Symmetry of phonon, magnetic, and spin-phonon excitations in GdSr$_2$RuCu$_2$O$_8$ single crystals

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We present a polarized Raman scattering study of GdSr$_2$RuCu$_2$O$_8$ single crystals. In this compound, the RuO$_6$ octahedra are rotated around the c axis in turn gives some Raman activity of the oxygen (O$_{Ru}$) vibrations at 265 cm$^{-1}$ ($A_{1g}$), 411 cm$^{-1}$ ($B_{2g}$) and 607 cm$^{-1}$ ($B_{1g}$). These vibrations, as well as those of the apical oxygen of RuO$_6$ at 654 cm$^{-1}$ ($A_{1g}$) and the Cu-plane oxygen at 318 cm$^{-1}$ ($B_{1g}$), clearly respond to the onset of magnetic ordering at $T_m$=140 K. In particular, the 265 cm$^{-1}$ mode hardens anomalously with decreasing temperature below $T_m$. Notably, the corresponding phonon line is absent in the Raman spectra of GdSr$_2$NbCu$_2$O$_8$ (Nb$^{5+}$:4$d^1$), a compound isomorphic to GdSr$_2$RuCu$_2$O$_8$ (Ru$^{5+}$:4$d^1$). We argue that the eigenvector of the 265 cm$^{-1}$ phonon (rotational mode) facilitates efficient modulation of the $Ru_{(1g)}$-O$_{Ru}(p)$ bands. This modulation gives both Raman scattering strength to the 265 cm$^{-1}$ mode and strong spin-phonon coupling.

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I. INTRODUCTION

Recent studies of ruthenate-cuprates have demonstrated the rather peculiar properties of these materials. In particular, earlier suggestions that superconducting GdSr$_2$RuCu$_2$O$_8$ is also ferromagnetically ordered have been challenged by neutron powder diffraction experiments where no sign of ferromagnetism has been found. Instead, G-type antiferromagnetic (AFM) order of Ru moments has been evidenced below $T_m$=138 K. On the other hand, magnetic measurements of GdSr$_2$RuCu$_2$O$_8$ have clearly demonstrated spontaneous magnetization below $T_m$ that is, an existence of a ferromagnetic (FM) component of magnetic ordering. It is, however, unclear whether this ferromagnetic component stems from a canted AFM structure or spatially separated AFM and FM phases. It is believed that ferromagnetic excitations have also been detected by Raman spectroscopy as a magnonlike peak (hereafter called the magnetic peak) at $\sim$150 cm$^{-1}$. This peak has also been observed in other compounds closely related to GdSr$_2$RuCu$_2$O$_8$. The behavior of the position and intensity of the magnetic peak under applied magnetic field is similar to that one when decreasing the temperature, which gives further support to a ferromagnetic origin. The Raman intensity of the magnetic peak varies in different GdSr$_2$Ru$_x$Cu$_2$O$_8$ samples and can be very weak or even vanishing. The Raman response of GdSr$_2$Ru$_x$Cu$_2$O$_8$ seems to be strongly influenced by crystalline morphology that is featured with fine granularity, heavy twinning, a variety of domains, and domain boundaries. Interestingly, the Raman spectra of polycrystalline GdSr$_2$Ru$_x$Cu$_2$O$_8$ reported so far have been mostly unpolarized albeit micron-size grains were probed.

In this paper we present a Raman scattering study performed on nonsuperconducting GdSr$_2$RuCu$_2$O$_8$ single crystals. We measured the polarized Raman spectra of GdSr$_2$RuCu$_2$O$_8$ in several exact configurations that allowed us to determine the symmetries of the phonon and coupled spin-phonon excitations. For comparison, we also recorded the Raman spectra of isomorphic GdSr$_2$NbCu$_2$O$_8$. We find essential differences between the two compounds that reveal the unique role of Ru in formation of magnetic moments, ordering, and doping of GdSr$_2$RuCu$_2$O$_8$.

II. EXPERIMENT

In the Raman experiment, we measured small GdSr$_2$Ru$_x$Cu$_2$O$_8$ single crystals with rectangular faces of $\sim30\times30$ $\mu$m$^2$ in size, embedded in a matrix of reaction residuals. The crystals were grown from CuO flux. First, presintered powders of GdSr$_2$Ru$_x$Cu$_2$O$_8$ and CuO with a molar ratio of 3:7 were thoroughly mixed. The mixture was put into a 30-ml Pt crucible, placed in a muffle furnace, and heated up to 1150°C in air at a rate of 15°C/h to ensure a homogeneous melting, and held for 15 h. In addition, a polycrystalline GdSr$_2$NbCu$_2$O$_8$ sample was prepared by solid-state reaction of stoichiometric powders of NbO$_2$, SrCO$_3$, Gd$_2$O$_3$, and CuO as described in Ref. 5.

