



Raman Phonons in RuSr₂GdCu₂O₈

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The Raman spectra of polycrystalline samples of RuSr₂GdCu₂O₈, annealed under high pressure (3 Gpa, 1000°C), were studied between 10 and 420 K. The ferromagnetic ordering has a little (if any) effect on the variations with temperature of the position and width of the Raman lines at 158, 318, 440 and 659 cm⁻¹. In contrast, for the line near 270 cm⁻¹ one observes a local maximum of the halfwidth near the magnetic transition and strong hardening upon cooling below T_c. The observation of the latter line, which has no analog in the YBCO-type compounds, supports either *I4/mcm* or *P4/mbm* crystal structure, where, due to the tilting of the RuO₆ octahedra, the unit cell is doubled and new Raman modes are activated. The lattice dynamical calculations (LDC) predict that the Raman mode with the closest wavenumber to that of the 270 cm⁻¹ line is the A_{1g} mode involving rotations of CuO₅ pyramids. Such an assignment alone cannot explain the anomalous behavior near T_c. A reasonable explanation could be given considering the 270 cm⁻¹ line as a superposition of two A_{1g} lines corresponding to rotations around *c*-axis of CuO₅ pyramids (265 cm⁻¹) and RuO₆ octahedra (275 cm⁻¹), respectively.

1. Introduction

RuSr₂GdCu₂O₈ (Ru1212) attracted significant interest since it was found that the ferromagnetic order below T_C ≈ 135 K may coexists with superconductivity below T_c = 15 – 40 K. In particular, definite attention has been paid to the structure and microstructure [1,2], lattice vibrations [3,4] and magnetic ordering effects [4,5] in this material.

Although the structure of Ru1212 is similar to that of the well known 1212 cuprate compounds, the Rietveld refinement of the x-ray [1,3] and neutron [2] powder diffraction data reveal some importance differences. Due to the mismatch of the Ru-O and Cu-O in-plane bonds, the RuO₆ octahedra are rotated around the *c*-axis, which results in large off-site in-plane displacement of the oxygens in the RuO₂ layers and a $\sqrt{2}a \times \sqrt{2}b$ superlattice with either *I4/mcm* or *P4/mbm* tetragonal symmetry [1–3,6]. The rotations of RuO₆ octahedra, however, are not coherent and the averaged structure of Ru1212 is *P4/mmm*.

Raman spectroscopy is among the most efficient techniques for study of the local atomic ar-

range. Indeed, each of the first order (Γ -point) Raman allowed phonon modes corresponds to vibrations of mainly one type of atoms, the mode frequency and selection rules being governed by mainly the positions of the nearest neighbors and the type of corresponding interatomic interactions. Pringle *et al.* [3] reported the room temperature Raman spectra of several Ru1212 samples with different rate of ¹⁸O for ¹⁶O isotopic substitution. It has been found that four of the five experimentally observed Raman lines (at 260, 317, 437 and 652 cm⁻¹) exhibit isotopic shift and therefore are related to oxygen vibrations. The 260 cm⁻¹, which has no analog in YBCO-type compounds, has been assigned to vibrations of the oxygens of the RuO₂ planes. The appearance of this line strongly supports a local structure with all oxygen atoms in noncentrosymmetrical sites. Hadjiev *et al.* [4] studied the variations of the Raman spectra of Ru1212 with lowering temperature. They observed appearance with magnetic ordering of new spectral features at ≈ 147 and 274 cm⁻¹ and connected them with magnetic ordering.

In this work we report our results on the vari-

ations with temperature of the Raman spectra of Ru1212 between 5 and 420 K. The observed Raman lines are assigned to definite modes of A_{1g} and B_{2g} symmetry by comparison to the predictions of lattice dynamical calculations (LDC) for the $I4/mcm$ and $P4/mbm$ structures. The only phonon line, which exhibits anomaly near the magnetic phase transition seems to be a superposition of two close A_{1g} lines corresponding to rotations around the c -axis of the CuO_5 pyramids and RuO_6 octahedra, respectively. No additional structures that could be related to magnetic excitations and no effect of superconductivity (below $T_c \sim 30$ K) were observed.

