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Journal of RAMAN SPECTROSCOPY

Received: 17 July 2013 Revised: 21 November 2013 Accepted: 21 November 2013 Published online in Wiley Online Library: 18 December 2013

(wileyonlinelibrary.com) DOI 10.1002/jrs.4431

Raman scattering in the magnetically frustrated double perovskite Sr_2YRuO_6

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The spin correlations and excitations of the Sr_2YRuO_6 double perovskite are investigated by means of Raman scattering, complemented by synchrotron X-ray diffraction measurements. Anomalous softening of a breathing mode of the oxygen octahedra is observed below ~200 K, much above the long-range antiferromagnetic ordering temperature, $T_{N1} = 32$ K, due to a spin-phonon coupling mechanism in the presence of magnetic correlations. A diffusive Raman signal is also observed, possibly associated with spin excitations within magnetically correlated regions. Our results point to a characteristic energy and temperature scale of ~25 meV/200 K below which unusual behavior associated with magnetic correlations is observed in this material. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: magnetic correlations; spin-phonon coupling; double perovskites; magnetic frustration; X-ray diffraction

Introduction

In geometrically frustrated magnetic materials, competing interactions destabilize the long-range-ordered ground states, resulting in exotic magnetic ground states such as spin glasses, spin ices, or spin liquids.[1,2] Despite the continuous interest in this topic, frustration in the simplest three-dimensional frustrated geometry, namely the face-centered cubic (FCC) lattice with a network of spin tetrahedra, has not been intensively investigated. This is likely because the second nearest-neighbor interaction is relatively strong in most FCC magnets, releasing the frustration. The family of double perovskites, $A_2B'RuO_6$, where Ru and non-magnetic B' ions adopt an ordered arrangement, fulfill the condition for significant geometric frustration, because Ru spins are arranged in an FCC lattice, and second-neighbor exchange coupling tends to be rather small because of the large separation between the Ru magnetic ions.[3]

Sr_2YRuO_6 (SYRO) crystallizes in a monoclinic structure,[4,5] where Ru and Y atoms are located at the center of regular tilted oxygen octahedra (see inset of Fig. 1). Even in the presence of rotations of these octahedra due to steric effects, the Ru ions alone define a nearly perfect FCC lattice. In addition, the Ru^{5+} ions possess an orbitally inert t_{2g}^3 configuration under an octahedral environment. Despite such simplicity, a fairly rich magnetic phase diagram has been observed, with two transitions captured by specific heat.[6] A subsequent neutron study showed that below $T_{N2} = 24$ K, the Ru spins order in a type I antiferromagnetic structure.[4,5] Between T_{N2} and $T_{N1} = 32$ K, a partially ordered state is found, while a state without long-range order with marked two-dimensional correlations is found above T_{N1} up to ~200 K.[5]

Raman scattering is a powerful tool to investigate magnetic correlations and can probe both the magnetic excitations associated with such state and the phonon anomalies caused by the spin-phonon coupling.[7,8] This technique has been employed to investigate magnetically frustrated materials such as $ZnCr_2O_4$ [9] and RMn_2O_5,[10] among others. In this work, Raman scattering measurements were performed in SYRO, complemented by synchrotron X-ray powder diffraction (XPD) experiments. The anomalous phonon behavior associated with spin-phonon coupling was investigated, and a diffusive Raman signal presumably due to magnetic fluctuations was also observed. Our results are discussed in terms of the magnetic correlations revealed by a recent neutron-scattering investigation on this material.[5]

Experimental details

The polycrystalline SYRO sample was synthesized by the solid-state reaction method. Stoichiometric amounts of high-purity RuO_2, Y_2O_3, and $SrCO_3$ were ground together thoroughly in an agate mortar, placed in an alumina crucible, and fired first at 900 °C for 3 days in air, with two intermediate regrindings. The resulting powder was ground again, pressed into pellets, and heat treated in air at 1350 °C for 3 days. High-resolution synchrotron XPD experiments were performed on the XPD beamline of the Brazilian synchrotron light laboratory (LNLS),[11] using an incident beam with $\lambda = 1.2399$ Å and a Ge(111) analyzer crystal with a scintillation detector in the diffraction arm. For high-intensity synchrotron X-ray diffraction experiments, the XRD-2 beamline of LNLS was employed with $\lambda = 1.7701$ Å and a highly oriented pyrolitic graphite analyzer with a scintillation detector in the diffraction arm. In both diffraction setups, the powder SYRO

