Raman Study of the Orbital-Phonon Coupling in $LaCoO_3$

A. Ishikawa*
Venture Business Laboratory, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

J. Nohara and S. Sugai
Department of Physics, Faculty of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan
(Received 31 May 2004; published 20 September 2004)

The magnetic state in $LaCoO_3$ changes from the low spin state ($S = 0$) to the mixed state with a thermally excited intermediate spin state (IS) ($S = 1$) above about 50 K. The partially filled e_g orbital in the IS state has a nature of Jahn-Teller (JT) distortion. The cooperative JT distortion causes an orbital order. We found that all Raman active phonon modes are affected by the excitation of IS Co^{3+} ions. Especially, the JT vibration mode shows anomalous temperature dependence.

DOI: 10.1103/PhysRevLett.93.136401 PACS numbers: 71.70.Ej, 63.20.Kr, 78.30.Hv

The orbital degree of freedom in partially filled d-electron orbitals arouses much interest such as orbital order, orbital waves, specific magnetic properties, and insulator-metal transitions. The interactions between orbital excitations and other excitations produce rich physical properties. In the cubic crystal field, $3d$ orbitals split into triply degenerated t_{2g} orbitals and doubly degenerated e_g orbitals. The configuration of occupied orbitals for six electrons causes two magnetic and electronic transitions around 50 K and 500 K [1–11]. The spin state of $LaCoO_3$ changes from the nonmagnetic low spin (LS) ($t_{2g}^6 e_g^0$, $S = 0$) state to the paramagnetic intermediate spin (IS) ($t_{2g}^5 e_g^1$, $S = 1$) state at about 50 K, as temperature increases [3,7,8,10,11]. The temperature dependence of the magnetic susceptibility can be fitted by the thermal excitation of the IS state with the excitation energy of about 180 K. In a pure ionic picture the ground state is the LS state for $\Delta(t_{2g} - e_g) > 3J$ and the high spin (HS) ($t_{2g}^4 e_g^2$, $S = 2$) state for $\Delta(t_{2g} - e_g) < 3J$, where $\Delta(t_{2g} - e_g)$ is the crystal field splitting between t_{2g} and e_g, and J is the intra-atomic exchange interaction. Korotin *et al.*[12] pointed out that the energy of the IS state decreases by the hybridization with the oxygen $2p$ state in the local density approximation + Hubbard U (LDA + U) approach. The energy of the IS state is a little higher than that of the LS state and much lower than the energy of the HS state. The partially occupied e_g orbitals have a strong Jahn-Teller (JT) nature and then the IS state may have an orbital ordering. They calculated that the orbital ordering stabilizes the IS state and causes the insulating property. In their model the transition to the metallic phase above 500 K is caused by the disordering of orbitals. On the other hand Asai *et al.* [8] showed from the temperature dependence of the lattice volume, that the insulator-metal transition is caused by the mixing of the HS state. Mizokawa *et al.* [13] also showed that the IS state is the second lowest in a proper parameter range.

Until lately the orbital order has not been observed in $LaCoO_3$ [14,15], but very recently Maris *et al.* [16] observed the alternate short and long bonds in the ab plane and the medium Co-O bond at the out of plane by x-ray diffraction. It indicates that the cooperative quadrupole JT distortion of the Q_2 type [17] is induced by the e_g orbital ordering. The crystal structure changes from rhombohedral $R\bar{3}c$ (D_{3d}^6) to monoclinic $I2/a$ (C_{2h}^6, $C2/c$ in the standard setting) by the cooperative JT effect [16]. The unit cell of $I2/a$ is twice the unit cell of $R\bar{3}c$. It is known that there are two types of orbital ordering in $KCuF_3$ [18]. In the a-type the $x^2 - z^2$ and $y^2 - z^2$ orbitals are alternately arranged along the x, y, and z directions. On the other hand, in the d type the orbitals are arranged alternately along the x and y axes, but the same orbitals are aligned along the z axis. Korotin *et al.* [12] supposed the d-type orbital order in $LaCoO_3$, but the x-ray diffraction [16] disclosed the a-type orbital order. The shortest Co-O bonds are alternatively arranged along the x and y directions as the Co site moves along the c axis, where $x = [110]$ and $y = [1\bar{1}0]$ in the $I2/a$ structure. Louca and Sarrao[19] also observed the local static JT distortion in the pair density function of neutron scattering. The phonon mode with the same atomic displacement should be strongly affected at the LS-IS transition. Yamaguchi *et al.* [20] observed temperature dependent rise and fall of transverse optical phonon peaks in the infrared spectra and attributed them to the cooperative JT effect.

