Phonon dynamics of the geometrically frustrated pyrochlore $Y_2Ru_2O_7$ investigated by Raman spectroscopy

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We investigate temperature-dependent Raman spectra of the geometrically frustrated pyrochlore $Y_2Ru_2O_7$, which shows a spin-glass-like transition at $T_G \sim 80$ K. Three discernable phonons appear around 315, 410, and 510 cm^{-1} without any abrupt change in the number of Raman-active modes within the temperature range of 10–300 K. Fitting each phonon with Lorentz oscillators, we examine the effects of temperature on phonon dynamics, in terms of the phonon frequency and the linewidth. The temperature dependence of the mode near 510 cm^{-1} shows abnormal behavior below T_G, while the other two phonons follow the usual thermal effect. This behavior can be understood in terms of spin-phonon coupling. Considering the atomic modulations of the phonon mode showing abnormal behavior, the 510-cm^{-1} phonon mode is isotropically coupled to the spin degree of freedom, while the other modes are not.

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I. INTRODUCTION

Recently, considerable effort has been devoted to study compounds with pyrochlore structure to find out intriguing properties connected with their geometrically frustrated spin configurations.[1–3] In the pyrochlore compound, $A_2B_2O_7$, it is difficult for magnetic moments to order antiferromagnetically since magnetic atoms at A or B sites compose a tetragonal unit. Nevertheless, pyrochlore $Y_2Ru_2O_7$ has many signatures with an antiferromagnetic ordering or a strong antiferromagnetic correlation.[4,5]

Our previous research on the infrared-active phonon modes of$Y_2Ru_2O_7$ demonstrated plentiful evidences on strong spin-phonon coupling.[5] Among seven infrared-active phonon modes, while three phonon modes exhibit normal temperature (T) dependences, the other four modes exhibit strong anomalies below the spin-glass-like transition temperature $T_G \sim 80$ K.[6] We suggested that the strong spin-phonon coupling effect should play a crucial role in the intriguing magnetic state of this compound. However, to understand the spin-phonon coupling mechanism on pyrochlore $Y_2Ru_2O_7$ more thoroughly, we should give an appropriate answer to the question why only specific phonons are involved in the anomaly of phonon dynamics in the spin-glass-like ground state below T_G.

Raman spectroscopy has been widely used in investigating the spin-phonon coupling effect in various magnetic compounds.[7–9] For example, Chen *et al.* investigated Raman spectra of cupric oxide both above and below the Néel temperature. They observed that a zone-folded phonon mode shifted to higher frequency under the Néel temperature. They interpreted an unusual large shift in frequency as an effect of a strong spin-phonon interaction.[7] Recently, Granado *et al.* reported that a phonon mode of the pyrochlore manganites, $A_2Mn_2O_7$ (A=Tl, In, and Y) becomes hardened below a ferromagnetic transition temperature.[8] And they demonstrated that the blueshift of the phonon frequency could be well scaled with magnetization.

In this paper, we investigated T-dependent Raman spectra of the spin-frustrated $Y_2Ru_2O_7$ system in order to provide a microscopic model for the intriguing spin-phonon coupling in the compound. We observed three strong Raman-active phonon modes around 315, 410, 510 cm^{-1} and other weak peaks. By fitting the observed phonon peaks with the Lorentz oscillator function, we obtained T dependences of phonon frequency and linewidth for each phonon. The phonon around 510 cm^{-1} shows interesting T-dependent behavior below T_G, while other modes show typical thermal effects. Considering eigenvectors for each phonon mode, we propose that isotropic lattice modulation should be closely related to a specific spin configuration in the magnetic ground state of the geometrically frustrated $Y_2Ru_2O_7$ system.

II. EXPERIMENTAL WORK

High-density $Y_2Ru_2O_7$ polycrystals were synthesized at 3 GPa with a solid-state reaction method.[10] T-dependent Raman-scattering measurements were performed using a

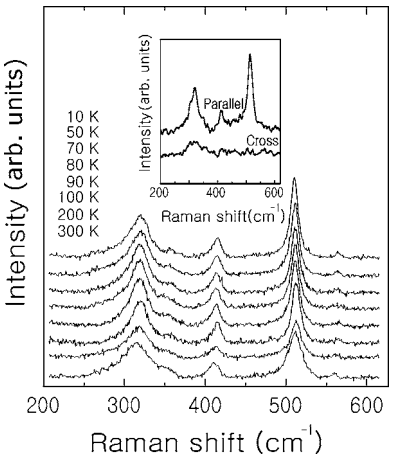

FIG. 1. T dependence of Raman spectra of $Y_2Ru_2O_7$. Three discernable peaks (315, 410, and 510 cm^{-1}) and small peaks (350 and 560 cm^{-1}) appear. The inset shows Raman spectra at 300 K in parallel and cross scattering geometries.