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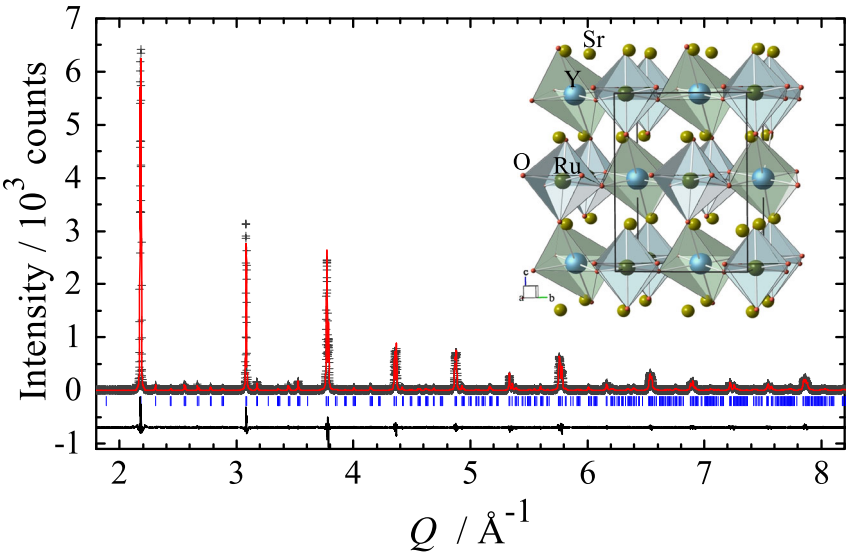

Figure 1. High-resolution synchrotron X-ray diffraction profile of Sr_2YRuO_6 at **T = 2** K (symbols). The calculated profiles as well as difference curves are given as solid lines. The short vertical lines in the bottom indicate the Bragg peak positions. The fitting residuals are $\mathbf{R_{wp}} = \mathbf{20.6}$%, $\mathbf{R_p} = \mathbf{13.1}$%, and $\chi^2 = \mathbf{1.91}$. The double perovskite structural model with **$P2_1/n$** space group is illustrated in the inset.

sample was mounted on the cold finger of a closed-cycle He cryostat in reflection ($\theta/2\theta$) geometry. Rietveld refinements were performed using the program GSAS + EXPGUI.[12] Raman scattering measurements were performed using a Jobin Yvon T64000 triple grating spectrometer (with 1800 g/mm gratings) equipped with a LN_2-cooled multichannel charge-coupled device detector. The Raman spectra were excited with the 488 nm Ar^+ laser line in a quasi-backscattering configuration. The incident laser power was kept below 12 mW focused into a spot of ~100 μm of diameter to avoid local heating. The *T*-dependent measurements were carried out by mounting the samples with fresh broken surfaces on a cold finger of a closed-cycle He refrigerator. The Raman measurement at 6 K was performed using a commercial superconducting optical magnetocryostat. All Raman spectra were corrected by the Bose–Einstein thermal population factor.