In order to clarify the orbital-phonon interaction the phonon modes were investigated by Raman scattering. Raman scattering has an advantage to find out the change induced by the orbital states, because the Raman activity of all phonon modes are created by the distortion from the cubic perovskite structure. The quadrupole mode, which has the same displacement as the JT distortion, is Raman active, but not infrared active.

$LaCoO_3$ crystals were synthesized by a solid-state reaction method from La_2O_3 and Co_3O_4 powder at 900°C in air for 12 h. Then the powder was pressed into a rod and sintered in air at 1050°C for 20 h. The rod was transformed into a single crystal by an infrared-radiation-heated floating zone method. The Raman scattering measurement was performed in a quasi-backscattering configuration on fresh cleaved surfaces of $LaCoO_3$ single crystals from 5 K to 300 K. The 514.5 nm Ar ion laser light was focused into the area of $50 \times 500\ \mu m^2$. The laser power was 20 mW.

In the rhombohedrally distorted perovskite structure $R\bar{3}c$, Raman active modes are $A_{1g} + 4E_g$ and the infrared active modes are $3A_{2u} + 5E_u$ [21,22]. The $2A_{1u} + 3A_{2g}$ modes are silent. In the cooperative JT phase of the IS state the number of phonon modes at $k = 0$ roughly doubles because the zone boundary modes are folded back into the $k = 0$ point. The A_{1g} and A_{2g} modes in $R\bar{3}c$ change into the A_g and B_g modes in $I2/a$, respectively. The E_g mode split into A_g and B_g modes. It should be noted that the crystallographic axes changed from $R\bar{3}c$ to $I2/a$. We measured the Raman spectra in the (x, x) and (x, y) polarization configurations, where x and y are crystallographic axes in the pseudocubic structure. Both A_{1g} and E_g modes are active in both polarization configurations in the $R\bar{3}c$ phase. We use the notation A_{1g} and E_g even in the $I2/a$ phase to distinguish the phonon modes.

Figs. 1(b) and 1(c) show the temperature dependence of the (x, x) and (x, y) Raman spectra, respectively. All the peaks have large temperature dependence. Based on the reported phonon energies in the rhombohedrally distorted perovskite $LaMnO_3$, $LaAlO_3$, $PrAlO_3$, and $NdAlO_3$, [21,22] the 261 cm^{-1} (at five K) mode is assigned to the A_{1g} rotational mode of O atoms around the c axis, the 86 cm^{-1} mode to the E_g rotational mode of O atoms around the a and b axes, the 172 cm^{-1} mode to the E_g vibrational mode of La atoms along the a and b axes, the 432 cm^{-1} mode to the E_g bending mode, and the 584 cm^{-1} mode to the E_g quadrupole mode. The atomic displacement of this mode is the same as the JT distortion in the IS state. The atomic displacement of the normal modes is presented by Abrashev *et al.* [22].

All the modes have strong temperature dependence. The intensity of the 86 cm^{-1} peak decreases rapidly as temperature increases from 5 K and 50 K. The peak spreads from 75 to 95 cm^{-1} at 50 K. The peak shifts to 72 cm^{-1} at 60 K and the energy decreases to 61 cm^{-1} at 300 K. The temperature dependence is shown in Fig. 2. The population of the IS state can be presented by the thermal excitation of the energy gap 160 K and the degen-

