

**Raman spectroscopy of CaRuO<sub>3</sub>**N. Kolev,<sup>1</sup> C. L. Chen,<sup>1</sup> M. Gospodinov,<sup>2</sup> R. P. Bontchev,<sup>3</sup> V. N. Popov,<sup>4</sup> A. P. Litvinchuk,<sup>1,3</sup> M. V. Abrashev,<sup>4</sup>  
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We report on the polarized Raman spectra of untwinned single crystals of CaRuO<sub>3</sub> (Ru<sup>4+</sup>) that reveal the phonon excitations in this compound. The observed Raman lines are assigned to definite atomic vibrations based on predictions of lattice dynamics calculations and by a comparison to the spectra of isostructural SrRuO<sub>3</sub>. Unlike some other Ru<sup>4+</sup> compounds such as ferromagnetic SrRuO<sub>3</sub> and antiferromagnetic Ca<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub>, the temperature dependence of the Raman spectra shows no anomalies related to magnetic ordering. This result is in favor of paramagnetic or short-range spin-glass-type magnetic interactions in CaRuO<sub>3</sub>.

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The properties of isostructural perovskitelike SrRuO<sub>3</sub>, CaRuO<sub>3</sub>, and Sr<sub>1-x</sub>Ca<sub>x</sub>RuO<sub>3</sub> (space group *Pnma*, *Z*=4) have attracted significant interest.<sup>1-13</sup> This was stimulated by the discovery of superconductivity in Sr<sub>2</sub>RuO<sub>4</sub>,<sup>14</sup> and predictions for strong electron correlations in SrRuO<sub>3</sub> and CaRuO<sub>3</sub>. The series Sr<sub>1-x</sub>Ca<sub>x</sub>RuO<sub>3</sub> is also of practical interest as these compounds can be used as normal metal barrier in Josephson junctions<sup>15,16</sup> and as electrodes in epitaxial heterostructures.<sup>1,2,17-19</sup>

While there is a consensus that SrRuO<sub>3</sub> is an itinerant ferromagnetic conductor with  $T_C \sim 160-165$  K, reports on the magnetic properties of CaRuO<sub>3</sub>, which also exhibits metallic conductivity, are rather controversial. Gibb *et al.*<sup>20</sup> found that CaRuO<sub>3</sub> remains a paramagnetic metal (or exchange-enhanced paramagnetic metal) down to at least 30 mK, while others claimed that CaRuO<sub>3</sub> exhibits a magnetic instability with a nearly ferromagnetic (nearly FM) (Refs. 3 and 21) ground state, or has an antiferromagnetic (AFM) (Ref. 22) or FM (Ref. 23) ground state. The conclusion for AFM ordering is consistent with the ordering found in Ca<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> and Ca<sub>2</sub>RuO<sub>4</sub> (Refs. 4 and 24) and a large negative Weiss constant.<sup>20,25</sup> Some recent results suggested a short-range magnetic interaction, possibly of spin-glass type.<sup>5</sup> Based on resistivity and magnetoresistance measurements, it was proposed that CaRuO<sub>3</sub> is a non-Fermi liquid metal.<sup>6,7</sup> It was also found that the Hall effect in SrRuO<sub>3</sub> and CaRuO<sub>3</sub> exhibits a sign reversal,<sup>4,8,26</sup> which implies that these compounds are highly compensated metals.

The Raman spectra of SrRuO<sub>3</sub> were reported by Kirillov *et al.*<sup>27</sup> and Iliev *et al.*<sup>28</sup> The temperature dependence of some Raman lines was found to exhibit a pronounced anomalous hardening upon cooling below  $T_C$ , attributed to spin-phonon coupling and reorganization of the electronic states.<sup>28</sup> Similar effects have been observed for the antiferromagnetic Ca<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub>.<sup>29</sup> To the best of our knowledge, there are no reports on the Raman spectra of CaRuO<sub>3</sub>. Given that the magnetic properties of SrRuO<sub>3</sub> and CaRuO<sub>3</sub> differ significantly, a comparison of their spectra is of definite interest.

