A Raman study of the temperature-induced low-to-intermediate-spin state transition in LaCoO₃

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Abstract

The effect of the thermally induced spin-state transition on the phonon mode behavior of LaCoO₃ has been investigated by using Raman spectroscopy. The number of observed Raman modes is larger than the number predicted by group theory for a rhombohedrally distorted perovskite structure with the space group \( R\bar{3}c \). There is a strong similarity between the Raman spectrum of LaCoO₃ and LaMnO₃ at ambient conditions due to the Jahn–Teller (J–T) distortion associated with the intermediate-spin (IS) state of Co\(^{3+}\). The J–T distortion splits the external mode associated with La–O vibration into a doublet above the spin-state transition temperature. There is an increase in the anharmonic coupling between the one-phonon states with increase in temperature above the transition temperature, due to the gradual increase in the population of Co\(^{3+}\) in the IS state.

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1. Introduction

The thermally induced spin-state transition in LaCoO₃ has been investigated for nearly five decades, but there are still some aspects which are not fully understood [1–10]. LaCoO₃ exhibits transitions related to spin state changes around 100 and 500 K [2,3]. At the first transition, the magnetic moment increases rapidly to \( 2.5 \mu_B \). It was earlier considered that the increase in the magnetic moment was due to a transition of 50% of the low-spin (LS, \(^1\)A\(_1\); \( t^6_2g^0 \); \( S = 0 \)) Co\(^{3+}\) ions to the high-spin (HS, \(^5\)T\(_2\); \( t^2_2g^2 \); \( S = 2 \)) state. Based on this premise, the second transition was considered to be associated with the ordering of the two spin states. Neutron diffraction studies do not, however, show any change in symmetry in the temperature range close to 500 K [11,12]. Subsequently, dynamic disorder of HS to LS Co\(^{3+}\) was proposed as a plausible explanation [8]. Polarized-neutron scattering measurements showed that the decrease in the magnetization to zero at 10 K was not due to antiferromagnetic ordering, but was due to the disappearance of average magnetic moment [13]. This was confirmed by \(^{59}\)Co and \(^{139}\)La Knight shift measurements as well [14]. Photoemission [15] and X-ray absorption spectroscopy (XAS) [16] studies also indicated that the transition could not be interpreted in terms of the HS–LS transition. Presence of an intermediate-spin (IS) state \((^3\!T_1; \ t^2_2g^1 \); \( S = 1 \)) has since been suggested as an alternative interpretation and the two transitions assigned to thermally activated LS to IS to HS state transitions [17]. Based on LDA + U calculations Korotin et al. [18], have suggested the presence of the IS state with local symmetry lowering and orbital ordering accompanied by a large bandwidth of the \( e_g \) states. The IS state was found to be energetically comparable to the LS state and much more stabilized than the HS state. Saito et al. [16], have analyzed their results from photoemission spectroscopy and XAS based on the LS, IS and HS states, with a gradual LS–IS state transition above \( \sim 90 \) K. The IS state with an asymmetrically filled \( e_g \) level is associated with Jahn–Teller (J–T) distortion [16]. One would therefore expect dynamic J–T distortion to occur arising from the LS–IS transition. Such a distortion may not be detected by diffraction measurements, but phonon spectra should

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provide useful information of the dynamical and local lattice distortions. Optical reflectivity as well as infrared spectroscopic measurements reported in the literature reveal the signature of the IS state [19–22].

Raman spectroscopy is a valuable tool to probe optical phonons, being sensitive to local structural distortions. To the best of our knowledge, there are no known reports on the Raman spectrum across the spin-state transition of LaCoO3. The purpose of the present study is to investigate the phonon mode behavior at the transition. The room temperature Raman spectrum of LaCoO3 is similar to that of LaMnO3 [23] and is not consistent with rhombohedrally distorted perovskite structure. This suggests that the Co 3+ ion is J–T distorted like the Mn 3+ ion, the extra modes appearing in the Raman spectrum are due to this distortion. In the Raman spectrum above the LS–IS transition temperature, we observe two external modes associated with the La–O vibration mode and originating from the J–T distorted CoO6 octahedra. We find that the temperature dependence of the two external modes can be described using a one phonon-coupled model. The coupling between the modes increases with the increase in temperature due to the increasing population of the IS state at high temperatures.

2. Experimental details

Polycrystalline LaCoO3 was prepared by the standard solid-state reaction. La2O3 was preheated in air at 900 °C for 12 h. Then it was mixed with CoC2O4·2H2O and heated to 900 °C for 12 h. The mixture was ground and reheated at 1200 °C for 24 h. Powder X-ray diffraction study shows a single phase pattern. Single crystals of LaCoO3 were grown by the floating zone melting technique by employing SC-M35HD double reflector infrared image furnace (Nichiden Machinery Ltd, Japan). The crystals were characterized by X-ray diffraction and chemical estimation of the oxygen content. Magnetization and resistivity measurements are consistent with the literature. The X-ray diffraction study shows it is a single phase LaCoO3.

