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3p–3d resonant photoemission study of $LaCoO_3$ at low temperature

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Abstract. We have studied the Co 3d state of $LaCoO_3$ in the temperature range 20–110 K by using resonant photoemission spectroscopy in the Co 3p→3d photoabsorption region. By raising the sample temperature from 20 to 110 K, the Co 3d derived emission near the top of the valence band is transferred to higher binding-energies, and the relative peak intensity of two peaks in the satellite is changed. This is interpreted by a spin-state transition of the Co ion.

1. Introduction

The electronic state of $LaCoO_3$ has been investigated extensively, because this material shows interesting behaviour in both electrical and magnetic properties. A semiconductor-to-metal transition occurs in the temperature range 400–600 K [1–3]. Magnetic measurements [1, 2, 4–7] have revealed a gradual nonmagnetic-to-paramagnetic transition around 90 K and another transition in the range 400–600 K. The magnetic transition around 90 K has been attributed to a low-spin (LS; t_{2g}^6: $^1A_1$)-to-high-spin (HS; $t_{2g}^4e_g^2$: $^5T_2$) transition [4–6]. Recently, several authors have suggested that the transition involves an intermediate-spin (IS; $t_{2g}^5e_g^1$) state instead of the HS state [7–9]. Band-structure calculations have shown that the IS state has lower energy than the HS state, and that the LS, IS and HS states have densities of states quite different from each other [8, 9]. Abbate *et al* have studied x-ray photoabsorption (XA) and x-ray photoemission (XP) spectra of $LaCoO_3$ at various temperatures along with theoretical calculations [10]. They have concluded that, in contrast to the results obtained from magnetic data [4–7], $LaCoO_3$ is in a highly covalent LS state up to 300 K, on the grounds that neither XA nor XP spectra change in the temperature range from 80 to 300 K.

The aim of the present work is to study experimentally the Co 3d state of $LaCoO_3$ in a temperature range 20–110 K by using Co 3p–3d resonant photoemission spectroscopy. The resonant photoemission technique has been proved to be a powerful tool for obtaining information concerning the 3d states of transition-metal compounds [11]. The energy separations between two spin states related to the transition around 90 K are estimated

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¶ Deceased.

to be 27 and 22 meV for LS-to-HS [6] and LS-to-IS [7] models, respectively. The band calculations [8, 9] and cluster-model analysis [7], however, suggest that LS, IS and HS states will give rise to valence-band (VB) photoemission spectra appreciably different from each other. Abbate *et al* performed the experiments down to 80 K [10]. It may be easier to detect differences between photoemission spectra by measuring at lower temperatures.

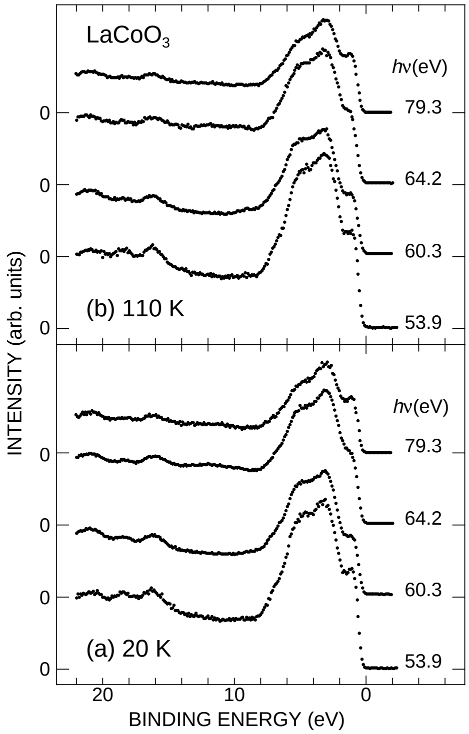

Figure 1. Energy distribution curves of LaCoO$_3$ at (a) 20 K and (b) 110 K measured with four different excitation photon energies around the Co 3p threshold. The photon energies are indicated on the right-hand side of each spectrum. Binding energies are given relative to the Fermi level estimated from a photoemission spectrum of an evaporated gold film.

