Lattice dynamics and the electron-phonon interaction in Ca$_2$RuO$_4$

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We present a Raman scattering study of Ca$_2$RuO$_4$, in which we investigate the temperature-dependence of the lattice dynamics and the electron-phonon interaction below the metal-insulator transition temperature ($T_{MI}$). Raman spectra obtained in a backscattering geometry with light polarized in the ab-plane reveal 9 B$_{1g}$ phonon modes (140, 215, 265, 269, 292, 388, 459, 534, and 683 cm$^{-1}$) and 9 A$_g$ phonon modes (126, 192, 204, 251, 304, 322, 356, 395, and 607 cm$^{-1}$) for the orthorhombic crystal structure (Pbca–D$_{4h}^4$). With increasing temperature toward $T_{MI}$, the observed phonon modes shift to lower energies and exhibit reduced spectral weights, reflecting structural changes associated with the elongation of the RuO$_6$ octahedra. Interestingly, the phonons exhibit significant increases in linewidths and asymmetries for $T > T_N$. These results indicate that there is an increase in the effective number of electrons and the electron-phonon interaction strengths as the temperature is raised through $T_N$, suggesting the presence of orbital fluctuations in the temperature regime $T_N < T < T_{MI}$.

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I. INTRODUCTION

Like many other transition-metal oxides that exhibit strong correlations among spin, charge, orbital, and lattice degrees of freedom, Ca$_{2-x}$Sr$_x$RuO$_4$ exhibits many exotic phenomena throughout its rich phase diagram. For instance, not only do the ruthenates exhibit orbital ordering, but also orbital-dependent superconductivity, heavy-mass Fermi liquid behavior, and metal-insulator transitions.

The single-layer ruthenate material Sr$_2$RuO$_4$ is a superconductor below $T_c = 1.5$ K, possibly with an unconventional $p$-wave pairing state. Substitution of Ca for Sr significantly distorts the lattice structure and lowers the crystal symmetry from cubic to orthorhombic, giving rise to remarkable changes in magnetic, electronic, and structural properties. The ground state of Ca$_2$RuO$_4$ is antiferromagnetic (AF) insulating with a Fano profile observed in the Raman response. In La$_2$-$\delta$Sr$_\delta$CuO$_4$, an increase of Sr concentration causes the appearance of an asymmetric phonon lineshape and a dramatic decrease of the phonon intensity associated with the apical oxygen vibration, indicating that the electron-phonon interaction is also important in this material. Inelastic neutron scattering and x-ray scattering studies have suggested the presence of orbital fluctuations in LaTiO$_3$. As described in Ref. 21, an electronic continuum and anomalous phonon behavior with a Fano profile observed in the Raman response of $RTiO_3$ ($R=$ rare earth) may also indicate the presence of orbital fluctuations in the insulating region of this system. Therefore, it is of great interest to study how spin, charge, orbital, and lattice correlations evolve in Ca$_2$RuO$_4$ through different phase transitions, particularly as a means of comparing the exotic properties of this system to those of complex oxides such as the cuprates, manganites, and titanates. In this paper, we use the unique strengths of Raman scattering to explore lattice dynamics and the electron-phonon interaction in Ca$_2$RuO$_4$ as a function of temperature between 10 K and...
TABLE I: Site symmetries and IR’s of the atoms in Ca$_2$RuO$_4$ with space group Pbca–D$_{2h}^{15}$. Mode classifications are: $\Gamma_{\text{Raman}}$ = 9 ($A_g + B_{1g} + B_{2g} + B_{3g}$), $\Gamma_{\text{infrared}}$ = 11 (B$_{1u}$ + B$_{2u}$ + B$_{3u}$), $\Gamma_{\text{silent}}$ = 12 A$_u$, and $\Gamma_{\text{acoustic}}$ = B$_{1u}$ + B$_{2u}$ + B$_{3u}$. The corresponding polarization tensor elements for each of the Raman-active factor group species are: $A_g$ → $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$; $B_{1g}$ → $\alpha_{xy}, \alpha_{yx}$; $B_{2g}$ → $\alpha_{xz}, \alpha_{zx}$; and $B_{3g}$ → $\alpha_{yz}, \alpha_{zy}$.