Figure 1 displays the results of magnetic measurements of GdSr$_2$Ru$_x$Cu$_2$O$_8$ sample consisting of a bunch of single crystals. The temperature dependence of magnetization reveals a relatively broad magnetic transition at $T_m$=140 K [defined as the inflection point of the field-cooled (FC) magnetization] and no indication of superconductivity at low temperatures. The increase of magnetization at very low temperatures is due to the antiferromagnetic ordering of Gd moments at 2.8 K. The deviation of FC magnetization from the zero-field cooled (ZFC) one persists up to 300 K, which may be due to minor phases between the crystals in the sample.
The Raman spectra were recorded using a notch-filter-equipped single-grating spectrometer with a liquid-nitrogen-cooled charge-coupled device detector. The 514.5-nm Ar⁺ ion laser line was used for excitation of the samples using a microprobe attachment with a ×50 objective for focusing the incoming beam on a spot of ≈2 μm in diameter and collecting the scattered light. The samples were attached to the cold finger of a helium microcryostat, held at different temperatures, and measured in backscattering geometry. The scattering configurations in the Porto notation \(i(k)l,m\), where \(i\) and \(m\) stand for the propagation direction of the incident and scattered photons, while \(k\) and \(l\) represent their polarization, respectively. The symbols \(x, y,\) and \(z\) denote directions parallel to the \(a, b,\) and \(c\) axes of the crystal, respectively, and \(x'\) and \(y'\) are two mutually orthogonal directions along \([110]\) and \([1 \bar{1} 0]\).

### III. EXPERIMENTAL RESULTS AND DISCUSSION

#### A. Symmetry analysis and lattice dynamics calculations

The crystal structure of GdSr₂RuCu₂O₈ can be derived from the tetragonal \((P4/mmm)\) GdBa₂Cu₃O₈ structure by substituting the basal plane Cu for Ru and Ba for Sr, and filling up the oxygen sites in the Ru plane. Thus formed RuO₆ octahedra (Ru, 4 O₉Ru, and two apical oxygen O₉ atoms) are rotated around the \(c\) axis by \(≈14°\) to match the in-plane Ru-O₉Ru bonds with the shorter Cu-O₉Cu ones in the CuO₂ planes. This rotation is facilitated by smaller ionic radius of Sr than that of Ba. The rotational displacements of O₉Ru lead to doubling of the unit cell and change of the space group according to \(P4/mmm(a,a,c) \rightarrow P4/mmbm(a,\sqrt{2}a,\sqrt{2}c)\), where \(a\) and \(c\) are the lattice constants.

The doubling of the unit cell increases the number of the Raman-active phonons from 10 \((4A₁g + B₂g + 5Eₙ, P4/mmm)\) to 22 \((6A₁g + 2B₁g + 4B₂g + 10Eₙ, P4/mmbm)\). The Raman intensity of the \(Eₙ\) phonons is usually very weak, and a doubling of the unit cell is expected to mostly add new lines of \(A₁g, B₁g,\) and \(B₂g\) symmetry in the Raman spectra. The additional two \(A₁g\) modes in the \(P4/mmbm\) structure correspond to rotational motion of the RuO₆ octahedra and the CuO₂ pyramids around the \(c\) axis, respectively. These modes should have vanishing frequency in \(P4/mmm\), that is, they are soft modes for the transition \(P4/mmm \rightarrow P4/mmbm\). We also note that this structural transition transforms the \(B₁g\) mode in \(P4/mmm\), that involves the out-of-phase vibrations of \(O_{Cu}\), to a \(B₂g\) mode in \(P4/mmbm\).

The \(\Gamma\)-point phonons were calculated using a shell model with model parameters taken from studies of a number of perovskite-like compounds. In this model the interionic interactions are described by long-range Coulomb potentials and short-range Born-Mayer potentials of the form \(V = a\exp(-br)-c/r^6\) with \(r\) being the interionic separation. The polarizability of the ions is accounted for in the dipole approximation representing each ion as a point-charged core surrounded it so that the free ionic polarizability \(\alpha\) is given by \(\alpha = Y^2/k\). The values of the shell model parameters used in the present calculation are given in Table I.