2. Experimental details

Photoelectron measurements were carried out at beamline 2 of SOR-RING at the Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo. Light from the beamline was monochromatized with a modified Rowland-mount monochromator. Energy distribution of photoelectrons was measured with a double-stage cylindrical mirror analyser (DCMA), which was set at 90° to the photon beam from the monochromator. The incidence angle of the photon beam was set at 45° to the surface normal. Photon energies were calibrated by referring to the energy of Li 1s core-exciton absorption (60.75 eV) of *in situ* evaporated LiCl film [12] and by measuring the Fermi edge of evaporated gold film at various photon energies. The deviation of photon energies was not observed at the end of this experiment. The energy resolution of the monochromator was about 0.1 eV full width at half maximum (FWHM) at a photon energy of 65 eV, and that of the DCMA was kept constant to 0.4 eV FWHM. The overall energy resolution was 0.45 ± 0.05 eV FWHM at 65 eV. Photoelectron spectra shown below are normalized for the number of incident photons, but not corrected for the transmittance of the DCMA. The sample used was single-crystalline $LaCoO_3$, which was grown by an infrared image furnace and cut from an ingot of 4 mm diameter. The sample was examined by x-ray diffraction before the photoemission measurements. The magnetic susceptibility measurement for the present sample was in accord with those reported previously [6, 7], and the Co^{2+} impurity was estimated to be within 1 at.% by the measurement. The sample was cooled through a Cu sample holder connected to a He cryostat. The pressure of the analysis chamber was 5×10^{-9} Pa when the sample was kept at 20 K, and rose to 2×10^{-8} Pa at 110 K. The sample surface was cleaned *in situ* by scraping with a diamond file before measurements. The sample position illuminated by photons was checked by the zeroth-order diffraction of the monochromator after every scraping procedure. The cleanliness of the sample surface was confirmed by the absence of the *dirty peak* well known in photoemission measurements of metal-oxide samples, whose binding energy is expected to be around 10 eV.

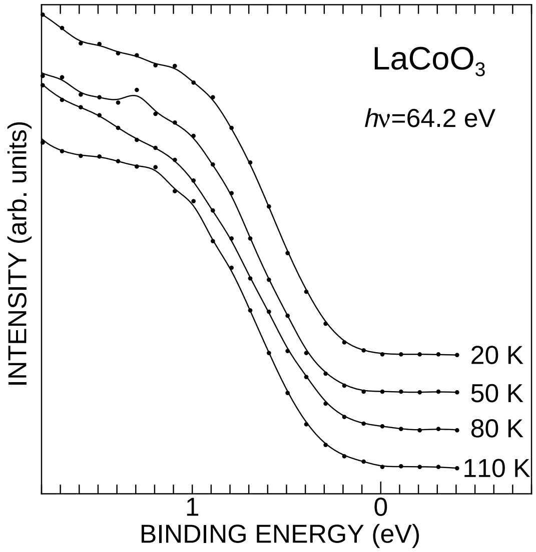

Figure 2. Energy distribution curves near the Fermi level of $LaCoO_3$ at 20, 50, 80 and 110 K measured with a photon energy of 64.2 eV. Each spectrum is normalized at the binding energy of 14 eV.

3. Results and discussion

Figures 1(a) and (b) show energy distribution curves (EDCs) of $LaCoO_3$ at 20 and 110 K, respectively, measured with four different photon energies around the Co 3p threshold. The photon energies are indicated on the right-hand side of each EDC. It is seen that the corresponding spectra in figures 1(a) and (b) are not distinctly different from each other, as observed in XP spectra by Abbate *et al* [10]. The temperature dependence of the Fermi-level position is examined by comparing the 64.2 eV EDCs at 20, 50, 80 and 110 K in figure 2. The EDCs are normalized at the binding energy of 14 eV. The onset of VB is moved toward higher binding energy at 50, 80 and 110 K in comparison with 20 K EDC, but the amount of shift is smaller than 0.1 eV. Similar shifts are also observed in EDCs obtained with photon energies other than 64.2 eV (not shown here). If the sample were charging up by irradiation at 20 K, the shift would be observed in the opposite direction. It is also observed that the onset becomes slightly less distinct at higher temperatures. Since $LaCoO_3$ is semiconducting at this temperature range [1–3, 6], these observations may be due to the thermal activation of carriers. Several photoemission bands are seen in figure 1. The band due to VB, which consists of Co 3d and O 2p, is located in a binding-energy range of 0–9 eV and apparently has three peaks at 1, 3 and 5 eV and a shoulder at 7 eV. The peaks at 16 and 18.5 eV are attributed to La 5p core levels and the one at 21 eV is attributed to O 2s. A satellite caused by many-body effects [7, 10] is observed around 11 eV.