Raman measurements were performed in a 90° geometry using a Jobin Yvon TRIAX 550 triple grating spectrometer equipped with a cryogenic charge-coupled device camera, using diode-pumped frequency doubled solid state Nd:YAG laser of 532 nm (Model DPSS 532-400, Coherent Inc., USA). The scattered light was collected using a microscope objective (10 × .25) and fibre optic cable. A super Notch filter (Kaiser Optical Systems, Inc.) was used to eliminate the Rayleigh scattering and residual laser light. The incident laser power was kept below 20 mW focused in a diameter of ~50 μm to avoid the laser heating of the sample. The sample was mounted on the cold finger end of a closed-cycle He cryostat (CTI cryogenics, USA). The sample temperature was measured with an accuracy of ±1 K. The variable Raman spectra were collected in the temperature range of 30–300 K.

3. Results and discussion

Group theoretical analysis gives the following optical phonon modes at the zone center of the rhombohedrally distorted perovskite (R3c) structure of LaCoO3 [19]:

\[
\Gamma(D_{3d}^f) = 2A_{1u} + 3A_{2g} + A_{1d}(R) + 3A_{2d}(IR) + 4E_g(R) + 5E_u(IR)
\]

Thus, LaCoO3 should have five modes (A_{1u} + 4E_g) which are Raman active. Fig. 1 shows the Raman spectrum of LaCoO3 as a function of temperature. We observe 11 modes, at 170, 180, 210, 228, 273, 313, 319, 380, 570, 650 and 750 cm\(^{-1}\) as can be seen from Fig. 1(a). The inset in Fig. 1 shows the expanded spectrum in the 500–700 cm\(^{-1}\) range at 300 K which reveals peaks around 580 and 650 cm\(^{-1}\). The spectrum is much richer than that expected from the rhombohedral distortion of the cubic perovskite structure. We believe that this is due to local lattice

![Fig. 1. Raman spectra of LaCoO3 at different temperatures: (a) 300 K, (b) 120 K, (c) 60 K and (d) 30 K and the inset shows the expanded region 500–700 cm\(^{-1}\) of (a). The asterisks show the new bands at low temperatures.](image-url)
distortion arising from static J–T distortion. Though the crystal was not cut along any specific crystallographic plane, we notice a distinct polarization dependence. As seen from Fig. 2, the modes at 170, 180, 210, 228, 273, 319, 650 and 750 cm\(^{-1}\) appear only in the VV while the others appear in HV configuration. Here, H and V stand, respectively, for parallel and perpendicular polarization of the electric field, with respect to the scattering plane.

In order to understand the Raman spectra of LaCoO\(_3\), it is instructive to examine the Raman spectra of other rhombohedrally distorted perovskites such as LaAlO\(_3\) and LaMnO\(_3\), reported in the literature [23]. LaMnO\(_3\) consists of J–T distorted Mn\(^{3+}\) ions unlike LaAlO\(_3\). This is reflected in the appearance of additional bands in the spectrum of LaMnO\(_3\), but absent in the spectrum of isostructural LaAlO\(_3\) [23]. The spectrum of LaCoO\(_3\) has strong resemblance to that of LaMnO\(_3\) rather than LaAlO\(_3\). This suggests that the Co\(^{3+}\) is in the IS state and is J–T distorted at room temperature. The J–T distortion of the Co\(^{3+}\)–O\(_6\) octahedra lowers the local atomic site symmetry followed by the appearance of extra modes, which is otherwise forbidden in the \(R\bar{3}c\) structure.

Polarization studies show that the peaks at 170 and 180 cm\(^{-1}\) are of \(E_g\) symmetry and assigned to the external mode (La–O vibration), just as in LaMnO\(_3\) and LaAlO\(_3\) [23].

In the latter oxide, there is only one mode at 165 cm\(^{-1}\). The appearance of two modes associated with the La\(^{3+}\) ion can arise from the partial conversion of the LS state to the IS state, also reflected in the variation in the La–O bond distance [24]. As shown in Fig. 3(a), these modes tend to merge around 120 K to give a single vibration mode of La–O bond, the frequency monotonically increases with decreasing in temperature. We believe that the origin of the two \(E_g\) modes is the presence of J–T distortion as well as a short range orbital ordering of undistorted CoO\(_6\) octahedra which affect the local environment of the two La\(^{3+}\) ions. At low temperatures, both the La\(^{3+}\) ions in the \(R\bar{3}c\) unit cell are surrounded by eight LS CoO\(_6\) octahedra. Hence, the vibrational mode frequencies associated with the two La\(^{3+}\) ions in the unit cell are degenerate. With increase in temperature, above LS–IS transition, the LS Co\(^{3+}\) ions partly convert to the J–T distorted (IS) state which lowers the symmetry. This distortion is accompanied by a change in bond length of La–O and Co–O as well as Co–O–Co bond angle [9,24,25]. Since the two La\(^{3+}\) ions in the unit cell are linked through oxygen of the CoO\(_6\) octahedra, the strain

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**Fig. 2.** Polarization dependence of the spectrum of LaCoO\(_3\) at ambient conditions. Upper panel shows the parallel polarization and the lower panel shows cross polarization.