closed cycle He refrigerator and a Jobin Yvon T64000 spectrometer equipped with a nitrogen-cooled charge-coupled device detector. The 514.5-nm line of an Ar-ion laser was used as the excitation source in the back scattering geometry. The diameter and power of the beam spot on the sample surface were about 5 μm and less than 0.4 mW, respectively. We measured Raman spectra in various scattering geometries in order to assign the phonon modes. Polarizations of the incident and scattered light were chosen so that they are parallel (parallel) or perpendicular (cross) to each other. In actual experiments, the axis of the polarization analyzer for the scattered light is fixed, and the polarization of the incident light is rotated by a half wave plate depending on parallel or cross measurements.

III. RESULTS AND DISCUSSION

Figure 1 shows the T-dependent Raman spectra of $Y_2Ru_2O_7$ from 300 to 10 K. For clarity, we displayed the spectra with an upward baseline shift, with T decreasing from 300 to 10 K. Three discernable phonon modes are observed around 315, 410, and 510 cm^{-1}. Additionally, two weak phonons seem to appear around 350 and 560 cm^{-1}. A broad hump near 680 cm^{-1} is not distinguishable for $Y_2Ru_2O_7$, while it becomes stronger as Bi is doped in $Y_{2-x}Bi_xRu_2O_7$ system.[11] It should be noted that no additional peak appears below T_G, which indicates that there is no abrupt change in the structural symmetry at T_G, in agreement with the neutron scattering and infrared phonon data.[4,5]

These observed phonon modes are well consistent with the results of the factor group analysis (FGA) predicting six Raman-active modes for the cubic pyrochlore with a space group $Fd3m$,[12] i.e.,

$$\Gamma(\text{Raman}) = A_{1g} + E_g + 4F_{2g}. \tag{1}$$

The inset of Fig. 1 shows Raman spectra of parallel and cross measurements at 300 K. The 510-cm^{-1} mode in cross geometry is much more suppressed than the other modes indicating that it is of A_{1g} character. Moreover, comparing the polarized Raman spectra of $Y_2Ru_2O_7$ with previous Raman results on other pyrochlore oxides, it is reasonable to assign the 510-cm^{-1} mode as an A_{1g} mode.[8,13]

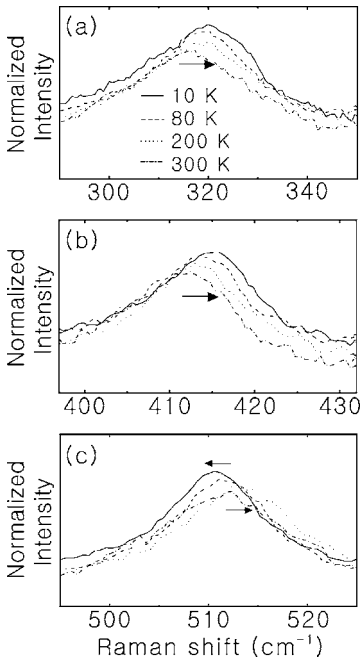

FIG. 2. T dependence of each phonon mode. (a), (b), and (c) show T dependence of the phonon mode near 315, 410, and 510 cm^{-1}, respectively. In each figure, the spectra from top to bottom are shown for temperatures of 10 (solid line), 80 (dashed line), 200 (dotted line), and 300 K (dash dotted line). For clarity, the Raman spectra are displaced with upward baseline shifts, as T decreases from 300 to 10 K.

Figures 2(a)–2(c) show the T dependences of the phonon modes around 315, 410, and 510 cm^{-1}, respectively. The intensities of Raman spectra were normalized by dividing the measured spectrum by its maximum. We notice that the mode near 510 cm^{-1} and the modes near 315 and 410 cm^{-1} show different T dependences.As T decreases, the latter two phonons show gradual blueshifts down to 10 K. On the other hand, the 510-cm^{-1} phonon mode shows a red shift below around T_G ($\sim$80 K), while it exhibits a similar blueshift down to 100 K.