2. Samples and Experimental

Samples of polycrystalline $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ were prepared by the standard solid state reaction and annealed under high pressure (3 GPa, 1000°C) for 1/2 hour. The x-ray diffraction pattern gave an averaged tetragonal $P4/mmm$ structure with $a = 0.384$ nm and $c = 1.16$ nm. The samples were ferromagnetic with $T_C = 135$ K and exhibited zero resistance below ~ 35 K.

The Raman spectra were measured in backward scattering configuration using the 514.5 nm Ar^+ laser line and a microscope with $\times 50$ objective for focusing the incident beam and collecting the scattered light. The spectrum of the scattered light was analyzed using a notch filter and a single spectrometer equipped with liquid-nitrogen-cooled CCD detector. The sample was mounted in a Microstat^{He} microcryostat where the temperature could be varied between 5 and 420 K.

3. Results and Discussion

Fig.1 shows the variations with temperature between 10 K and 300 K of the Raman spectra of Ru1212 as obtained with parallel polarization of the incident and scattering radiation. The relative peak intensity was the same for all spots checked: an indication that the size of the microcrystal grains is less the focus spot ($3\text{--}4 \mu\text{m}$). With a crossed analyzer one observes the same Raman lines with a reduced intensity. The only exception is the line at 318 cm^{-1} , which relative

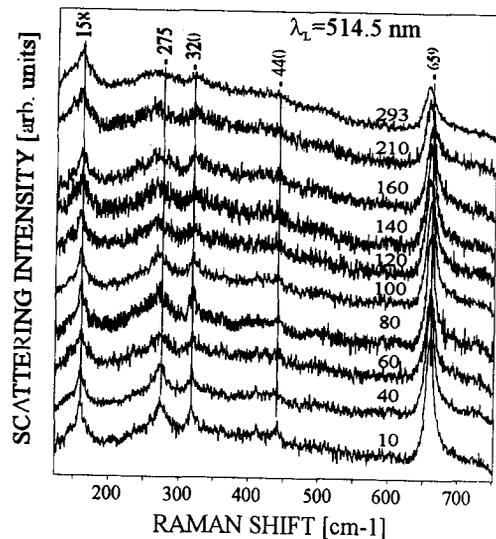


Figure 1. Variations with T of the Raman spectra of Ru1212.

intensity increases in crossed polarization. With lowering temperature the Raman lines sharpen and shift towards higher wavenumbers. The line near $265\text{--}275 \text{ cm}^{-1}$ is the only one which exhibits anomaly near the magnetic transition. This is illustrated on Fig.2 where are compared the temperature dependencies of the positions and widths of the lines at 158 , 270 , 318 , and 659 cm^{-1} . In contrast to the report of Hadjiev *et al.* [4] no new spectral features that could be related to magnetic excitations were observed at low temperatures. A possible reason for this discrepancy could be the resonant properties of magnetic excitations (in Ref.[4] the 647.1 nm laser line has been used for excitation).

In Table I are given the atomic site symmetries and irreducible representations for Ru1212 with $P4/mbm$ structure. In this structure one expects in total 23 ($6A_{1g} + 2B_{1g} + 4B_{2g} + 11E_g$) Raman allowed modes. This number is much higher than the experimentally observed Raman lines. It is plausible to expect, however, that similarly to the case of YBCO-type compounds, the E_g lines are of low intensity and most of the lines correspond to modes of A_{1g} , B_{1g} and B_{2g} sym-

Table 1

Wyckoff notations, atomic site symmetries and irreducible representations and phonon mode frequencies (experimental and calculated) in RuSr₂GdCu₂O₈ [space group *P4/mbm*, No.127, Z = 2].

