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Ryo Fukaya, Nao Yamaya, Tadahiko Ishikawa, Shin-ya Koshihara,
Yoichi Okimoto, Ken Onda, Akira Isayama, Takao Sasagawa
and Kazumasa Horigane

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Picosecond dynamics in layered cobalt perovskites studied by time-resolved Raman spectroscopy

Ryo Fukaya^a, Nao Yamaya^a, Tadahiko Ishikawa^a, Shin-ya Koshihara^a,
Yoichi Okimoto^{*, a}, Ken Onda^b, Akira Isayama^c, Takao Sasagawa^c
and Kazumasa Horigane^d

^a Department of Chemistry, Tokyo Institute of Technology, 2-12-1, Ookayama, Tokyo, 152-8551, Japan

^b Department of Chemistry, Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan

^c Laboratory for Materials and Structures, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama, 226-8503, Japan

^d Research Institute for Interdisciplinary Science, Okayama University, 3-1-1, Tsushimanaka, Okayama, 700-8530, Japan

Current address: Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan (R. Fukaya)

E-mails: ryo.fukaya@kek.jp (R. Fukaya), tishi@chem.titech.ac.jp (T. Ishikawa), skoshi@chem.titech.ac.jp (S.-y. Koshihara), okimoto.yaa@m.titech.ac.jp (Y. Okimoto), konda@chem.kyushu-univ.jp (K. Onda), sasagawa.taa@m.titech.ac.jp (T. Sasagawa), k-horigane@okayama-u.ac.jp (K. Horigane)

Abstract. Picosecond dynamics of the photoexcited charge-ordered perovskite-type cobalt oxides $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$ and $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ were investigated based on time-resolved Raman and reflection spectroscopy. These cobalt oxides show strong Raman scattering at around 700 cm^{-1} , originating from the breathing vibration mode of the CoO_6 octahedron coupled with the checkerboard-type charge ordering of Co^{2+} and Co^{3+} . We performed time-resolved Raman and reflection spectroscopy by photoirradiating with picosecond pulses at 400 nm, exciting the charge transfer (CT) transition from the O $2p$ site to the Co $3d$ site. As a result of the excitation, the Raman intensity of the breathing mode was suppressed by 10% on a similar time scale in the reflectance change without changing the frequency of the mode, directly indicating ultrafast suppression of the order parameter of the charge-ordered state by CT transition.

Keywords. Spin crossover cobaltite, Perovskite-type oxide, Time-resolved spectroscopy, Raman spectroscopy, Femtosecond technology.

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* Corresponding author.

1. Introduction

The spin crossover (SC) phenomenon is a variation of the spin state in a strong ligand field, and is especially observed in materials containing divalent Fe^{2+} or trivalent Co^{3+} ions. These transition metal cations have six d electrons, and when the crystal field is greater than Hund coupling energy, the low spin (LS) state appears in which all the spins occupy t_{2g} levels (t_{2g}^6). By contrast, when the crystal field is weak, a high spin (HS, $t_{2g}^4 e_g^2$) or an intermediate spin (IS, $t_{2g}^5 e_g^1$) state is realized. An interesting point of the SC material is that the external perturbation such as temperature variation, applying pressure, and light illumination can cause the spin state change [1]. Hence, SC systems have attracted much interest as an example of exotic phase control with external stimuli.

As one of the SC materials, perovskite-type cobalt oxides with Co^{3+} ions have been investigated during the past quarter century [2]. A typical SC cobalt example is LaCoO_3 (LCO). The LCO crystal shows the SC transition with changing temperature at around 100 K [3–5]. Although it remains to be seen whether the excited state is an HS or IS state, a lot of experiments to understand the mechanism of the SC phenomena in the LCO system have been reported [2–5].

