the experiment. In the present work, however, the energy of the half-breathing mode is already higher than experiment, so inclusion of $U$ might probably not improve the result.

In summary, the phonon frequencies for the time-reversal symmetry breaking superconductor Sr$_2$RuO$_4$ have been calculated using the real-space cumulative force-constant approach and the overall agreement with experiment is excellent, except for the highest $\Delta_1 (\xi \xi 0)$ and $\Sigma_3 (\xi \xi 0)$ dispersions. We find that the softening of the rotational mode of the RuO$_6$ octahedra is not due to the anharmonic effects, as the calculated results are the same among the finite difference approach and density-functional-perturbation theory, together with the difference in supercell shape and $k$ mesh in calculating the force constants.

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