In this paper we report results from Raman measurements of oriented untwinned single crystals of CaRuO<sub>3</sub>. Most of the observed Raman lines are assigned to definite atomic vibrations based on their symmetry, comparison to the phonon frequencies predicted by lattice dynamics calculations (LDC's) and by a comparison to SrRuO<sub>3</sub>. The temperature dependence of the Raman spectra provides no evidence of phonon anomalies related to long-range magnetic ordering.

Ceramic CaRuO<sub>3</sub> was prepared by mixing CaCO<sub>3</sub> and RuO<sub>2</sub>, preheating the pressed pellets at 1000 °C for 24 h, and then sintering at 1200 °C for 72 h under oxygen. Small single crystals of CaRuO<sub>3</sub> were grown in Pt crucibles, from a self-flux using a mixture of ground CaRuO<sub>3</sub> and CaCl<sub>2</sub> (ratio 1:30), which was heated to 1260 °C, maintained for homogenization for 48 h, cooled at a rate of 2 °C/h to 1000 °C and then quenched to room temperature. Most of the crystals were of rectangular shape and of typical size 0.1 × 0.1 × 0.5 mm<sup>3</sup>. The elemental content was confirmed by energy dispersive x-ray analysis. For structural analysis a SIEMENS SMART single-crystal x-ray diffractometer was used. The orientation matrix and data were collected at room temperature using graphite-monochromatized Mo-*K*α radiation ( $\lambda = 0.71073$  Å). The x-ray diffraction of most of the crystals showed twinning with six orientational variants of domains, identical to those in orthorhombic manganites.<sup>30</sup> Some of the crystals, however, turned out to be merohedral twins with as low as 80:20 exchanged **a** and **c**, the twinning law being expressed by the matrix [(0 0 1)(0 -1 0)(1 0 0)]. The exposed crystal faces for such a crystal (further used in the Raman experiments) were identified using the SIEMENS SAINT program and the structure was solved by direct methods followed by full matrix least-squares refinement with the SHELXTL package. The main crystal parameters: space group *Pnma* (#62), **a**<sub>o</sub> = 5.5216(8) Å, **b**<sub>o</sub> = 7.6416(11) Å, **c**<sub>o</sub> = 5.3542(8) Å, and *Z* = 4 were in agreement with previously reported data.

The polarized Raman spectra were collected in back-scattering configuration using a single spectrometer equipped with a microscope, notch filters and a liquid-nitrogen-cooled

CCD detector. To obtain the spectra in all exact scattering configurations, the crystal was mounted on a pin, which allowed one to obtain spectra with incident polarizations along the [100], [001], [010], [101], and [101] directions (further denoted as  $x$ ,  $z$ ,  $y$ ,  $x'$ , and  $z'$ , respectively). For low-temperature measurements an optical Microstat<sup>He</sup> (Oxford Instruments) was used. The temperature of the cold finger could be varied between 10 and 300 K.

Perovskite-like  $ABO_3$  compounds with a  $Pnma$  structure yield a total of 60  $\Gamma$ -point phonons. Twenty-four of them are Raman active ( $7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$ ) and 25 are infrared active ( $9B_{1u} + 7B_{2u} + 9B_{3u}$ ). In the available scattering configurations, the Raman-allowed  $A_g$  modes are expected to appear in the parallel  $xx$ ,  $zz$ ,  $yy$ ,  $x'x'$ , and  $z'z'$  polarizations and should not be seen in the crossed  $xz$ ,  $yx'$ , and  $yz'$  polarization. The first and second letters in these notations denote the polarizations of the incident and scattered light, respectively. The  $B_{2g}$  modes are allowed in the  $x'x'$ ,  $z'z'$ , and  $xz$  polarizations and are forbidden in the  $xx$ ,  $zz$ , and  $yy$  polarizations. The  $B_{1g}/B_{3g}$  modes are expected to appear in only  $yx'$  and  $yz'$  of the available configurations. The notation of the  $xx/zz$  type refers to an experimental indistinguishability between the  $x$  and  $z$  axes. As a rule, the assignment of a Raman line to a definite phonon mode is based on its symmetry and comparison to the results of LDC's. The LDC model used by us to predict both the eigenfrequencies and eigenvectors of phonon modes of  $CaRuO_3$  was described in detail in Ref. 31.