In addition to LCO, it is known that layered perovskite-type cobalt oxides such as $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$ (LCCO) and $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ (LSCO) also show the SC transition. The crystal structure is the so-called K_2NiF_4 type [6, 7], which is identified with that of the high- T_c cuprate. In LCCO and LSCO, the nominal valence of the cobalt ion is $2.5+$ and $\text{Co}^{2+} : \text{Co}^{3+} = 1 : 1$. Note that in the layered cobaltite there is real-space ordering of Co^{2+} and Co^{3+} as shown in the inset of Figure 1(a), and the charge order makes the cobaltites insulating [8]. X-ray diffraction measurement suggests that the two types of cobalt ions show a checkerboard-type ordering in the ab -plane of the K_2NiF_4 structure below $T_{\text{co}} = 800$ K [9]. Thus, both LCCO and LSCO are highly insulating with the charge ordering at room temperature. In LSCO, some experimental [10, 11] and theoretical works [12] revealed that the electronic states of Co^{2+} and Co^{3+} were HS and LS at room temperature, respectively. A magnetic study [13] suggests that an SC transition occurs in Co^{3+} between the LS and HS state at T_{co} . These results indicate that the layered cobaltites can also be viewed as an SC system like LCO.

Besides the viewpoint of the exotic spin state change, we noticed such SC cobalt oxides as a target of photoactive materials. Some SC materials, especially Fe^{2+} complexes are known to show the perpetual photoinduced spin state transition between the HS and LS state in several iron complexes [1], and furthermore, the detailed dynamics of SC has also recently been investigated using a femtosecond (fs) laser and/or X-ray pulses [14, 15]. From this respect, we have conducted ultrafast spectroscopy on several cobalt perovskites and so far demonstrated some works concerning the photoinduced electronic change involved in the SC phenomena [16–18]. One example is the LSCO system [19], on which we conducted time-resolved fs reflection spectroscopy and revealed that photoirradiation with 400 nm laser pulses could realize an exotic photoexcited state that is different from the thermally induced HS state. By comparing the observed transient absorption spectrum with the theoretically suggested one by using theoretical [20] and experimental reports [21], it is reasonable to consider that the local (polaronic) HS domains appear in response to light, although further experiments other than those on the reflection change on the ultrafast time scale would be needed.

In this paper, we report on the photonic change of Raman scattering in the layered cobaltites, LCCO and LSCO, using picosecond (ps) laser pulses. The layered perovskites show strong breathing Raman mode as depicted in the inset of Figure 1(b) [19, 22]. The symmetry of the mode is A_{1g} in the tetragonal setting ($I4mmm$) and is inactive without the checkerboard-type charge ordering in the ab -plane [22]. Thus, the intensity of the Raman peak reflects the degree of the charge order. We investigate the transient change of the breathing mode after photoirradiating with 400 nm ps