| Atom | Site symmetry | IR’s |
|------|---------------|------|
| Ru   | C$_1$         | 3 (A$_u$ + B$_{1u}$ + B$_{2u}$ + B$_{3u}$) |
| Ca   | C$_1$         | 3 (A$_g$ + B$_{1g}$ + B$_{2g}$ + B$_{3g}$ + A$_u$ + B$_{1u}$ + B$_{2u}$ + B$_{3u}$) |
| O(1) | C$_1$         | 3 (A$_g$ + B$_{1g}$ + B$_{2g}$ + B$_{3g}$ + A$_u$ + B$_{1u}$ + B$_{2u}$ + B$_{3u}$) |
| O(2) | C$_1$         | 3 (A$_g$ + B$_{1g}$ + B$_{2g}$ + B$_{3g}$ + A$_u$ + B$_{1u}$ + B$_{2u}$ + B$_{3u}$) |

300 K.

II. EXPERIMENT

A single-crystal sample of Ca$_2$RuO$_4$, which was grown by a floating-zone method, was mounted inside a continuous He-flow cryostat. The 647.1-nm excitation wavelength from a Kr-ion laser was used in a backscattering geometry with the propagation vector ($\mathbf{k}$) oriented along the c axis of the sample, $\mathbf{k} \parallel c$-axis. Scattered light from the sample was dispersed using a triple-stage spectrometer, and then recorded using a liquid-nitrogen-cooled charge-coupled device (CCD) detector. Various polarization configurations of the incident and scattered light were employed in order to identify the scattering symmetries of the Raman spectra obtained for Ca$_2$RuO$_4$: ($\mathbf{E}_i$, $\mathbf{E}_s$) = (x, y), B$_{1g}$ symmetry; ($\mathbf{E}_i$, $\mathbf{E}_s$) = (x, x), A$_g$ symmetry; and ($\mathbf{E}_i$, $\mathbf{E}_s$) = (x’, x’), B$_{1g}$ + A$_g$ symmetry, where $\mathbf{E}_i$ and $\mathbf{E}_s$ are the incident and the scattered polarization directions, respectively. B$_{1g}$ and A$_g$ are irreducible representations (IR’s) of the space group D$_{2h}$, and x | [1,0,0], y | [0,1,0], and x’ | [1,1,0]. All the Raman spectra were corrected, first, by removing the CCD dark current response, and second, by normalizing the spectrometer response using a calibrated white light source. Finally, the corrected spectra were divided by the Bose thermal factor, giving rise to the spectral responses displayed in this paper. These responses are proportional to the imaginary part of the Raman susceptibility.

III. RESULTS AND DISCUSSION

Ca$_2$RuO$_4$ has an orthorhombic crystal structure (space group Pbca–D$_{2h}^{15}$) with four formula units per unit cell. A factor-group analysis, summarized in Table I, yields a total of 81 Γ-point phonons, of which 36 [9 (A$_g$ + B$_{1g}$ + B$_{2g}$ + B$_{3g}$)] are Raman-active modes involving Ca, in-plane oxygen [O(1)], and apical oxygen [O(2)] ions, 33 [11 (B$_{1u}$ + B$_{2u}$ + B$_{3u}$)] are infrared-active modes, and 12 (12 A$_u$) are silent modes. The Ru ions are located at a center of inversion symmetry and, thus, do not participate in any Raman-active phonon modes. Unlike tetragonal Sr$_2$RuO$_4$, in which 2 A$_{1g}$ and 2 E$_g$ symmetry optical phonons are Raman-active, orthorhombic Ca$_2$RuO$_4$ exhibits numerous phonon lines. This reflects the fact that substitution of Ca for Sr strongly distorts the RuO$_6$ octahedra, causing a rotation of the octahedra around the c axis, and a tilt of the octahedra around an axis on the RuO$_2$ plane. As shown in Fig. 1, polarized Raman spectra in a backscattering geometry (with the propagation vector $\mathbf{k} \parallel c$-axis) reveal all of the phonon modes corresponding to each of scattering symmetries: 9 B$_{1g}$ symmetry modes in ($\mathbf{E}_i$, $\mathbf{E}_s$) = (x, y), 9 A$_g$ symmetry modes in ($\mathbf{E}_i$, $\mathbf{E}_s$) = (x, x), and 9 B$_{1g}$ + 9 A$_g$ symmetry modes in ($\mathbf{E}_i$, $\mathbf{E}_s$) = (x’, x’) polarization configurations, respectively. Note in the inset of Fig. 1 that the B$_{1g}$ phonon peak energies assigned at 265 and 269 cm$^{-1}$ are clearly resolved in a high-resolution Raman spectrum. More specific assignments of the observed optical phonons to particular atomic normal modes will require lattice dynamic...
In order to elucidate the temperature-dependence of the lattice parameters and the electron-phonon interaction below $T_{MI}$, both $B_{1g}$ and $A_g$ symmetry Raman spectra from Ca$_2$RuO$_4$ were studied as a function of increasing temperature from 10 to 300 K, as summarized in Figs. 2(a) and 2(b). There are several key features observed in the Raman spectra as a function of increasing temperature, including (i) a softening of all the $B_{1g}$ and the $A_g$ optical phonon energies, (ii) a decrease of phonon spectral weights, and (iii) a significant broadening and increased asymmetry of phonon lineshapes across $T_N$.