Results and analysis

X-ray diffraction

Figure 1 shows a high-resolution synchrotron XPD profile at 2 K. A monoclinic double perovskite phase of SYRO (space group $P2_1/n$) was successfully employed in the structure refinement. Intensities of impurity peaks are below 0.3% of the strongest peak of the major phase. Refined structural parameters at selected temperatures (2, 10, 25, 40, 200, and 295 K, not shown) are consistent with previous reports.[5,13] No structural phase transition associated with the magnetic transitions occurs between 2 and 300 K, a feature in line with previous reports.[5,13] High-intensity X-ray diffraction experiments were also performed for $0.3 < Q < 2.4$ Å^{-1} (not shown). No detectable X-ray scattering centered at $Q \sim 0.75$ Å^{-1} was observed between 20 and 300 K, strongly supporting the purely magnetic nature of the broad neutron-scattering signal seen at this position between 25 and 300 K.[5] In fact, the detection level in this X-ray diffraction experiment is 0.02% of the intensity of the main peak, while the neutron signal at $Q \sim 0.75$ Å^{-1} is as strong as ~1% of the main peak at 40 K.[5]

Raman scattering

Figure 2(a) displays the Raman spectra of SYRO at selected temperatures. The spectrum is dominated by two pronounced peaks at relatively high wavenumbers, 572 and 770 cm^{-1}, which are characteristic of double perovskites.[15–17] The high-wavenumber mode at 770 cm^{-1} is assigned to a symmetric stretching vibration of the oxygen octahedra, while the other strong mode, at 570 cm^{-1}, is associated with oxygen anti-stretching and/or bending vibrations. In addition, a number of weak modes are observed at 109, 166, 215, 237, 384, 397, 430, 656, and 741 cm^{-1}, less than the 24 expected Raman active modes for the crystal structure of SYRO ($\Gamma_{Raman} = 12A_g + 12B_g$). Finally, broad modes at high wavenumber associated with multi-phonon Raman scattering are observed at 852, 974, 1005, 1170, 1320, and 1490 cm^{-1}. Similar high-wavenumber modes were also observed by Rao and coworkers using 514.5 nm excitation line.[18]

The wavenumber and linewidth of the two main peaks at 572 and 770 cm^{-1} as a function of temperature are plotted in Fig. 2 (b) and 2(c), respectively. The solid curves represent the expected behavior of the anharmonic phonon–phonon interaction.[14] The error bars are statistics and refer to the standard deviation obtained by fitting the experimental curve with a Lorentzian curve. An anomalous softening of the 770 cm^{-1} mode wavenumber is seen on cooling below a characteristic temperature T^* ~200 K, well above the magnetic ordering temperatures, T_{N1} ~32 K. Temperature dependence of the obtained linewidths of the selected modes shows no significant anomaly in the measured temperature interval, within our experimental resolution (see right panels of Fig. 2(b)–(c)).

Figure 3(a) shows the temperature dependence of the Raman spectra in the low-wavenumber region, obtained by correcting the intensities by the Bose–Einstein population factor. A broad diffusive signal below 250 cm^{-1} emerges for $T < T^*$, which seems to be another manifestation of the magnetically correlated state below T^*. The strong diffusive signal of the low-wavenumber scattering at low temperatures can also be an artifact effect as, for example, a frost layer formed on the sample. In order to