The polarized Raman spectra of  $CaRuO_3$ , as obtained at room temperature with several exact scattering configurations, are shown in Fig. 1. The Raman peaks at 172, 265, 357, 418, 557, 706, and 737  $cm^{-1}$  have exact  $A_g$  symmetries. Peaks of  $B_{2g}$  symmetry are observed at 172, 243, 447, and 616  $cm^{-1}$  in the  $x'x'/z'z'$  and  $xz/xz$  spectra. No pronounced Raman lines are seen in the cross-polarized  $yx'/yz'$  or  $x'y/z'y$  spectra, an indication that the  $B_{1g}$  and  $B_{3g}$  lines are of negligible intensity.

The results of LDC's and the experimental data for  $CaRuO_3$  and  $SrRuO_3$  are presented in Table I. The atomic motions for the  $A_g$  and  $B_{2g}$  modes of  $CaRuO_3$  as predicted by LDC's are shown in Fig. 2. The three high-frequency  $A_g$  modes have very similar eigenvectors in the two compounds, although the relative amplitudes of the O1 movements for the  $A_g(5)$  mode are different. For the four low-frequency modes, however, there is no such one-to-one correspondence. In the  $SrRuO_3$  modes the amplitudes of the main atomic motions in a particular mode are at least three times greater than the secondary motions, while the  $CaRuO_3$  modes involve quite mixed atomic motions. Some of the eigenvectors are rather different, and that is why the  $A_g(4)$  mode in  $SrRuO_3$  is closer in its eigenvectors to  $A_g(2)$  in  $CaRuO_3$ , and  $A_g(3)$  in  $SrRuO_3$  to  $A_g(1)$  in  $CaRuO_3$ . The Sr(Ca)-O distances in  $SrRuO_3$  and  $CaRuO_3$  are very similar [respectively, 1.98 and 1.98 Å for Sr(Ca)-O1 and 1.99 and 2.00 Å for Sr(Ca)-O2], and one reasonably expects close frequencies for the high-frequency  $A_g$  modes, involving mainly stretching and bending vibrations of the  $RuO_6$  octahedra. These frequencies are predicted to lay below 560  $cm^{-1}$ , which has experimentally been confirmed for  $SrRuO_3$ .<sup>28</sup> This indicates that the  $CaRuO_3$  complex band around and above 700  $cm^{-1}$ , although of nominally  $A_g$