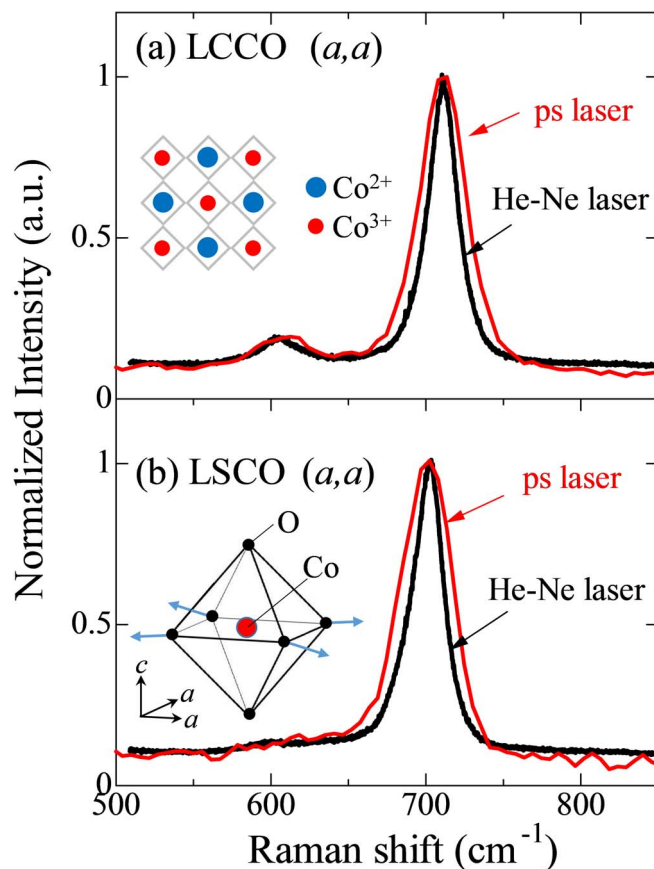


Figure 1. Static Raman spectra in (a) LCCO and (b) LSCO obtained by CW He–Ne laser light (black lines) and the ps laser pulse (red lines). The Raman intensities are normalized with the maximum value. The inset in (a) shows schematics for the ordering of Co^{2+} and Co^{3+} and in (b) for the breathing mode of the CoO_6 octahedron.

laser pulses and discuss the ps dynamics of the photoexcited state in the charge-ordered system, introducing the simultaneous measurement system used for the pump–probe reflection and Raman spectroscopy.

2. Experiment

Single crystal rods of LCCO and LSCO were grown by the floating zone method [6, 7, 19]. The crystal orientation of the grown crystal rods was examined by X-ray diffraction. The *ab*-plane of the crystal was precisely cut from the crystal rods, and the surfaces were polished with alumina powder.

Figure 2(a) shows the schematics of simultaneous measurement system with the pump–probe reflection and Raman spectroscopy. We used a mode-locked Ti-Sapphire laser powered by the regenerative and multipass amplifier (Quantronix Titan-I-3p) with the wavelength of ≈ 800 nm and the pulse width of ≈ 1.5 ps as a light source for probing the reflection and Raman scattering signals, and photoexcitation of the samples. The output beam was divided into pump and probe beams by the beam splitter (BS). By using fundamental beam, we obtained reflection signal and

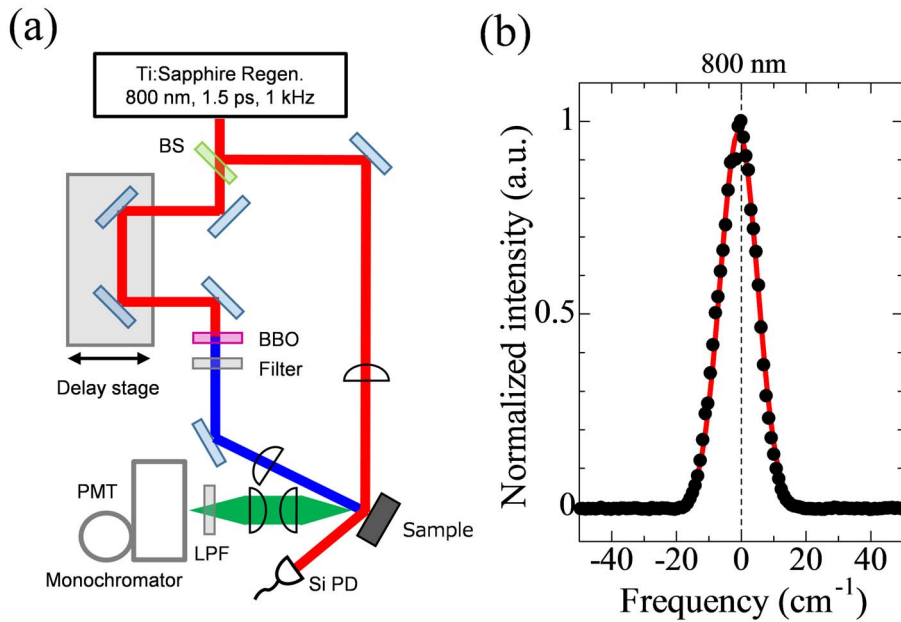


Figure 2. (a) Schematics of the experimental system for the time-resolved reflection and Raman spectroscopy. (b) A spectrum of ps laser pulse used for the time-resolved Raman spectroscopy (black circle). The red line indicates the fitted result based on the Gaussian function.