**Fig. 3.** (a) Temperature dependence of the coupled mode. Of the two modes, one at 180 cm\(^{-1}\) shows softening and the other at 170 cm\(^{-1}\) shows hardening followed by merging at 140 K. (b) Variation of the coupling constant with temperature. The coupling strength decreases with decrease in temperature.
induced by the presence of the IS state couples anharmonically to the vibrational mode, lifting the degeneracy. As the temperature is increased, the population of the Co\(^{3+}\) ion in the IS state increases, in turn increasing the anharmonicity. Fig. 3(b) shows this increase in the anharmonic coupling with temperature. We have used the coupled-mode equation, to elucidate the effect of anharmonicity on the two modes to explain the behavior of these modes above 145 K, similar to the one and two-phonon coupling in quartz and AlPO\(_4\) [26,27]

\[
\omega_\pm = \frac{1}{2}(\omega_1 + \omega_2) \pm \frac{1}{2}[\omega_1 - \omega_2]^2 + 4|\omega_1|^{3/2} \tag{1}
\]

Here, \(\omega_1\) and \(\omega_2\) are the frequencies of the two modes and \(\omega_{12}\) is the anharmonic term connecting the two modes. In Fig. 4, we show the fit using the coupled-mode equation to the spectra at the three different temperatures along with the deconvoluted spectra. The mode coupling is consistent with Yamaguchi’s model with two different types of internal

\[
\text{Fig. 4. Deconvoluted spectrum of the coupled modes at three different temperatures. The coupled-mode equation was used to fit the two modes as described in the text. The solid circles represent experimental data, the solid line is the fitting obtained. Dotted lines represent deconvoluted spectra.}
\]

modes associated with the IS or HS sites which start losing their identity below 130 K, leaving the La sites identical [20].

In the 400–700 cm\(^{-1}\) region (see Figs. 1 and 5) we observe the following: (i) there are two broad bands centered around 580 and 650 cm\(^{-1}\), (ii) the line shape of the broad band changes with temperature and (iii) a sharp peak appears around 450 cm\(^{-1}\) below 120 K (Fig. 1(b)–(d)). We believe that the origin of these features is linked to the J–T distortion in LaCoO\(_3\).

The widths and shape of the 580 and 650 cm\(^{-1}\) bands can not be explained with such a simple approach and it is pertinent to examine similar broad bands observed above \(T_c\) in the doped lanthanum manganites. Non-coherent J–T distortion can be small or large. Small lattice perturbation affects the phonon lifetime, causing line broadening. In the case of large distortions, the translational symmetry of the oxygen sublattice can be totally lost in certain crystallographic planes. This relaxes the selection rules and makes all the phonon states of the corresponding phonon branches

\[
\text{Fig. 5. Temperature dependence of the Raman shift of (a) the new band at 450 cm}^{-1}\text{, which appears at 120 K, (b) 580 cm}^{-1}\text{ band which splits into three distinct peaks of which two are shown here and (c) the 650 cm}^{-1}\text{ band which also shows the similar behavior at low temperature.}
\]
to become Raman active. The resulting phonon spectrum will represent a one-phonon density of state. Keeping this in mind, we assume that the density-of-states as the origin of the broad band around 550–700 cm$^{-1}$ (Fig. 1). Such a feature has been observed in LaMnO$_3$ as well [23]. At room temperature, the J–T effect is strong but as one lowers the temperature this effect decreases leading to decrease in the phonon broadening. This shows up as fine structure in the density-of-states at low temperatures in the Raman spectrum, giving rise to new features in the broad band in the 550–700 cm$^{-1}$ range. The appearance of new features as well as the behavior of the bands at below and at 120 K arise from the decrease in the population of the IS state in the mixed state (Fig. 5(b) and (c)). If the fine structure in the Raman spectrum is ignored, the average frequency of the modes shows no anomaly across the transition. This is consistent with the behavior of the high frequency mode in the variable temperature infrared spectra [21].

The temperature variation of the integrated intensity of the broad bands centered around 580 and 650 cm$^{-1}$ is shown in Fig. 6. The intensity increases in the 300–100 K range and decreases below around 100 K, consistent with the decrease in the percentage of total distorted CoO$_6$ octahedra at low temperatures [16]. We also observe a sharp band near 450 cm$^{-1}$ surrounded by the weak satellites at low temperatures (see Figs. 1(c) and 2(b)). Its position is comparable to that of the bending E$_g$ mode in rhombohedral LaMnO$_3$ [23].

4. Conclusion

Raman studies of LaCoO$_3$ suggest the presence of the IS Co$^{3+}$ state above 120 K. The lifting of degeneracy of the internal mode of E$_g$ symmetry associated with La–O bond vibration and the presence of broad bands around 400–700 cm$^{-1}$ can only be explained on the basis of the J–T distortion of the IS Co$^{3+}$ ions. The unusual mode splittings as well as their intensity variation in the 30–300 K range show that the spin-state transition in LaCoO$_3$ takes place around 120 K, which induces the local lattice distortion.

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