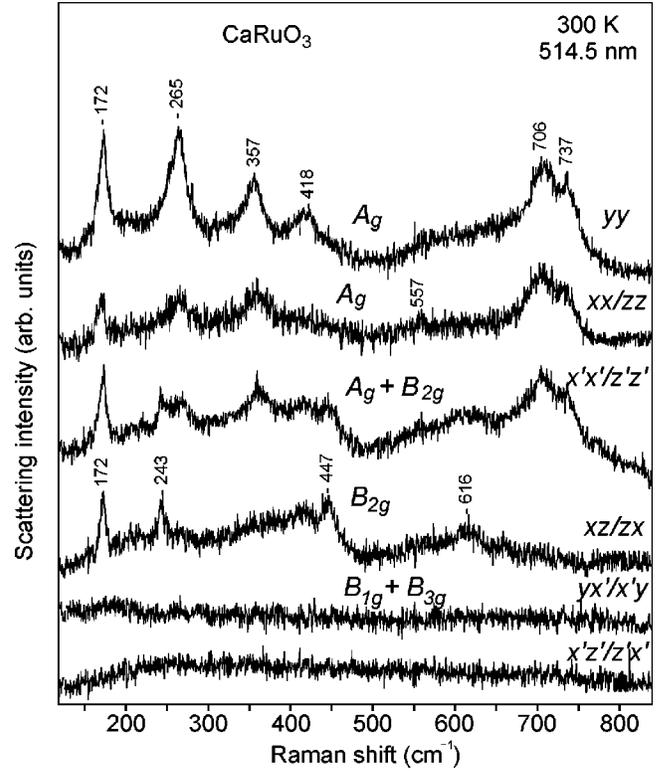


FIG. 1. Raman spectra of  $CaRuO_3$  in several exact scattering configurations.

symmetry, is not related to  $\Gamma$ -point  $A_g$  mode(s). Indeed, both the intensity and the profile of this complex band are sample dependent. At this stage we tentatively assume that it is of a density-of-states origin. The calculated one-phonon density

TABLE I. Calculated and experimental frequencies (in  $cm^{-1}$ ) of the  $A_g$  and  $B_{2g}$  Raman modes in  $SrRuO_3$  and  $CaRuO_3$ .

Mode	$SrRuO_3$		$CaRuO_3$		Main atomic motions in $CaRuO_3$
	calc.	expt. Ref. 28	calc.	expt. this paper	
$A_g(1)$	254	253	198	172	$RuO_6$ $y$ rotations, Ca
$A_g(2)$	296	291	228		Ca, $RuO_6$ $x$ rotations
$A_g(3)$	188	225?	268	268	$RuO_6$ rotation/stretching
$A_g(4)$	149	123?	297		Ca( $z$ ), $RuO_6$ rotation/stretching
$A_g(5)$	350	393	342	357	Ca( $x$ ), $RuO_6$ stretching/bending
$A_g(6)$	482	–	467	418	O1-Ru-O1, O2-Ru-O2 bendings
$A_g(7)$	540	–	555	557	Ru-O2 in-phase stretching
				705?	
				737?	
$B_{2g}(1)$	181	–	222	172	Ca( $z$ ), $RuO_6$ breathing
$B_{2g}(2)$	246	–	243	–	$RuO_6$ $z$ rotation, Ca
$B_{2g}(3)$	158	–	284	–	Ca( $x$ ); $RuO_6$ $z$ rotation
$B_{2g}(4)$	391	390	315	–	O1, O2 stretching
$B_{2g}(5)$	465	412	451	447	O1-Ru-O1, O2-Ru-O2 bendings
$B_{2g}(6)$	490	–	495	–	O2-Ru-O2 bending
$B_{2g}(1)$	725	–	706	616?	Ru-O2 stretching (breathing)