#### B. Phonons

In Fig. 2 we present the low-temperature Raman spectra of \((a)\) GdSr₂RuCu₂O₈ single crystals, measured for various scattering configurations, and \((b)\) polycrystalline GdSr₂NbCu₂O₈. The Raman selection rules for tetragonal groups assert that \(y'(zz')y'\) selects spectral components of \(A₁g\) symmetry, \(z'(xx')z'\) selects components of \(B₂g\) symmetry, \(z(xx)z\) selects components of \(A₁g\) symmetry. We assign the line at \(318\) cm⁻¹ to \(A₁g\) modes in \(P4/mmbm\). From Fig. 2(a) it follows that the excitations at \(158, 275, 439,\) and \(654\) cm⁻¹ are \(A₁g\) modes, those at \(318\) and \(439\) cm⁻¹ are \(A₁g\) modes, and the one at \(608\) cm⁻¹ is of \(B₁g\) symmetry. We assign the line at \(158\) cm⁻¹ to a superposition of the two \(A₁g\) modes involving Cu and Sr vibrations along the \(c\) axis. This assignment is consistent with the results of the lattice dynamical calculations given in Table II. Additional support is found in the spectrum in Fig. 2(b), where somewhat different interatomic distances in GdSr₂NbCu₂O₈ lead to better resolved separation of the Cu and Sr modes. The \(A₁g\) modes at \(318\) and \(439\) cm⁻¹ in Fig. 2(a) correspond to the out-of-phase and in-phase \(O_{Cu}\) vibrations along the \(c\) axis, respectively. The \(A₁g(O_{Cu})\) vibration appears at \(654\) cm⁻¹.

The three \(A₁g\) vibrations along the \(c\) axis in GdSr₂NbCu₂O₈ are easily identified in the spectrum in Fig.

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**TABLE I. Shell model parameters for GdSr₂RuCu₂O₈.**

| Ion | Z \((|e|\)) | \(\alpha(\text{Å}^3)\) | Ionic pair | \(a(\text{eV})\) | \(b(\text{Å}^{-1})\) | \(c(\text{eVÅ}^6)\) |
|-----|-------------|-----------------|------------|-------------|-------------|-------------|
| Ru  | 4.75        | 1.4             | 0.0        | Ru-O        | 3900        | 3.565       | 0           |
| Sr  | 1.90        | 3.0             | 2.5        | Sr-O        | 888         | 2.536       | 0           |
| Gd  | 2.85        | 1.7             | 0.7        | Gd-O        | 1631        | 2.854       | 0           |
| Cu  | 1.90        | 3.0             | 1.3        | Cu-O        | 1600        | 3.476       | 0           |
| O   | -1.90       | -3.0            | 3.0        | O-O         | 22764       | 6.711       | 20.37       |

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**FIG. 1.** Temperature dependence of magnetization of GdSr₂RuCu₂O₈ single crystals in zero-field cooled (ZFC) and field-cooled (FC at 2 Oe) regimes.
valence of the cation $Z$. A model for oxygen vibrations in cuprates gives that the square of the apical oxygen frequency mentally measured frequencies straightforward comparison gives that the ratio of experimentally observed frequencies and those predicted by lattice dynamical calculations. Four of the $A_{1g}$ modes and one $B_{2g}$ mode are clearly seen in the Raman spectra of both the Ru- and the Nb-based compounds. From Table II it follows that these modes include predominantly vibrations along the $c$ axis. On the other hand, the phonons at 275 ($A_{1g}$), 411 ($B_{2g}$) and 607 ($B_{1g}$) cm$^{-1}$ in the spectra of GdSr$_2$RuCu$_2$O$_8$ have no counterpart in the spectra of GdSr$_2$NbCu$_2$O$_8$. We note that all these phonons involve $O_{Ru}$ vibrations.