Raman scattering spectra in the configuration of quasi-backscattering geometry. The reflection signal was detected by silicon photodiode (Si PD). The scattering light through appropriate low-pass filter (LPF) with the edge wavelength at 813.7 nm ($\approx 210.5 \text{ cm}^{-1}$) was dispersed by a single grating monochromator (JASCO CT-25, $f = 250 \text{ mm}$), and then detected with a photomultiplier (PMT, Hamamatsu R2658). The polarization directions of the incident and scattered light were both along the a -axis of the crystal.

To photonically excite the crystals, we used a second harmonic beam (400 nm) generated by $\beta\text{-BaB}_2\text{O}_4$ (BBO) crystal, which excites the charge transfer transition from the O $2p$ band to the empty Co $3d$ band [23]. After the photoexcitation, we measured the transient change of the reflection at 800 nm and the Raman signal scarcely changing the optical configuration, as depicted in Figure 2(a).

First, let us clarify the type of ps laser pulse we used for Raman spectroscopy. Figure 2(b) shows the spectrum of the ps laser pulse used in this work that was obtained by the monochromator shown in Figure 2(a). The peak intensity is normalized with the maximum value. Reflecting the ps pulse width, the spectrum has a finite bandwidth. The red curve shows a fitted result based on the Gaussian function, indicating that the spectral resolution of the time-resolved measurement system is about 13.6 cm^{-1} full width at half maximum (FWHM).

In general, Raman spectroscopy is measured using continuous wave (CW) laser light whose wavelength is well determined. Therefore, it seems that it is difficult to get an exact Raman spectrum by ps laser pulse with a wider bandwidth. In Figures 1(a) and (b), to respond to this problem, we show Raman spectra for LCCO and LSCO obtained by ps laser pulse with the system depicted in Figure 2(a) by the red curves and ones obtained by CW He-Ne laser light and a commercially purchased Raman spectrometer (Jobin Yvon T64000) by the black lines.

As mentioned above, the conspicuous peaks were observed at around 714 cm^{-1} (LCCO) and 700 cm^{-1} (LSCO), which are assigned as the breathing mode of the CoO_6 octahedron [19]. The Raman shift in LCCO is 14 cm^{-1} greater than that in LSCO, indicating that the ionic crystal is more robust in the former than in the latter, partly because the ionic radius of Ca^{2+} is smaller than that of Sr^{2+} . An important parameter is the FWHM of the Raman peak. The values of the FWHM measured with the ps pulse are 36.7 cm^{-1} for LCCO and 39.7 cm^{-1} for LSCO, while those obtained with CW He–Ne laser light are 25.8 cm^{-1} for LCCO and 28.1 cm^{-1} for LSCO, respectively. In both the crystals, the former value with ps pulse was little greater than the latter one with He–Ne laser, but you can see that the ps laser pulse detected the Raman signal well. The breathing mode is so broad that the ps pulse can measure the Raman spectra despite the fact that the bandwidth is larger than that of the CW laser light.

3. Results and discussions

Hereafter, we discuss the ps dynamics of the layered cobaltites. In Figures 3(a) and (b), we show the time dependence of the relative change of reflectivity at 800 nm in LCCO and LSCO. In both cases, the reflectivity suddenly decreases abruptly by about 1% just after the photoirradiation and then gradually decays (the excitation fluence is $\approx 1.7\text{ mJ/cm}^2$). To see the dynamics more quantitatively, we fit the time profile according to the following function:

$$I(t) = I_1 \exp(-t/\tau) + I_2. \quad (1)$$

The first term denotes an exponential decay (τ is the decay time) and the second a constant component relaxed from the first state. The actual fitting was performed with the convolution between $I(t)$ and the response function of the present time-resolved system. The fitted results are shown in Figures 3(a) and (b) with black lines, which well reproduce the experimental data. The estimated values of $\tau = 6.4 \pm 0.84\text{ ps}$ for LCCO and $6.0 \pm 1.1\text{ ps}$ for LSCO. Taking account of the pulse width we used ($\approx 1.5\text{ ps}$), the decaying time is comparable in the two crystals.