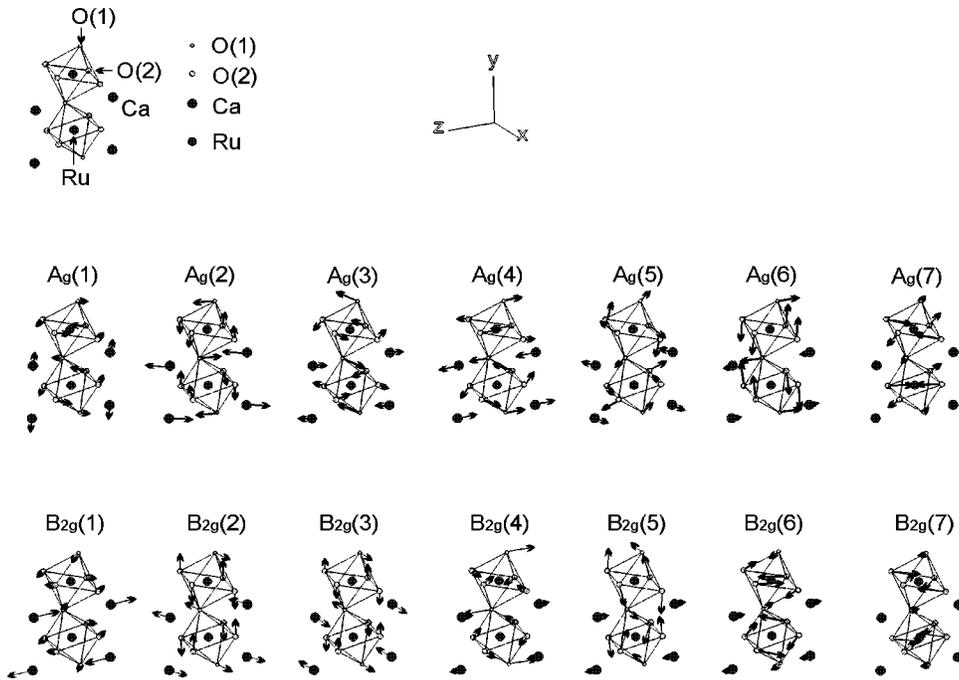


FIG. 2. Atomic displacements for the  $A_g$  and  $B_{2g}$  modes in  $\text{CaRuO}_3$ , as obtained by LDC's. The mode frequencies are given in Table I.

of states for  $\text{CaRuO}_3$  does exhibit a strong sharp peak centered at  $720 \text{ cm}^{-1}$ . The activation of otherwise forbidden non- $\Gamma$ -point phonons is usually caused by a break of the translational symmetry due to nonstoichiometry or other lattice distortions. Such defects are expected to affect the magnetic ordering too, which may explain the controversial results on magnetic properties.

The  $B_{2g}$  modes in  $\text{CaRuO}_3$  and  $\text{SrRuO}_3$ , like the  $A_g$  modes, have similar eigenvectors for the high-frequency

modes, while two of the low frequency modes, namely,  $B_{2g}(2)$  and  $B_{2g}(3)$  in the case of  $\text{CaRuO}_3$ , involve more than one type of atoms with comparable amplitudes in a particular vibration. Figure 3 shows the Raman spectra of  $\text{CaRuO}_3$  at various temperatures between 10 and 300 K. The  $\omega_{ph}(T)$  dependencies for the well pronounced lines at 172

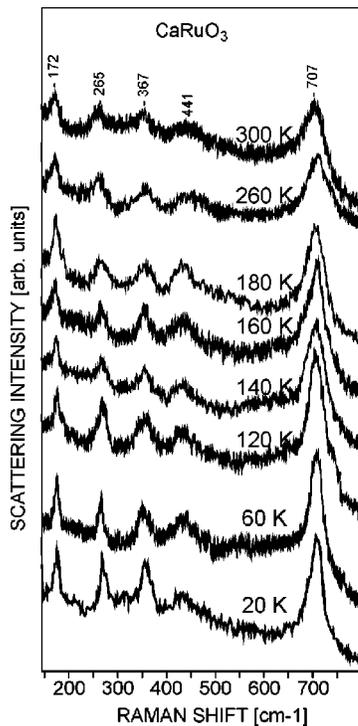


FIG. 3. Variations with  $T$  of the Raman spectra of  $\text{CaRuO}_3$ .