**C. Magnetic excitations**

An interesting Raman feature is the relatively broad peak at $\sim 150$ cm$^{-1}$ in the $z(xx)z$ and $z(x'x'')z$ spectra at 5 K in Fig. 2(a). This peak resembles the magnetic peak in GdSr$_2$RuCu$_2$O$_8$ reported in Refs. 6–8, but has much lower intensity. In addition, the spectral weight of the 150 cm$^{-1}$ peak rapidly decreases with increasing temperature, and we were not able to follow the temperature dependence previously observed$^{6–8}$ in polycrystalline samples. On the other hand, the shape and position of the 150 cm$^{-1}$ peak, as well as the fact that it appears below $T_m$, are much in favor of the magnetic peak assignment. Despite these uncertainties it is tempting to describe the peculiar symmetry properties of the 150 cm$^{-1}$ peak. From the spectra in Fig. 2(a) it follows that the magnetic peak in GdSr$_2$RuCu$_2$O$_8$ has $A_{1g}$ symmetry, a rather unusual symmetry for Raman-active magnetic excitations. Raman scattering from magnons proceeds predominantly through spin-orbit interaction. Creation of a magnon in the Raman process requires a spin-flip in the intermediate state that rotates the scattered light polarization by $90^\circ$, that is, magnons are usually seen for crossed incident and scattered light polarizations. The latter property excludes the $A_{1g}$

![FIG. 2. Polarized Raman spectra of (a) GdSr$_2$RuCu$_2$O$_8$ single crystals and (b) polycrystalline GdSr$_2$NbCu$_2$O$_8$ at 5 K. All the polarization configurations are given in (a) except for the $y(zx)y$ ($E_g$) one for which no phonon peaks have been detected. The upper two spectra in (a) are taken from one and the same crystal, and the bottom four from another one.](image)

2(b) at 331, 444, and 732 cm$^{-1}$. The higher frequency of the $O_{a}$ mode in GdSr$_2$NbCu$_2$O$_8$ is due to the shorter $d_{O_{a},Nb}$ = 1.856 Å bondlength$^{12}$ compared to $d_{O_{a},Ru}$ = 1.914 Å in GdSr$_2$RuCu$_2$O$_8$. It is well established that the corresponding $O_{a}$-Cu(chain) bondlength in RBa$_2$Cu$_3$O$_7$ ($R$ is rare earth) controls the $A_{1g}$ apical oxygen frequency.$^{15}$ A simple model for oxygen vibrations in cuprates gives that the square of the apical oxygen frequency $\omega_{O_{a}}^2$ varies with the valence of the cation $Z_{Me}$ and the metal-oxygen distance as $Z_{Me} d_{O_{a},Me}^2$, due to the change of ionic binding energy. A straightforward comparison gives that the ratio of experimentally measured frequencies $\omega_{O_{a},Ru}^2/\omega_{O_{a},Nb}^2$ agrees well with $Z_{Ru} d_{O_{a},Ru}^{-3}/Z_{Nb} d_{O_{a},Nb}^{-3}$ provided $Z_{Nb} = +5$ and $Z_{Ru} = +4.3$. Interestingly, this particular valence of Ru corroborates well that obtained from the valence bond sum in GdSr$_2$RuCu$_2$O$_8$.$^{10}$

Table II summarizes the experimentally measured phonon frequencies and those predicted by lattice dynamical calculations. Four of the $A_{1g}$ modes and one $B_{2g}$ mode are clearly seen in the Raman spectra of both the Ru- and the Nb-based compounds. From Table II it follows that these modes include predominantly vibrations along the $c$ axis. On the other hand, the phonons at 275 ($A_{1g}$), 411 ($B_{2g}$) and 607 ($B_{1g}$) cm$^{-1}$ in the spectra of GdSr$_2$RuCu$_2$O$_8$ have no counterpart in the spectra of GdSr$_2$NbCu$_2$O$_8$. We note that all these phonons involve $O_{Ru}$ vibrations.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Experiment (5 K)</th>
<th>Calculations (shell model)</th>
<th>Atomic motions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}(1)$</td>
<td>158</td>
<td>176</td>
<td>Cu stretching vibration along the $c$ axis</td>
</tr>
<tr>
<td>$A_{1g}(2)$</td>
<td>158+</td>
<td>186</td>
<td>Sr stretching vibration along the $c$ axis</td>
</tr>
<tr>
<td>$A_{1g}(3)$</td>
<td>256</td>
<td>323</td>
<td>Rotation of $CuO_4$ around the $c$ axis</td>
</tr>
<tr>
<td>$A_{1g}(4)$</td>
<td>439</td>
<td>448</td>
<td>Rotation of $RuO_4$ around the $c$ axis</td>
</tr>
<tr>
<td>$A_{1g}(5)$</td>
<td>659</td>
<td>644</td>
<td>In-phase vibrations of $O_{Cu}$ along the $c$ axis</td>
</tr>
<tr>
<td>$A_{1g}(6)$</td>
<td>659</td>
<td>644</td>
<td>$O_{s}$ stretching vibration along the $c$ axis</td>
</tr>
<tr>
<td>$B_{1g}(1)$</td>
<td>497</td>
<td>497</td>
<td>In-plane antistretching vibrations of $O_{Cu}$</td>
</tr>
<tr>
<td>$B_{1g}(2)$</td>
<td>607</td>
<td>688</td>
<td>In-plane antistretching vibrations of $O_{Ru}$</td>
</tr>
<tr>
<td>$B_{2g}(1)$</td>
<td>178</td>
<td>178</td>
<td>Sr Along the $c$ axis</td>
</tr>
<tr>
<td>$B_{2g}(2)$</td>
<td>297</td>
<td>297</td>
<td>Out-of-phase vibrations of $O_{Cu}$ along the $c$ axis</td>
</tr>
<tr>
<td>$B_{2g}(3)$</td>
<td>425</td>
<td>425</td>
<td>“Scissors” type, in-plane $O_{Ru}$ vibrations</td>
</tr>
<tr>
<td>$B_{2g}(4)$</td>
<td>488</td>
<td>488</td>
<td>“Scissors” type, in-plane $O_{Cu}$ vibrations</td>
</tr>
</tbody>
</table>