In Figures 3(c) and (d), we display time profiles of relative change of Raman scattering intensity at 714 cm^{-1} for LCCO and 700 cm^{-1} for LSCO by red circles, respectively. In the breathing mode depicted in the inset to Figure 2(a), when Co^{2+} and Co^{3+} can be distinguished with the charge ordering, the mode is Raman active. Hence, the cross-section of Raman intensity denotes the degree of the charge ordering in the CoO_2 layer [22]. Similar to the case of the reflection change, the time profiles of Raman intensity also suddenly decreases just after the photoexcitation in both the crystals. The magnitude of the change is more than 10%, directly indicating instant and partial melting of the charge order caused by extra injected electrons due to the CT excitation. For comparison, we plotted the time profiles of reflectivity, which seem to resemble those of Raman intensity change, implying that there are similar dynamics in the electronic change and the charge ordering. To see the photoinduced frequency change of Raman peaks, in Figures 4(a) and (b) we show the transient spectral change (ΔI) just after the photoirradiation. After the photoexcitation, ΔI shows a dip-like decrease at $\approx 714\text{ cm}^{-1}$ (LCCO) and $\approx 700\text{ cm}^{-1}$ (LSCO), which almost correspond to the Raman shift for the breathing mode before the photoexcitation (see Figures 1(a) and (b)), indicating a scarce change of the stiffness of the CoO_6 octahedron in both the crystals at least on the ps time scale.

It is interesting to compare these results with the study using $\approx 10\text{ fs}$ laser pulse performed in LSCO [19]. On the fs time scale, according to the literature, the time profile of the reflectivity of LSCO oscillates from the excitation time to $\approx 500\text{ fs}$, originating from a coherent motion of the breathing mode. The estimated frequency and decay time of the coherent mode are $\approx 680\text{ cm}^{-1}$ and $\approx 410\text{ fs}$, suggesting that softening of the phonon instantly occurs, and the observed softening vanishes within 1 ps. This work reveals the successive dynamics and reveals that after 1 ps, partial