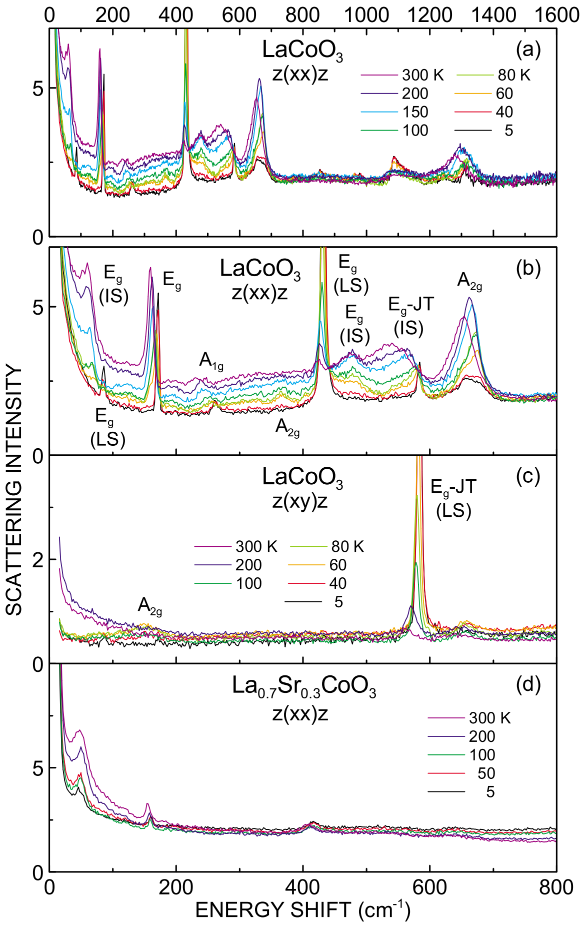

FIG. 1 (color). Temperature dependence of Raman spectra of $LaCoO_3$ and $La_{0.7}Sr_{0.3}CoO_3$. Note that the energy scale of the uppermost panel is twice the other panel.

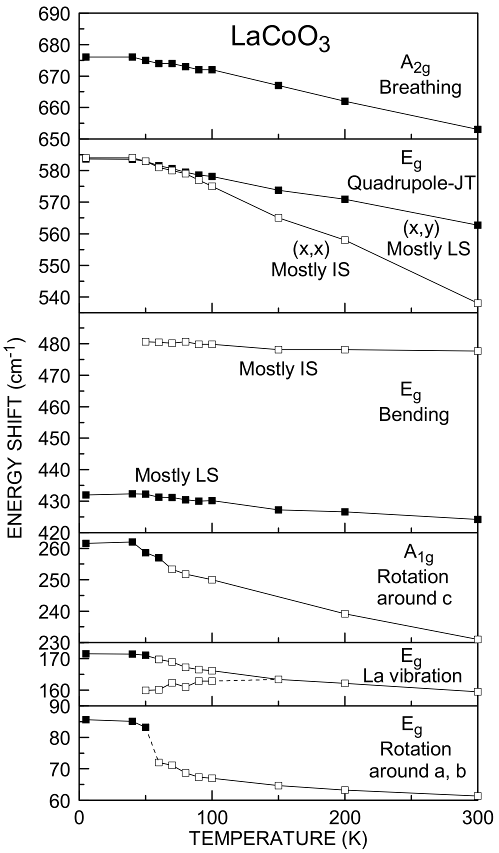

FIG. 2. Temperature dependence of phonon energies.

eracy nine as discussed later. The occupancy of the IS state increases rapidly above 40 K and reaches 84% at 300 K. In the JT phase the nearest neighbor e_g orbitals at Co sites are coupled via the displacement of a sharing O atom. This favors the formation of a cluster. The phase separation occurs if the clustering develops. In $LaCoO_3$ the clustering develops intermediately as discussed later. It is known that there are two types of phonon modes in the mixed crystal [23]. One is a single-mode type that the phonon energy shifts gradually as the mixing ratio changes from the pure compound A to the other compound B. Another is a two-mode type that the two-phonon modes are preserved in the whole concentration range. Many phonon modes in $LaCoO_3$ look like the two-mode type, probably due to the clustering.