Atom	Wyckoff notation	Site symmetry	Irreducible representations	
Ru	2(a)	4/m [<i>D</i> ₄]	$A_{2g} + A_{2u} + E_g + E_u$	
Sr	4(f)	2. <i>mm</i> [<i>C</i> _{2v} ^d]	$A_{1g} + A_{2u} + B_{1u} + B_{2g} + 2E_g + 2E_u$	
Gd	2(c)	<i>m.mm</i> [<i>D</i> ' _{2h}]	$A_{2u} + B_{1u} + 2E_u$	
Cu	4(e)	4.. [<i>C</i> ₄]	$A_{1g} + A_{1u} + A_{2g} + A_{2u} + 2E_g + 2E_u$	
O1	4(g)	<i>m.2m</i> [<i>C</i> ' _{2v}]	$A_{1g} + A_{2g} + A_{2u} + B_{1g} + B_{1u} + B_{2g} + E_g + 2E_u$	
O2	8(k)	. <i>m</i> [<i>C</i> _s ^d]	$2A_{1g} + A_{1u} + A_{2g} + 2A_{2u} + B_{1g} + 2B_{1u} + 2B_{2g} + B_{2u} + 3E_g + 3E_u$	
O4	4(e)	4.. [<i>C</i> ₄]	$A_{1g} + A_{1u} + A_{2g} + A_{2u} + 2E_g + 2E_u$	
Selection rules		Modes classification		
$A_{1g} \rightarrow \alpha_{xx} + \alpha_{yy}, \alpha_{zz}$		$\Gamma_{\text{Raman}} = 6A_{1g} + 2B_{1g} + 4B_{2g} + 11E_g$		
$B_{1g} \rightarrow \alpha_{xx} - \alpha_{yy}$		$\Gamma_{\text{ir}} = 7A_{2u} + 13E_u$		
$B_{2g} \rightarrow \alpha_{xy}$		$\Gamma_{\text{silent}} = 5A_{2g} + 3A_{1u} + 5B_{1u} + B_u$		
$E_g \rightarrow \alpha_{xz}, \alpha_{yz}$		$\Gamma_{\text{acoustic}} = A_{2u} + E_u$		
Mode	Exp. 300 K	Exp. 10 K	Calc. <i>P4/mbm</i> (<i>I4/mcm</i>)	Main atomic motions
<i>A</i> _{1g} (1)	152?	156?	176 (163)	Sr, Cu along <i>z</i>
<i>A</i> _{1g} (2)	152?	156?	186 (172)	Sr, Cu along <i>z</i>
<i>A</i> _{1g} (3)	264	?	256 (277)	rotations of O2 in the <i>xy</i> plane
<i>A</i> _{1g} (4)	?	274	323 (318)	rotations of O1 in the <i>xy</i> plane
<i>A</i> _{1g} (5)	440	442	448 (453)	in-phase vibrations of O2 along <i>z</i>
<i>A</i> _{1g} (6)	653	659	644 (657)	apex O4 along <i>z</i>
<i>B</i> _{1g} (1)			497 (510)	O2 in the <i>xy</i> plane antistretching
<i>B</i> _{1g} (2)			688 (676)	O1 in the <i>xy</i> plane antistretching
<i>B</i> _{2g} (1)			178 (171)	Sr along <i>z</i> axis
<i>B</i> _{2g} (2)	318	320	297 (315)	out-of-phase vibrations of O2 along <i>z</i>
<i>B</i> _{2g} (3)			425 (416)	O1 in <i>xy</i> plane "scissors"
<i>B</i> _{2g} (4)			488 (452)	O2 in <i>xy</i> plane "scissors"

metry. Thus, an assignment of the Raman lines can be done by direct comparison of the experimental frequencies with the predictions of lattice dynamical calculations (LDC) for the frequencies of the *A*_{1g}, *B*_{1g} and *B*_{2g} modes of Ru1212. The results of such calculations, using a shell model [7] with atomic positions for the *P4/mbm* structure from Ref.[2] and for the *I4/mcm* structure from Ref.[6], are shown in the lower part of Table I. The calculated wavenumbers for both structures are close, although for the *I4/mcm* structure the atomic positions of GdSr₂TaCu₂O₈ (Ta1212) instead of those of Ru1212 were used. Out of