The systematic shifts of phonon peaks to lower energies with increasing temperature through $T_N$ primarily reflect an elongation of the RuO$_6$ octahedra along the $c$ axis. Figures 3(a) to 3(f) summarize the phonon energy changes with increasing temperature for some representative $B_{1g}$ (140, 215, 388, and 459 cm$^{-1}$) and $A_g$ (126 and 607 cm$^{-1}$) optical phonon modes. The phonon-
energy shifts are negligible for $T < T_N$, indicating little or no change in the lattice parameters in this temperature regime. In contrast, remarkable phonon-energy shifts are observed for $T > T_N$. Most of phonon modes display downward shifts of $\sim 15 \text{ cm}^{-1}$ as temperature is raised from 10 to 300 K. Interestingly, the $B_{1g}$ phonon at 215 cm$^{-1}$ shows a much more dramatic energy shift of $\sim 30 \text{ cm}^{-1}$. These Raman results are consistent with neutron scattering measurements, which show that there is little change in the lattice parameters for $T < T_N$, but that there is a significant change in the lattice parameters for $T_N < T \sim T_{\text{MI}}$. All the other $B_{1g}$ and $A_g$ optical phonons decrease in energy with increasing temperature. Note that all the $B_{1g}$ phonon modes exhibit a dramatic decrease in intensity as temperature is raised toward $T_{\text{MI}} (∼ 357 \text{ K})$, possibly reflecting increased damping of the modes by thermally activated carriers.

One notes in Figs. 2(a) and 2(b) that the $B_{1g}$ and the $A_g$ phonon lineshapes at low temperatures for $T < T_N$ are quite symmetric and narrow. In contrast, with increasing temperature through $T_N$, the phonon linewidths broaden significantly and the lineshapes become increasingly asymmetric. The latter reveals a Fano effect, caused by the interaction between the discrete phonon state and a broad electronic continuum of states. Similar behavior has been observed in Raman spectra of numerous other strongly correlated materials such as Ca$_2$RuO$_4$, La$_1-x$Ca$_x$MnO$_3$, Ca$_3$Ru$_2$O$_7$, Sr$_2$RuO$_4$, and RTiO$_3$ ($R = \text{rare earth}$).