The 172 cm^{-1} peak decreases continuously in energy as temperature increases. The peak height is low and the width is broad at 60–100 K where the mixing ratio of LS and IS is close to 50%. A satellite peak is observed at 160 cm^{-1} at 50–100 K and merges into the main peak above 100 K. The energy of the 261 $cm^{-1} A_{1g}$ peak decreases continuously in keeping the intensity constant as temperature increases.

The intensity of the 432 $cm^{-1} E_g$ peak decreases rapidly above 40 K. A broad peak appears at about 480 cm^{-1} at 40 K and the intensity increases as temperature increases. This mode is assigned to the same bending mode in the IS phase. The temperature dependent intensity (area) of the sharp 432 cm^{-1} peak is shown in Fig. 3. This temperature dependence can be fitted well by the occupancy ratio of the LS state given by,

$$p_{LS}(T) = \frac{1}{1 + \eta(2S + 1)e^{-\Delta/k_B T}}, \quad (1)$$

where the energy gap Δ between the LS state and the IS state is 160 K, the spin degeneracy of the IS state is three, and the orbital degeneracy η is three. The temperature dependent peak intensity cannot be fit by $\eta = 1$, which is expected in the split t_{2g} levels by the JT distortion. It suggests that the quasistatic cooperative JT distortion decreases by a fluctuation.

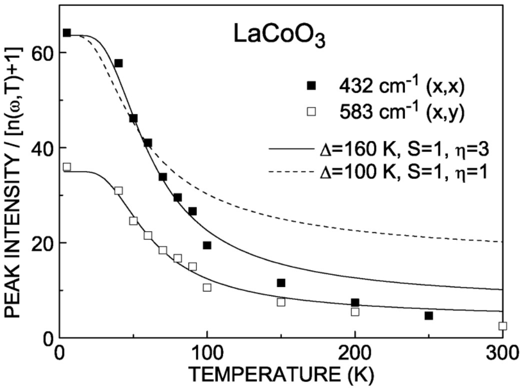

FIG. 3. Temperature dependent intensities in the LS state. The curves denote the occupancy ratio of the LS state calculated by Eq. (1). $n(\omega, T)$ is the Bose statistical factor.

The 584 cm^{-1} E_g peak is strong in the (x, y) spectra at 5 K. The corresponding small peak is observed in the (x, x) spectra at 5 K. This peak is the quadrupole mode the atomic displacement of which is the same as the JT distortion. The intensity in the (x, y) spectra decreases rapidly and the energy decreases a little above 40 K as shown in Figs. 2 and 3. The temperature dependent intensity can be fitted well by the occupancy ratio of the LS state given by Eq. (1). However, the temperature dependence of the peak in (x, x) is very different. The 584 cm^{-1} peak in (x, x) broadens asymmetrically to the low energy side and the peak energy decreases as temperature increases. A broad satellite peak appears near 550 cm^{-1} at 50 K and the intensity increases as temperature increases. The main and the satellite peaks are merged into a large broad peak at 536 cm^{-1} as temperature increases to 300 K. The intensity of this mode is enhanced by the strong electron-phonon interaction with the e_g orbitals. The growing up of the cooperative JT distortion is important for the large softening as shown in Fig. 2. If the cooperative effect does not work, the phonon energy does not change around the individual IS Co^{3+} ions.

Next let us pay attention to the peaks which are small or not detected at 5 K, but increase in intensity at the mixed IS and LS states. Those are the 153 cm^{-1} peak in the (x, y), the 367 cm^{-1} in (x, x), 656 cm^{-1} in (x, x) and (x, y), and 677 cm^{-1} in (x, x) at 50 K. The 153, 367, and 677 cm^{-1} modes are assigned to the A_{2g} modes which are Raman inactive in the rhombohedral $R\bar{3}c$ phase. Those modes become active in the monoclinic $I2/a$. The introduction of randomness by the mixing of the IS and LS phases also relaxes the selection rule. The 153 cm^{-1} mode is the stretching motion of the La atoms. The intensity of the peak takes a maximum at 50 K. The 367 cm^{-1} peak also takes a maximum at 50 K. The 656 cm^{-1} peak increases a little, while the 677 cm^{-1} peak increases rapidly in (x, x) as temperature increases. In many cases the breathing mode has large scattering intensity, even if it is inactive. Therefore the 677 cm^{-1} mode is assigned to the breathing A_{2g} mode.