TABLE II. Experimental and calculated Raman phonon mode frequencies of GdSr$_2$RuCu$_2$O$_8$ within the $P4/mmbm$ space group.
symmetry. In addition, this peak is absent in the $y'(x'x')y'$ spectrum in Fig. 2(a). This suggests that either the Raman scattering from magnetic excitations at $\sim 150$ cm$^{-1}$ also depends on the $k$-vector direction of the exciting light or that the two crystals characterized by the $y'(x'x')y'$ and $z(x'x')z$ spectra are different. Unfortunately, the reason for the magnetic-peak-intensity variation in GdSr$_2$RuCu$_2$O$_8$ between different samples remains still unclear. More experimental studies on samples with diverse crystalline morphology are needed to clarify the origin of the 150 cm$^{-1}$ excitation.

D. Phonon anomalies correlated with the magnetic transition

Coupling of phonons to magnetic excitations in solids results in phonon self-energy, that is, the frequency and linewidth of the phonons change due to interaction. Magnetic ordering can also influence the phonon self-energy by a variety of mechanisms known as spin-dependent phonon Raman scattering.\(^{18,19}\) Usually these effects manifest themselves in a peculiar behavior of phonon frequency or intensity near or below $T_m$.

Figure 3 displays the Raman spectra of GdSr$_2$RuCu$_2$O$_8$ measured at temperatures slightly above and below $T_m$. Close examination of the temperature dependence of phonon frequency suggests that at least three of the phonons show anomalous behavior below $T_m$. Two of these phonons (264 cm$^{-1}$ and 652 cm$^{-1}$) involve oxygen vibrations of RuO$_6$ and one (318 cm$^{-1}$) of CuO$_2$ planes. Their frequencies as a function of temperature are shown in Fig. 4. The 264 cm$^{-1}$ mode frequency shifts strongly upward to 275 cm$^{-1}$ at 5 K [Fig. 4(a)] in a manner that resembles the temperature dependence of the field-cooled magnetization (Fig. 1). Similar behavior has also been observed in polycrystalline GdSr$_2$RuCu$_2$O$_8$ samples.\(^{6-9}\) We discuss this in more detail in Sec. II E.