In order to address the T-dependent phonon dynamics in detail, we analyzed the Raman spectra by fitting with a series of Lorentz oscillators of the spectral response,

$$S(\omega) = [1 + n(\omega)] \sum_i \frac{A_i \Gamma_i \omega}{(\omega^2 - \omega_i^2)^2 + \Gamma_i^2 \omega^2} \tag{2}$$

where ω_i, Γ_i, and A_i represent the frequency, linewidth, and amplitude of the ith phonon mode, respectively. The quantity $[1+n(\omega)]$ is the Bose-Einstein thermal factor. Figure 3 shows the T dependences of the fitted values of the Raman frequency and the linewidth of each phonon mode. We evaluated (a) $\Delta\omega = \omega(T) - \omega$ (0 K) and (b) $\Delta\Gamma/\Gamma$ (300 K) $= [\Gamma(T) - \Gamma(300\text{ K})]/\Gamma$ (300 K). All three phonons shift to higher frequencies and their linewidths become narrower as

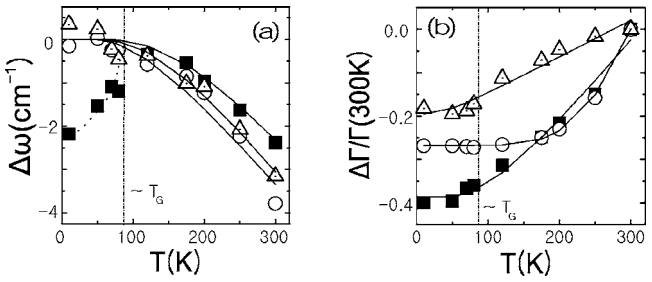

FIG. 3. T dependences of (a) frequencies in $\Delta\omega=\omega(T)-\omega(0\ K)$ and (b) linewidths in $\Delta\Gamma/\Gamma(300\ K)=[\Gamma(T)-\Gamma(300K)]/\Gamma(300\ K)$ of the three phonon modes. Empty circles, triangles, and solid squares indicate data for the 315, 410, and 510 cm^{-1} phonon mode, respectively. The thin solid lines are results of the fitting taking into account the temperature-induced anharmonicity and the dotted line is a guide to the eye only.

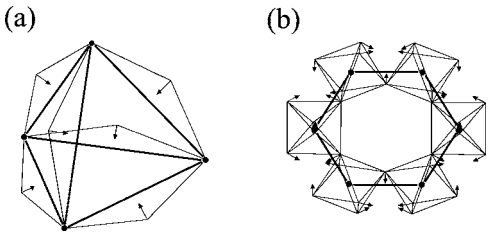

FIG. 4. Atomic displacement for the 510-cm^{-1} phonon mode related to (a) the tetrahedron and (b) the hexagon of the Ru^{4+} ions. Bold dots indicate the magnetic Ru^{4+} ions. The root of each arrow corresponds to the position of the O ion at the equilibrium state, and the arrows indicate the direction in which the O ions should move. With these displacements of the O ions, all of the Ru-O-Ru bond angles should be larger than θ_0, and the antiferromagnetic interaction between the magnetic Ru^{4+} ions becomes stronger, which is indicated by the bold solid line in each figure.

Tdecreases down to around T_G. However, going down below T_G, the peak frequency of the mode near 510 cm^{-1} drops abruptly around T_G.

The temperature-induced anharmonicity gives rise to shifts in the phonon frequency and changes in linewidth,[14]

$$\omega_T=\omega_T^0+A\left(1+\frac{2}{e^{\hbar\omega_0/2k_BT}-1}\right) \tag{3}$$

and

$$\Gamma=\Gamma^0+B\left(1+\frac{2}{e^{\hbar\omega_0/2k_BT}-1}\right), \tag{4}$$

where ω_T^0 and Γ^0 are the intrinsic frequency of the optical mode and the line broadening due to defect, respectively. A and B are the anharmonic coefficients, and $1/(e^{\hbar\omega_0/2k_BT}-1)$ corresponds to the thermal population factor of the acoustic modes.

For the phonon modes around 315 and 410 cm^{-1}, their T dependences could be well explained in terms of the usual thermal effect.[14] As T decreases, the anharmonic thermal motion should decrease, so it leads to the decrease of the lattice constants. Then the lattice vibration costs more energy, resulting in shift to higher phonon frequencies. Decrease of the anharmonic thermal motion should also make the linewidths of phonons narrower.[15] On the other hand, the T dependences of the 510-cm^{-1} mode cannot be simply understood in terms of the thermal effect. Since the phonon anomalies occur near the magnetic transition T, i.e., T_G, we suppose that they should be closely related to the coupling between the lattice and the spin degrees of freedom.[5]