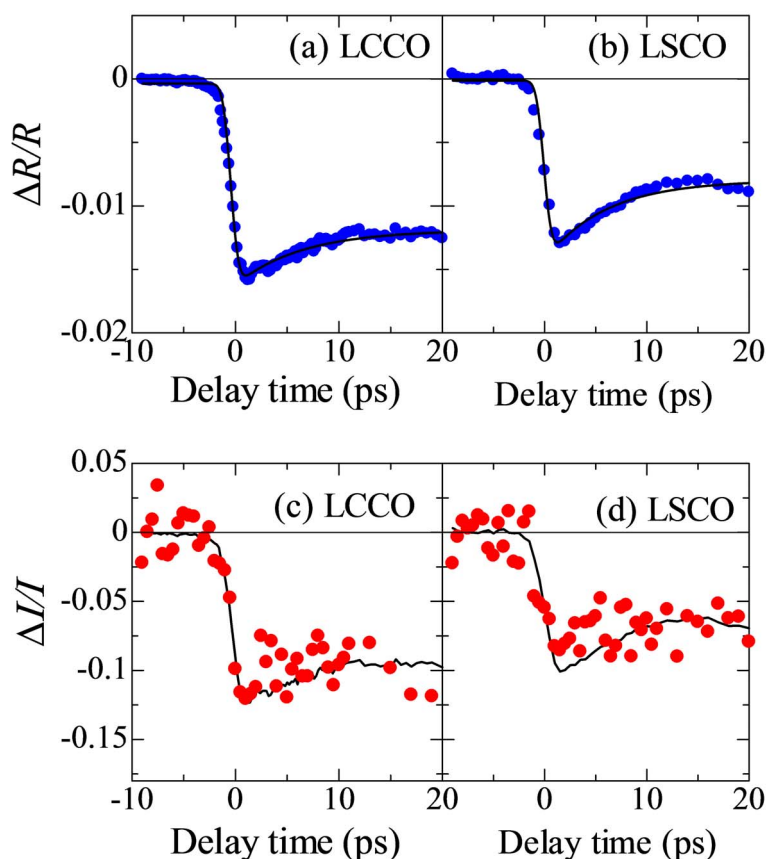


Figure 3. (a, b) Time profiles of relative change of reflectivity at 800 nm (blue circles) after the photoexcitation for LCCO and LSCO. The solid lines denote the fitting result considering the pulse width of ps laser pulse (see text). (c, d) Time profiles of relative change of Raman intensity (red circles) after the photoexcitation for LCCO at 714 cm^{-1} and LSCO at 700 cm^{-1} , respectively. The solid lines show the time profile of reflectivity.

melting of the charge ordering still persists even after the phonon softening has been recovered from the photoexcited state. This conclusion is consistent with the idea of the local formation of HS polarons by light in the layered cobaltites, and some studies such as time-resolved X-ray and/or electron diffraction measurements deserve further investigation.

4. Summary

In summary, we constructed a simultaneous time-resolved measurement system for reflection and Raman scattering using ps laser pulses and investigated the ps dynamics of the perovskite-type layered cobaltites, LCCO, and LSCO, based on pump-probe reflection and Raman spectroscopy. With the CT excitation, the Raman scattering intensity reflecting the degree of the charge ordering decreased within 1 ps by more than 10% without softening the Raman mode reflecting the stiffness of the lattice. Compared with the previous results of fs reflection spectroscopy, the lattice is relaxed on the time scale of 100 fs, while photonic melting of charge order-

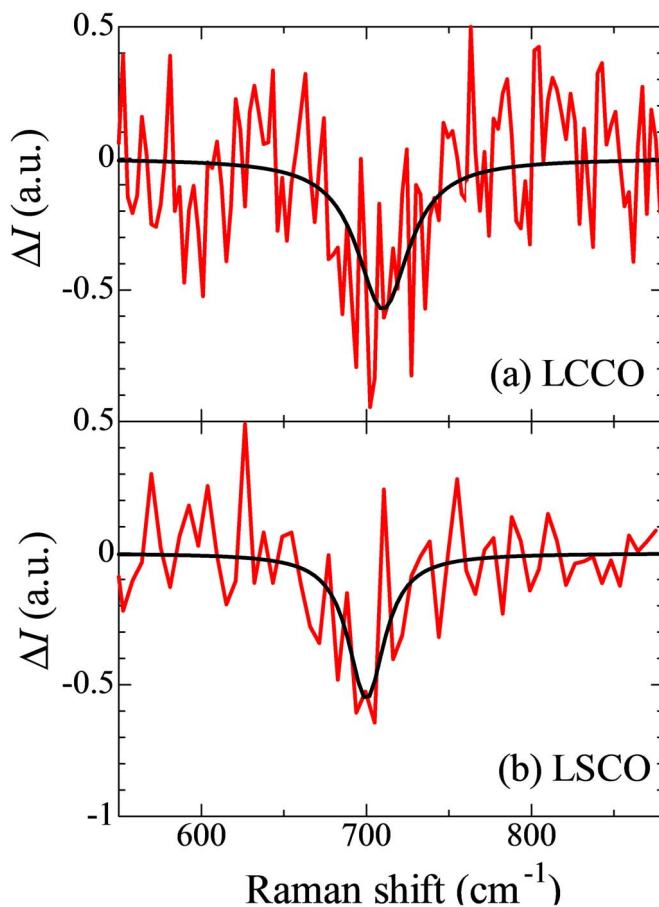


Figure 4. Change of Raman scattering spectrum (solid red line) just after the photoexcitation for (a) LCCO and (b) LSCO. The black lines denote the fitting results using Gaussian function.

ing persists with a longer life time (>1 ps), which not only implies that local spin polaronic state survives on the ps time scale but also reveals a novel aspect of photoinduced SC cobaltites.

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