The temperature dependence of the $A_{1g}(O_a)$ mode frequency in Fig. 4(b) looks at a first glance typical of a phonon in a shrinking lattice as that of GdSr$_2$RuCu$_2$O$_8$.\(^{3}\) However, we note that the neutron diffraction study by Chmaissem et al. indicated that the $O_a$-Ru bondlength $d_{O_aRu}$ increases with decreasing temperature.\(^{3}\) If this is the case, the frequency of the $O_a$ mode should decrease with temperature according to $\omega_{O_a} \propto d_{O_aRu}^{-3/2}$ (see, e.g., Sec. II B) unless other mechanisms contribute to the real part of the phonon self-energy (i.e., frequency). The solid curve in Fig. 4(b) is a fit of $\omega_{lat} = ad_{O_aRu}^{-3/2} + b(N_{\omega_{lat}} + 1)$ ($a$ and $b$ are parameters) to the frequencies measured in the paramagnetic region. The first term accounts for the frequency change due to the altered ionic binding energy resulting from the varying bond length. The second term, where $N_{\omega_{lat}} = 1/\left[\exp(h\omega_{lat}/2k_BT) - 1\right]$, gives the contribution from the anharmonic two-phonon decay process. In other words, the solid curve in Fig. 4(b) shows the expected temperature dependence of the $O_a$ phonon frequency based on the bondlength data in Ref. 3 and our measured high-temperature phonon frequencies. Clearly, they do not agree when $T < T_m$, suggesting the existence of a spin-phonon interaction contribution to the real part of the $A_{1g}(O_a)$ phonon self-energy.

The 320 cm$^{-1}$ $B_{2g}$ mode frequency versus temperature is given in Fig. 4(c). It shows a nonmonotonous behavior and an abrupt softening below $T_m$. At the end, we note the implication of these observations: oxygen atoms mediate magnetic interactions in GdSr$_2$RuCu$_2$O$_8$ and can in principle be used to probe the magnetic ordering.
We point out that as the ordered phase, the Raman intensity changes with temperature. An example of apparent spin-dependent phonon Raman scattering in GdSrRu₂Cu₃O₈ is demonstrated by the 411 cm⁻¹ (B₂g) and 607 cm⁻¹ (B₁g) phonons. These lines become observable below Tₘ and their Raman intensity increases further with decreasing temperature. The enhancement of Raman intensity of the two phonons is evidence for a spin-dependent scattering mechanism. In a magnetically ordered phase, the Raman intensity changes with temperature as

\[ I_{ph}(T) \propto R_{ph}^2 \frac{E_{ph}}{S^2}, \]

where \( R_{ph} \) is the nearest-neighbor spin correlation function and \( S^2 \) is the spin-independent Raman amplitude. This equation is valid for both ferromagnetic and antiferromagnetic magnetic ordering. The type of magnetic ordering reflects only on the sign of \( S/M \), provided the vertices are real, being opposite for the two types of ordering. Our experiment shows that the Raman intensity of the 411 cm⁻¹ and 607 cm⁻¹ lines is vanishing above Tₘ, that is, \( I_{ph}(T>T_m) \propto R_{ph}^2 \approx 0 \), and therefore \( I(T<T_m) \propto |M(S_0 \cdot S_{nn})|S^2| \). We point out that the (411 cm⁻¹ and 607 cm⁻¹) phonons in GdSr₂RuCu₃O₈ alone cannot distinguish to which of the magnetic ordering components the two phonons couple.

**E. Phonon renormalization due to interaction with magnetic excitations**

It is essential for the magnetic-order-dependent phonon self-energy effects that the phonon modulates those electronic bands that take part in formation of magnetic moments and the spin-spin coupling constants (exchange interaction). The effectiveness of this modulation depends on the phonon eigenvector. In Fig. 5 we display the eigenvectors of the 265 cm⁻¹ \((A_{1g})\) phonon obtained by symmetry considerations and lattice dynamics calculations (LDC). The oxygen displacements in this mode are similar to those of the RuO₆ rotation that causes the P₄/mmm to P₄/mmm structural transition. First-principles electronic and magnetic structure calculations show that this rotation results in significant narrowing of the 4d-electron bands that drives the system to AFM order. Indeed, an earlier calculation within the P₄/mmm structure (without RuO₆ rotations) of the same compound has given FM ground state. In the FM ordered P₄/mmm phase the Ru-O₆ hybridized bands, in particular Ru \( d_{xy}-O_{Ru} \), strongly contribute to the density of states (DOS) at the Fermi energy \((E_F)\), which gives itinerant character of Ru magnetism. A comparison with the DOS of the FM-P₄/mmm phase shows that the RuO₆ rotation leads to more localized majority spin \( d_{xy} \) states dipped below \( E_F \), and depleted \( d_{yz} \) states, which is, much less itinerant character of ferromagnetism. The FM ordering of Ru moments in P₄/mmm GdSr₂Ru₂Cu₂O₈, however, has been found energetically less favored than AFM. In the AFM-P₄/mmm phase the more localized \( d_{xy} \) and \( d_{yz} \) states of a given Ru hybridize with the \( d_{xy} \) and \( d_{yz} \) states on the nearest-neighbor Ru sites through \( O_{Ru} \). Therefore, the spin-spin coupling is carried through the superexchange mechanism. Interestingly, a soft mode similar to that at 265 cm⁻¹ in GdSr₂RuCu₃O₈ has been found to freeze at the surface of the Sr₅RuO₆ superconductor and stabilize the FM fluctuations in the surface layer. On the other hand, Mazin and Singh have given an example in which the in-plane RuO₆ rotation in Sr₅RuO₆ is coupled to AFM ordered Ru spins. In this compound the RuO₆ octahedra do not share common oxygen atoms. For these RuO₆ clusters the authors of Ref. 23 predict that a RuO₆ rotational mode with frequency of \( \sim 270 \) cm⁻¹ couples to magnetic excitations that flip the spin (magnons) of a RuO₆ cluster. From the above analysis we conclude that whatever type of magnetic ordering is established in GdSr₂Ru₂Cu₂O₈ the \( A_{1g} \) mode at 265 cm⁻¹ should couple strongly to the magnetic excitations either through strong modulation of the \( d_{xy} \) bands in the FM phase or by perturbing the superexchange path in the AFM phase.