Figure 1(a) shows the (x, x) spectra in the energy range twice the range of other spectra for the convenience to compare the two-phonon spectra to the single-phonon spectra. The small 854 cm^{-1} peak at 5 K is the two-phonon peak of the 432 $cm^{-1} E_g$ mode. The 1310 and 1351 cm^{-1} peaks at 5 K are the two-phonon peaks of the 656 and the 677 cm^{-1} mode. The 1087 cm^{-1} (at 5 K) peak has no corresponding single-phonon peak in the (x, x) and (x, y) spectra, but the energy is twice the infrared active 543 cm^{-1} (67.3 meV) mode which has large oscillator strength at 9 K in the imaginary part of the dielectric constant [20]. An infrared active mode is Raman inactive in the $R\bar{3}c$ and $I2/a$ phases. The excitation of two Raman inactive modes, however, becomes

Raman active in the two-phonon scattering. Yamaguchi *et al.* [20] showed that this mode has anomalous temperature dependence in the IS state. The temperature dependence of this two-phonon peak in (x, x) spectra is nearly the same as that in the infrared spectra.

Figure 1(d) shows the (x, x) Raman spectra in $La_{0.7}Sr_{0.3}CoO_3$. This crystal undergoes the magnetic transition from ferromagnetic metal to paramagnetic metal at 225 K with the increase of temperature as reported [24–29]. The spin states of both Co^{3+} and Co^{4+} are in the IS state. The sharp phonon peaks at 86, 172, and 432 cm^{-1} (at 5 K) in the LS state of $LaCoO_3$ are not observed in $La_{0.7}Sr_{0.3}CoO_3$. Similarly the 584 cm^{-1} (at 5 K) peak in the (x, y) spectra of the LS state of $LaCoO_3$ is not observed in $La_{0.7}Sr_{0.3}CoO_3$. Some phonon peaks in the IS state of $LaCoO_3$ are observed in $La_{0.7}Sr_{0.3}CoO_3$. The 48, 155, and 409 cm^{-1} (at 300 K) peaks in the IS state correspond to the 61, 160, and 424 cm^{-1} (at 300 K) peak in the IS state of $LaCoO_3$. On the other hand, the broad peaks enhanced by the JT distortion in the IS state of $LaCoO_3$ do not appear in $La_{0.7}Sr_{0.3}CoO_3$. Such modes are the 478 cm^{-1} (at 300 K) bending E_g mode, the 536 cm^{-1} (at 300 K) quadrupole E_g mode, and the 653 cm^{-1} (at 300 K) breathing A_{2g} mode. It indicates that the quasistatic cooperative JT distortion does not occur in the metallic $La_{0.7}Sr_{0.3}CoO_3$. Louca and Sarrao[19] observed the split of the short and long Co-O bonds in the paramagnetic *insulating phase* at room temperature. The present crystal is paramagnetic *metal* above 225 K. The absence of the enhancement suggests that the static JT distortion does not occur in the metallic phase by the rapid change of the orbital state through the interaction with the itinerant carriers. The similar effect was also reported in $RMnO_3$ [30].

The present Raman scattering experiment shows clear change of the phonon mode from the LS state to the IS state in $LaCoO_3$. It can be compared with the change in the infrared active phonons observed by Yamaguchi *et al.* [20]. They assigned the three stretching modes around 540 cm^{-1} to the vibration of an oxygen atom between (1) Co^{3+} atoms of LS and LS, LS and IS $(z^2 - x^2)$, and LS and IS $(z^2 - y^2)$; (2) IS $(z^2 - x^2)$ and IS $(z^2 - x^2)$; and (3) IS $(z^2 - x^2)$ and IS $(z^2 - y^2)$. The decrease of intensity for the mode (1) and the increase of intensity for the modes (2) and (3) was interpreted by the population of thermally excited IS Co^{3+} ions. However, their local mode analysis for only one oxygen atom does not present the normal phonon modes. Louca and Sarrao [19] observed the phonon modes at 177 cm^{-1} (22 meV) and 194 cm^{-1} (24 meV) in the inelastic neutron scattering. These energies are close to the 172 cm^{-1} E_g mode in which La atoms are vibrating.