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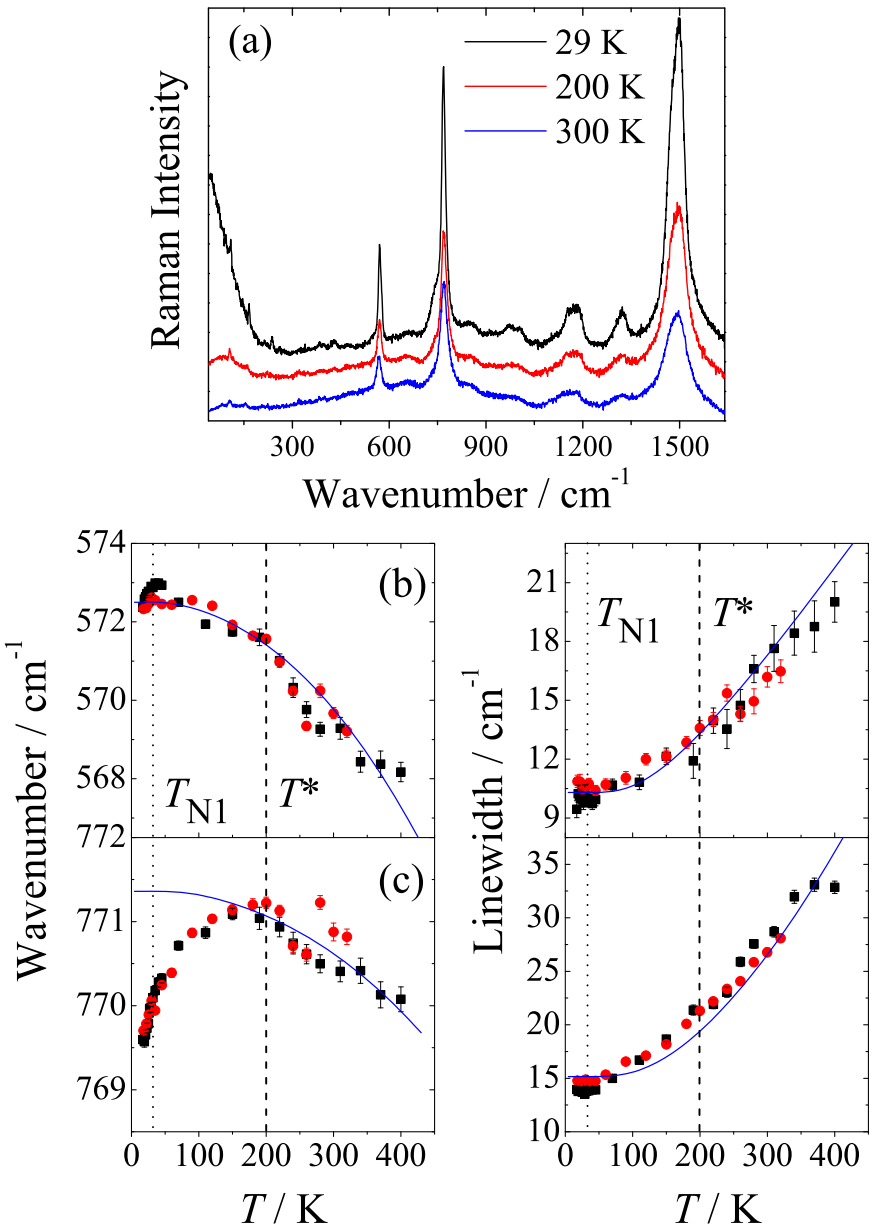

Figure 2. (a) Raman spectra of Sr_2YRuO_6 at three selected temperatures. Raman spectra were translated vertically for better visualization. (b)–(c) Temperature dependence of the wavenumber and linewidth of the selected Raman modes of Sr_2YRuO_6. The plots show the fits for two different Raman measurements. The solid curves represent the behavior of the normal phonon–phonon scattering.[14] The vertical dashed lines mark $\mathbf{T}^*$ ~200 K below which anomalous behavior is observed in the 770 cm^{-1} mode, while the vertical dotted lines represent the AFM partial ordering temperature, $\mathbf{T_{N1}} = \mathbf{32}$ K.[5]

discard this, temperature variations of the Raman spectra were made (Fig. 3(b)), where measurements were taken with cooling starting from room temperature and with warmed starting from the lowest temperature after cooling, obtaining similar behavior as in Fig. 3(a) for selected temperatures.

Discussion

Recently, a neutron diffraction study in SYRO reported two-dimensional magnetic correlations between frustrated Ru moments below ~ 200 K.[5] This suggests a magnetic origin for the anomalous phonon softening found by Raman scattering below the same characteristic temperature (Fig. 2(c)). The nearest-neighbor Ru–O–O–Ru superexchange is the only significant magnetic interaction in this material.[4,3,19] From all this, we can interpret the anomalous softening of the stretching mode in terms of the spin-phonon coupling in this material. The phonon renormalization may be associated with the modulation of the magnetic energy of the system by the lattice vibrations.[7,8] In fact, the optical phonon acts as a local probe to short-range magnetic correlations, because the anomalous phonon softening or hardening is proportional to the spin correlation function, $\rightarrow S_i \cdot \rightarrow S_j$. Our result in Fig. 2(c) supports the scenario of significant magnetic correlations at temperatures much above the long-range ordering temperature T_{N1}, being in accordance with the inherent geometric magnetic frustration of this material and consistent with the previous neutron-scattering study.[5]