To study the temperature dependence of the electron-phonon interaction in Ca$_2$RuO$_4$ in detail, the temperature-dependence of the phonon linewidths and asymmetries of the $B_{1g}$ and $A_g$ phonon modes were extracted by fitting these modes to a Fano lineshape, $I(\omega) = I_0(q + \epsilon)^2/(1 + \epsilon^2)$, where $\epsilon = (\omega - \omega_0)/\Gamma$, $\omega_0$ is the phonon energy, $\Gamma$ is the effective phonon linewidth, and $q$ is the asymmetry parameter. In this way, one obtains information on the electron-phonon interaction. The inverse of the asymmetry parameter, $1/|q|$, is proportional to the electron-phonon coupling strength $V$ and the imaginary part of the electronic susceptibility $\rho$ according to $1/q \sim V\rho$. Moreover, the electron-phonon coupling contribution to the phonon linewidth can be estimated from the fractional change in the phonon damping rate below $T_{\text{MI}}$, $\Gamma(T) - \Gamma(RT))/\omega_0 = \Delta\Gamma/\omega_0 \propto N(0)V\rho\lambda$, where $N(0)$ is the electronic density of states at the Fermi surface, $\omega_0$ is the phonon energy, and $\lambda$ is the dimensionless electron-phonon coupling parameter. The parameter $\lambda$ is related to the BCS parameter $N(0)V_{\text{ph}}$, where $V_{\text{ph}}$ is the pairing potential arising from the electron-phonon interaction. Therefore, by carefully monitoring the phonon linewidths, as well as the inverse asymmetry parameters, as a function of temperature, one can obtain useful information regarding the evolution of the electronic density of states and the electron-phonon coupling strengths in Ca$_2$RuO$_4$.

The role of the electronic contribution to the system above $T_N$, which influences the substantial phonon energy renormalizations observed above $T_N$, can be explored by plotting as a function of temperature the phonon linewidth changes divided by the corresponding phonon energy at $T = 10 \text{ K}$, $\Delta\Gamma/\omega(10 \text{ K})$, as a function of temperature normalized to $T_N$. The plots are displayed in Fig. 4(a). Interestingly, in contrast to the negligible change in phonon linewidths observed below $T_N$, there is significant broadening in the phonon linewidths above $T_N$. For example, the phonon linewidths at 300 K are significantly broader than those at 10 K, $\Delta\Gamma/\omega_0 \sim 5.3 \%$, which is even larger than the fractional broadening observed in the correlation gap material FeSi, $\Delta\Gamma/\omega_0 \sim 3.5 \%$. We attribute the systematic broadening of the phonon linewidths with increasing temperature above $T_N$ to an increase of the effective number of electrons in the system for $T > T_N$. Indeed, Jung et al. recently reported that the effective number of electrons systematically increases, and the optical gap closes, with increasing temperature above $T_N$ in Ca$_2$RuO$_4$. 

![FIG. 4: (a) Phonon linewidth changes divided by the corresponding phonon energy at $T = 10 \text{ K}$, $\Delta\Gamma/\omega(10 \text{ K})$, as a function of temperature normalized to $T_N$. (b) Magnitudes of inverse of the asymmetry parameters, $1/|q|$, as a function of temperature normalized to $T_N$.](image-url)
The evolution of the electron-phonon interaction in Ca$_2$RuO$_4$ can be carefully illustrated by plotting the inverse of the asymmetry parameter, $1/|q|$, for different modes as a function of temperature, as shown in Fig. 4(b). Note that the magnitudes of the inverse asymmetry parameters, $1/|q|$, which are obtained from the representative B$_1g$ and the A$_g$ phonon modes, are negligible at low temperatures, but increase significantly as temperature is raised through $T_N$. Even when the temperature is much lower than the MI transition temperature, there is no additional increase of the inverse asymmetry parameters for $T/N > ~1.2$. These results strongly suggest that the largest increase in the electron-phonon coupling strength occurs near $T_N$, rather than near $T_{MI}$. By contrast, between $x = 0.45$ and 0.76 in La$_{1-x}$Ca$_x$MnO$_3$, the $1/|q|$ value decreases linearly with increasing $x$ in the ferromagnetic low-temperature metallic region ($x \leq 0.52$), and vanishes in the AF region (for $x > 0.52$)\textsuperscript{14} Note also that the magnitudes of the inverse asymmetry parameters, $1/|q|$, in the PM insulating region of Ca$_2$RuO$_4$ for $T_N < T < T_{MI}$ are comparable to those in the metallic region of Sr$_2$RuO$_4$ (Ref. 29) and La$_{1-x}$Ca$_x$MnO$_3$.\textsuperscript{27,27}