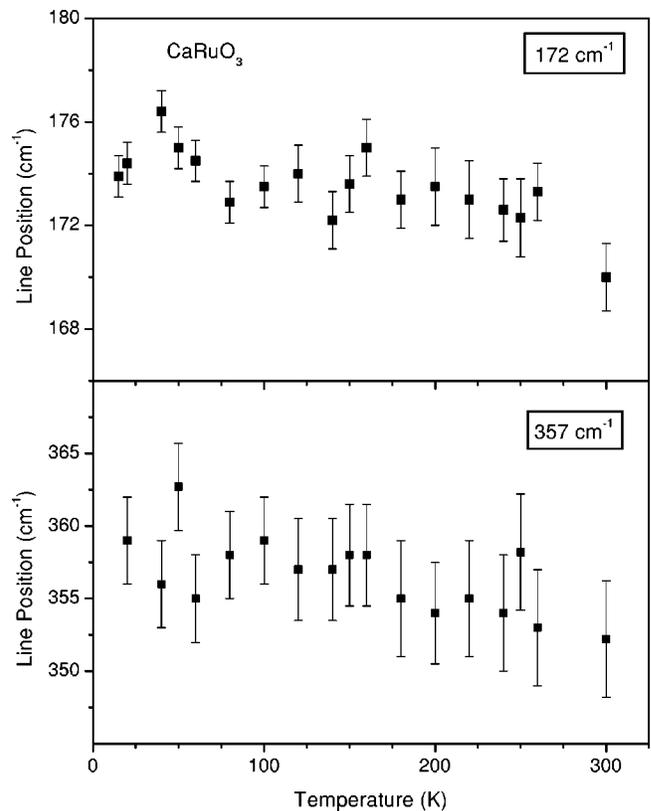


FIG. 4. Temperature dependence of the position of the two most pronounced Raman lines of  $\text{CaRuO}_3$ .

and  $357\text{ cm}^{-1}$  are given in Fig. 4. Unlike  $\text{SrRuO}_3$ ,<sup>28</sup> no anomaly in either line positions or linewidths that could be related to magnetic ordering was observed within the experimental error. Such an anomaly was expected to occur in the case of magnetic ordering. Indeed, it is well known that spin-phonon-coupling-induced phonon renormalization is due to a modulation of the spin-spin exchange integral by lattice vibrations. Ru in  $\text{CaRuO}_3$  is in the same valence (4+), spin state ( $S=1$ ) and crystal-field symmetry as in ferromagnetic  $\text{SrRuO}_3$  and antiferromagnetic  $\text{Ca}_3\text{Ru}_2\text{O}_7$ . The latter two compounds exhibit a strong phonon renormalization at the magnetic phase transition.<sup>28,29</sup> First-principles calculations<sup>9</sup> also confirm the closeness of magnetic moments in  $\text{SrRuO}_3$  and  $\text{CaRuO}_3$ , and therefore spin-spin correlations and corresponding magnetic ordering are what would make a difference. Model calculations<sup>29,32</sup> demonstrated that the degree of rotation of the  $\text{RuO}_6$  octahedra is crucial for establishing one type of magnetic ordering or another. With an increasing rotation angle, the long-range ordering changes from ferromagnetic ( $\text{SrRuO}_3$ ) to antiferromagnetic (expected for  $\text{CaRuO}_3$ ). Therefore, it is plausible to expect renormalization

near the magnetic phase transition at least for phonons that have an eigenvector containing rotational components. The lack of an anomaly with a variation of temperature in the phonon parameters of  $\text{CaRuO}_3$  is consistent with the conclusion of Ref. 5 that  $\text{CaRuO}_3$ , unlike  $\text{SrRuO}_3$  and  $\text{Ca}_3\text{Ru}_2\text{O}_7$ , remains paramagnetic over the whole temperature range covered by our studies.

In conclusion, the polarized Raman spectra of  $\text{CaRuO}_3$  were measured and the symmetry of all observed lines was determined. The lines below  $600\text{ cm}^{-1}$  were assigned to definite zone-center phonon modes by comparison to the spectra of  $\text{SrRuO}_3$  and the predictions of lattice-dynamics calculations. The high-frequency lines above  $700\text{ cm}^{-1}$  are tentatively assigned to non- $\Gamma$ -point phonon modes, activated by the break of translational symmetry. Our results provide no evidence of an effect of magnetic ordering, if present, on the Raman-active vibrations.

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