In summary, the effects of the e_g orbital order on the phonon modes were investigated by Raman scattering in $LaCoO_3$, which has JT distortion in the IS phase, and $La_{0.7}Sr_{0.3}CoO_3$, which does not have JT distortion in the IS ferromagnetic metallic phase. All the Raman active phonon modes change by the excitation of the IS state in $LaCoO_3$. The quadrupole mode, which has the same displacement as the JT distortion, shows the anomalous softening, enhancement, and broadening as the occupancy of the IS state increases. The large softening indicates the growing up of the cooperative JT distortion and the orbital order.

---

*Present address: Department of Physics, Faculty of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan
Electronic address: a_ishikawa@nucc.cc.nagoya-u.ac.jp

[1] R. R. Heikes, R. C. Miller, and R. Mazelsky, Physica (Amsterdam) **30**, 1600 (1964).
[2] G. H. Jonker, J. Appl. Phys. **37**, 1424 (1966).
[3] P. M. Raccah and J. B. Goodenough, Phys. Rev. **155**, 932 (1967).
[4] K. Asai *et al.*, Phys. Rev. B **40**, 10 982 (1989).
[5] M. Itoh *et al.*, J. Phys. Soc. Jpn. **64**, 3967 (1995).
[6] S. Yamaguchi *et al.*, Phys. Rev. B **53**, R2926 (1996).
[7] T. Saitoh *et al.*, Phys. Rev. B **55**, 4257 (1997).
[8] K. Asai *et al.*, J. Phys. Soc. Jpn. **67**, 290 (1998).
[9] Y. Tokura *et al.*, Phys. Rev. B **58**, R1699 (1998).
[10] Y. Kobayashi *et al.*, Phys. Rev. B **62**, 410 (2000).
[11] C. Zobel *et al.*, Phys. Rev. B **66**, 020402(R) (2002).
[12] M. A. Korotin *et al.*, Phys. Rev. B **54**, 5309 (1996).
[13] T. Mizokawa and A. Fujimori, Phys. Rev. B **54**, 5368 (1996).
[14] G. Thornton, B. C. Tofield, and A. W. Hewat, J. Solid State Chem. **61**, 301 (1986).
[15] P. G. Radaelli and S.-W. Cheong, Phys. Rev. B **66**, 094408 (2002).
[16] G. Maris *et al.*, Phys. Rev. B **67**, 224423 (2003).
[17] J. Kanamori, J. Appl. Phys. **31**, 14S (1960).
[18] A. Okazaki, J. Phys. Soc. Jpn. **26**, 870 (1969).
[19] Despina Louca and J. L. Sarrao, Phys. Rev. Lett. **91**, 155501 (2003).
[20] S. Yamaguchi, Y. Okimoto, and Y. Tokura, Phys. Rev. B **55**, R8666 (1997).
[21] E. Granado *et al.*, Phys. Rev. B **58**, 11 435 (1998).
[22] M. V. Abrashev *et al.*, Phys. Rev. B **59**, 4146 (1999).
[23] A. S. Barker, Jr. and A. J. Sievers, Rev. Mod. Phys. **47**, S-2 (1975).
[24] M. Itoh *et al.*, J. Phys. Soc. Jpn. **63**, 1486 (1994).
[25] M. A. Señarís-Rodríguez and J. B. Goodenough, J. Solid State Chem. **118**, 323 (1995).
[26] D. Louca *et al.*, Phys. Rev. B **60**, 10 378 (1999).
[27] M. Paraskevopoulos *et al.*, Phys. Rev. B **63**, 224416 (2001).
[28] S. Tsubouchi, T. Kyômen, and M. Itoh, Phys. Rev. B **67**, 094437 (2003).
[29] J. Wu and C. Leighton, Phys. Rev. B **67**, 174408 (2003).
[30] M. N. Iliev *et al.*, Phys. Rev. B **67**, 212301 (2003).