The observed diffusive signal (Fig. 3) may be ascribed to spin excitations within the spin correlated layers that develop below ~ 200 K.[5] It is interesting to note that no significant modification

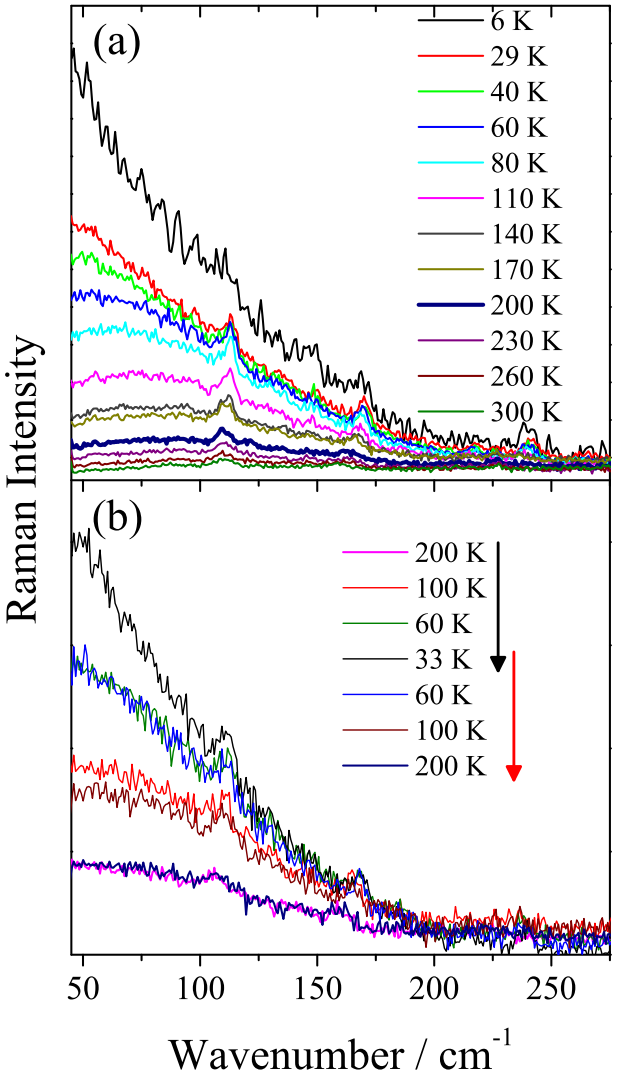

Figure 3. (a) Temperature dependence of the low-wavenumber Raman spectra of Sr_2YRuO_6. The spectral weight shows a pronounced temperature evolution on cooling below ~200 K. (b) Temperature variations of the Raman spectra where measurements were taken with cooling starting from room temperature (black arrow) and with warmed starting from the lowest temperature after cooling (red arrow) for four selected temperatures.

of this signal is observed through the long-range ordering temperature, suggesting that the high-energy spin excitations observed in the energy scale of our Raman experiment are insensitive to the three-dimensional long-range order.

Conclusions

In summary, Raman scattering measurements were performed in high-quality SYRO double perovskite ceramic samples, as verified by high-resolution X-ray diffraction. A renormalization of the symmetric stretching mode of the oxygen octahedra is observed below a characteristic temperature ~200 K, which is ascribed to a spin-phonon coupling mechanism in a scenario of strong Ru–Ru two-dimensional magnetic correlations. Also, a remarkable low-wavenumber Raman scattering structure response was observed below ~ 200 K, which is attributed to dynamic spin excitations within the correlated magnetic layers.

Acknowledgements

This work was supported by CAPES, CNPq, and Fapesp, Brazil.

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