**F. Raman scattering intensity of the 265 cm⁻¹ mode**

At the end we discuss the origin of the 265 cm⁻¹ mode Raman intensity. The band structure calculations of AFM-GdSr₂Ru₂Cu₂O₈ give that three bands cross the Fermi surface. These are a Ru-O₆ bands derived from the antibonding \( dp_x \cdot d_{xy} \cdot p_{xy} \) orbitals and two Cu-O₆ bands with \( dp_x \sigma \cdot d_{xy} \cdot p_{xy} \) character, as those in bilayer cuprates. In a FM ordered structure a fourth band, namely of the \( d_{yz} \cdot p_z \) orbitals, also crosses \( E_F \). In view of the weak 265 cm⁻¹ peak spectral weight, we suggest that it gains \( xx \) Raman intensity from transitions between the \( Ru(d_{xy})-O_{Ru}(p_{xy}) \) and \( Ru(d_{xy})-O_{Ru}(p_{xy}) \) bands, that is, transitions without charge transfer. Within the crystal-field approximation of \( Ru^{3+}\) \((4d^{5})\), these transitions correspond to \( ^4A_{2g} \rightarrow ^4T_{2g} \) or \( ^4T_{2g} \) spin-allowed but parity-forbidden intraionic transitions that have relatively weak oscillator strength. The Raman scattering is expected to be under resonance due to the energy gap of \( \sim 2.5 \) eV between the two Ru-O₆ bands. Indeed, a preliminary resonance study of GdSr₂Ru₂O₆ has found an enhancement of the 265 cm⁻¹ phonon intensity by increasing the excitation laser energy from 1.92 eV to 2.41 eV. The \( xx \) Raman intensity of the modes that involve Cu and O₆ vibrations most likely comes from Cu \( d_{xy} \cdot O_{Cu}(p_{xy}) \) transitions similar to those in...
Interestingly, the Raman spectrum of GdSr$_2$NbCu$_2$O$_8$ resembles more closely that of YBa$_2$Cu$_3$O$_6$, a fact that is consistent with insulating character of this compound.\textsuperscript{12} In GdSr$_2$NbCu$_2$O$_8$ (Nb$^{5+}$:4$d^0$) the Nb(4$d$)-O$_{Nb}$ bands are empty. Therefore, the Nb(4$d$)-O$_{Nb}$ band-to-band transitions that give strength to the $xx(\gamma\gamma)$ Raman intensity of the rotational mode are not available anymore and the process is off resonance. We believe that this most likely is the reason for the vanishing intensity of the rotational mode in GdSr$_2$NbCu$_2$O$_8$.

IV. CONCLUSIONS

We have determined the symmetry of the phonon, magnetic, and coupled magnetic-phonon excitations in GdSr$_2$RuCu$_2$O$_8$ from polarized Raman spectra of single-crystal samples. Spin-phonon interactions are found to produce phonon self-energy effects for all the Raman-active oxygen vibrations in GdSr$_2$RuCu$_2$O$_8$. These effects are particularly apparent for the $A_{1g}$ rotational mode at 265 cm$^{-1}$. We have given arguments that this phonon strongly perturbs the spin-spin correlations.

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