It is interesting to note that previous Raman results on Ca$_{2-x}$Sr$_x$RuO$_4$ have revealed that substitution of Sr for Ca increases the electron-phonon coupling strength, as evidenced by an increase of both the inverse asymmetry parameters and the phonon linewidths with Sr substitution at $T = 10$ K.\textsuperscript{27} Moreover, for the Sr-substituted samples ($x = 0.06$ and 0.09), a charge gap observed at 10 K was found to close well below the MI transition temperature, suggesting that the intermediate temperature regime $T_N$ and $T_{MI}$ consists of a coexistence of insulating S-Pbca and metallic L-Pbca phases.\textsuperscript{22} In contrast, in this study, the broadening of phonon linewidths and the increase of the $1/|q|$ values upon heating through $T_N$ ($< T_{MI}$ in Ca$_2$RuO$_4$ are probably not attributable to the coexistence of metallic and insulating phases in this temperature regime for several reasons, including the high stoichiometry of the sample, and the absence of any residual low frequency conductivity in Ca$_2$RuO$_4$ in the temperature regime $T_N < T < T_{MI}$.\textsuperscript{54}

In Ca$_2$RuO$_4$, the observed increase in both the electron-phonon coupling strength and the number of effective carriers with increasing temperature near $T_N$ strongly suggests that enhanced orbital fluctuations, which are associated with increased electron transfer between the $d_{xy}$ and $d_{xz/yz}$ orbitals, are responsible for the behavior observed in this temperature regime. Indeed, a recent O 1s x-ray absorption spectroscopy study of Ca$_{2-x}$Sr$_x$RuO$_4$ ($x = 0.0$ and 0.09) has suggested that orbital fluctuations gradually increase upon heating even in the insulating region well below $T_{MI}$. Note that the inverse asymmetry parameters and the spectral linewidths for the phonon mode near 300 cm$^{-1}$ in the insulating R$TiO_3$ ($R = Gd, Sm, Nd, Pr, Ce, La$) exhibit the largest values in La$_2$TiO$_4$,\textsuperscript{22} suggesting that orbital fluctuations are important in LaTiO$_3$, as pointed out by Keimer et al.\textsuperscript{22}

IV. CONCLUSIONS

In summary, temperature-dependent Raman spectra of Ca$_2$RuO$_4$ allow us to explore the lattice dynamics near the MI transition temperature of this system. With increasing temperature through the Néel temperature, the B$_1g$ and the A$_g$ phonon modes exhibit a substantial shift to lower energies. Moreover, the phonons significantly broaden and exhibit increasingly asymmetric lineshapes upon heating in the vicinity of $T_N$. These results demonstrate that both the electron-phonon coupling strength and the effective number of electrons increase as temperature is raised through $T_N$, suggesting that orbital fluctuations are present in the PM insulating region in the temperature regime $T_N < T < T_{MI}$.

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1. Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J.G. Bednorz, and F. Lichtenberg, Nature (London) 372, 532 (1994).
2. S. Nakatsuji and Y. Maeno, Phys. Rev. Lett. 84, 2666 (2000); S. Nakatsuji and Y. Maeno, Phys. Rev. B 62, 6458 (2000).
3. T. Hotta and E. Dagotto, Phys. Rev. Lett. 88, 17201 (2002).
4. S. Nakatsuji, D. Hall, L. Balicas, Z. Fisk, K. Sugahara, M. Yoshioka, and Y. Maeno, Phys. Rev. Lett. 90, 137202 (2003).
5. V.I. Anisimov, I.A. Nekrasov, D.E. Kondakov, T.M. Rice, and M. Sigrist, Eur. Phys. J. B 25, 191 (2002).
6. J.S. Lee, Y.S. Lee, T.W. Noh, S.-J. Oh, J. Yu, S. Nakatsuji, H. Fukazawa, and Y. Maeno, Phys. Rev. Lett. 89, 257402 (2002).
7. J.H. Jung, Z. Fang, J.P. He, Y. Kaneko, Y. Okimoto, and Y. Tokura, Phys. Rev. Lett. 91, 56403 (2003).