the in total 23 Raman allowed modes in Ru1212 10 ($4A_{1g} + B_{2g} + 5E_g$) are analogs of the Raman modes in YBCO-type compounds and correspond to out-of-plane ($4A_{1g} + B_{2g}$) and in-plane ($5E_g$) vibrations of Cu, Sr, O2(in-phase), O4, and O2 (out-of-phase), respectively. The additional $2A_{1g} + 2B_{1g} + 3B_{2g} + 6E_g$ modes arise from the doubling of the unit cell due the shift of the O1 atoms (in the RuO₂ planes) into non-centrosymmetrical positions. The new *A*_{1g} modes (*A*_{1g}(3) and *A*_{1g}(4)) represent rotations around the *z*-axis of the O2 atoms (CuO₅ pyramids) and O1 atoms (RuO₆ octahedra), respectively.

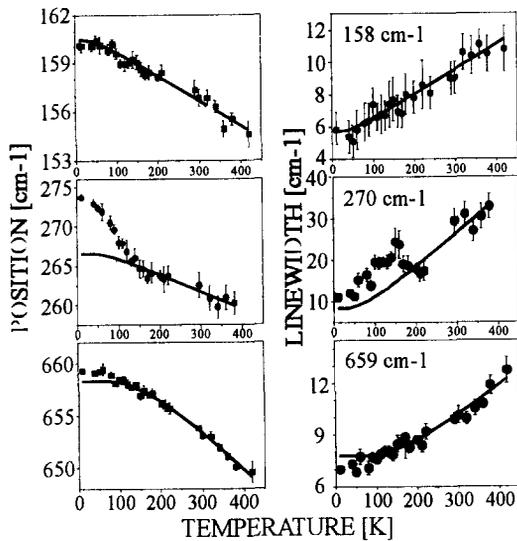


Figure 2. Variations with T of the position and width of the 158, 275 and 659 cm^{-1} Raman lines.

As it follows from Table I, the assignment of all experimentally observed Raman lines to definite atomic vibrations is not straightforward. The line at 155 cm^{-1} corresponds to either a single [$A_{1g}(1)$ or $A_{1g}(2)$] mode involving Cu and Sr vibrations, or to a superposition of these modes. The line at 318 cm^{-1} is very close to the prediction for the $A_{1g}(4)$ mode (rotations of RuO_6 octahedra). Its relative enhancement in crossed polarization, however, indicates that it rather represents the $B_{2g}(2)$ (out-of-phase vibrations of O2 along z) mode. As to the 442 and 659 cm^{-1} , there is no doubt that they correspond to the $A_{1g}(5)$ (in-phase vibrations of O2 along z) and $A_{1g}(6)$ (apex O4 vibrations along z) modes, respectively.

The assignment of the Raman line at 265–275 cm^{-1} , which exhibits anomaly with ferromagnetic ordering is of special interest as it has no analog in YBCO-type compounds. Following the LDC results, this line represents the $A_{1g}(3)$ mode, i.e. the rotations of CuO_5 pyramids around the z axis. Such an assignment, however, can hardly explain why the magnetic ordering affects only

the rotational vibrations of the O2 atoms, which are far enough from Ru. A more plausible explanation could be given assuming that this Raman line as a superposition of two lines centered at about 265 and 275 cm^{-1} , respectively. Given the 265 cm^{-1} component corresponds to the $A_{1g}(3)$ mode, the higher 275 cm^{-1} component can be assigned to the $A_{1g}(4)$ mode (rotations of RuO_6 octahedra). It is reasonable to expect that the latter component will be sensitive to magnetic ordering and related reorganization of the electronic structure. This interpretation is consistent with earlier results of Hadjiev et al. [4,8] where separate peaks at 260 and 274 cm^{-1} have been observed at low temperatures.

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