It should be noted that these phonon anomalies near T_G are similar to those for some infrared-active phonon modes. In our previous infrared phonon study,[5] we proposed that a decrease of several phonon frequencies below T_G would be a clear evidence of a strong spin-phonon coupling effect. If an ion is displaced by x from an equilibrium position, the crystal potential is given by $U=\frac{1}{2}kx^2+\Sigma_{i,j}J_{ij}(x)\vec{S}_i\cdot\vec{S}_j$. Here, k is the force constant. The latter term is from the exchange interaction. The exchange energy constant $J_{ij}(x)$ depends on the structural parameters, such as the lengths between the Ru^{4+} magnetic ions and the Ru-O-Ru angles. Its second derivative, $\partial^2U/\partial x^2=k+\Sigma_{i,j}(\partial^2J_{ij}/\partial x^2)\langle S_iS_j\rangle$, gives a harmonic force constant, where the second term represents spin-phonon coupling. As a result of such perturbation in the force constant, the Raman frequency can be affected by an additional contribution $\Delta\omega\equiv\lambda\langle S_iS_j\rangle$.[16] The spin-phonon coupling coefficient λ is different for different phonons, and can have either a positive or a negative sign.[7,9]

Our Raman results show that the magnetic ordering below T_G results in decrease of the frequency of the 510-cm^{-1} mode, meaning that the spin-phonon coupling interaction, i.e., $\lambda\langle S_iS_j\rangle$ is negative for this mode. The T-dependent value of $\langle S_iS_j\rangle$ can be evaluated from the integrated intensities of the neutron-scattering peaks of magnetic origin[4] as $\langle S_iS_j\rangle\simeq\frac{1}{4}$. As shown in Fig. 3(a), $\Delta\omega$ for the 510-cm^{-1} phonon mode is around 2 cm^{-1}. Since $\Delta\omega=\lambda\langle S_iS_j\rangle$, we estimate the value of λ for the 510-cm^{-1} mode as about 8 cm^{-1}, which is comparable to those of the infrared-active phonon modes[5] located around 420 and 490 cm^{-1}.

In order to get a more thorough understanding of the unusual behaviors of phonons near 510 cm^{-1}, we tried to compare the atomic displacements of each phonon mode based on the previous work.[13,17] We focus on the 510-cm^{-1} mode, which shows a distinct difference from the other two. We sketched atomic displacements of the 510-cm^{-1} mode and showed them in Fig. 4(a) in view of the tetrahedron of the Ru^{4+} ions, which is basically related to the geometrical frustration in the pyrochlore $Y_2Ru_2O_7$. Note that atomic modulations of Raman-active phonon modes are related to displacements of only O ions. Magnetic ions, Ru^{4+}, are marked by a bold dot and oxygen ions are located at the base of the arrows. The directions in which the O ions should move are indicated by the arrows. Extended atomic modulation and its corresponding Ru-O-Ru angle modulations are depicted in Fig. 4(b) in order to describe the Ru^{4+} hexagon more clearly. In the figure, each octahedron is RuO_6 on the $\langle 111\rangle$ plane, and oxygen atoms are at vertices of the octahedra. The 510-cm^{-1} mode shows in-phase change of all the Ru-O-Ru angle under the lattice modulation. For the other two modes, on the other hand, they have mixture of increase, decrease, and nonchange of the Ru-O-Ru angles resulting in small net change in the superexchange energy.[18]

In-phase changes of bond angles of the 510-cm^{-1} mode result in the modulation of the magnetic interaction in the spin ground state. We consider a superexchange interaction between magnetic Ru^{4+} ions mediated by O ions, which is very sensitive to the Ru-O-Ru angle. We paid attention to the modulations of the bond angle due to the O displacements. Let the Ru-O-Ru angle without any atomic displacement be θ_0 about 129°.[10] Bold solid lines connect two Ru^{4+} ions, of which the Ru-O-Ru bond angle is larger than θ_0 at a particular moment during the lattice vibration. Interestingly, the atomic displacements for the 510-cm^{-1} mode, depicted in Figs. 4(a) and 4(b), show in-phase increase and decrease of all the Ru-O-Ru angles under the lattice modulation. In-phase (isotropic) change in all the Ru-O-Ru angles results in a net change in the superexchange energy in the phonon around 510 cm^{-1}. Consequently, the isotropic change of superexchange interaction brings about spin-phonon coupling in the pyrochlore$Y_2Ru_2O_7$ system. This happens in the magnetic ground state of geometrical frustration with incomplete antiferromagnetic state.[4]

IV. CONCLUSION

We measured Raman spectra of $Y_2Ru_2O_7$ and observed intriguing temperature dependence for the phonon mode near 510 cm^{-1}, which shows an abrupt decrease of the peak frequency below the spin-glass-like transition temperature, T_G (~80 K). Considering that there appears no additional peak below T_G, the anomaly does not seem to be caused by a structural distortion. Rather, we discovered that the phonon mode around 510 cm^{-1} is coupled with the spin degree of freedom in the magnetic ground state below T_G. Only the 510-cm^{-1} mode has in-phase (isotropic) change in all the Ru-O-Ru angles, which results in net change in the superexchange energy. Our Raman results demonstrate that the magnetic phase transition experiences a coupling with an isotropic lattice modulation.

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