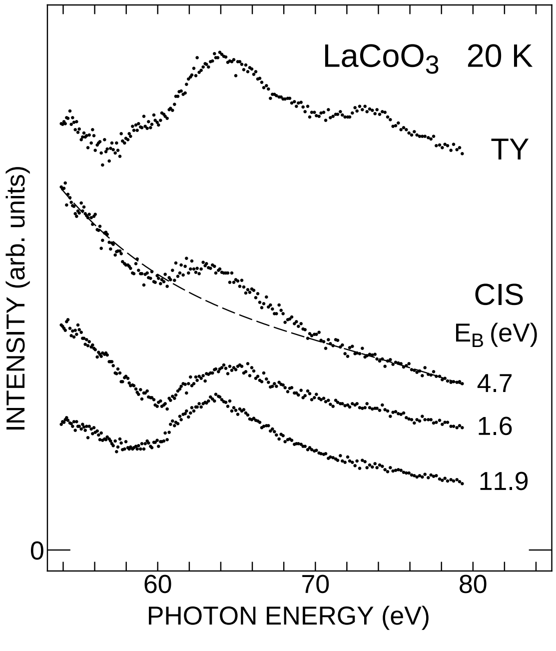

Figure 3. Constant initial state (CIS) spectra obtained at binding energies (E_B) of 1.6, 4.7 and 11.9 eV and a total photoelectric yield (TY) spectrum of $LaCoO_3$. The origin and scale of the ordinates of all CIS spectra are common. An assumed photon energy dependence of the non-resonant component is shown by a broken line.

The enhancement of photoemission at the Co 3p→3d photoexcitation is evident at 1.5 eV and around 11 eV in EDCs. We show the constant initial state (CIS) spectra at 20 K in figure 3, in order to examine the dependence of the enhanced features on photon energy. The binding energies at which CIS spectra were taken are indicated on the right-hand side. A total photoelectric yield (TY) spectrum is also shown in figure 3. The second-order reflection of the La 4d→4f giant absorption is observed at 59 eV in the TY spectrum [13]. The resonant enhancement is clearly seen for the 1.6 eV CIS spectrum: an anti-resonance dip is observed at 60.3 eV and a maximum around 64–65 eV. This indicates that the direct photoemission $3d^n + h\nu \rightarrow 3d^{n-1} + \varepsilon l$ interferes with the indirect one $3d^n + h\nu \rightarrow 3p^5 3d^{n+1} \rightarrow 3d^{n-1} + \varepsilon l$, and that the Co 3d state in $LaCoO_3$ is localized to some extent. Here n is the number of 3d electrons in the initial state, $h\nu$ is an incident photon and εl is an ejected photoelectron. The 11.9 eV CIS spectrum shows an enhancement following TY. The enhancement in the 4.7 eV

CIS spectrum is small, and it follows that the contribution from Co 3d is small at 4.7 eV.

In order to clarify the spectral distribution of the enhanced Co 3d component in EDCs of LaCoO$_3$, we show difference spectra along with on- and off-resonance EDCs at 20 and 110 K in figure 4. In figure 5 we compare difference spectra (dots) at 20, 50, 80 and 110 K. The difference spectra are made by subtracting the off-resonance (60.3 eV) EDC from the on-resonance (64.2 eV) one in the same way as described in [13]. First, the background due to secondary electrons is subtracted from each EDC. Second, the on- and off-resonance EDCs are multiplied by the photoionization cross-section of non-resonant components, mainly O 2p, at each photon energy, to remove the contributions of non-resonant components to the difference spectra. We have assumed that a smooth broken line shown in figure 3 represents the photoionization cross-section of non-resonant components. Figures 4(a) and (b) show the on- and off-resonance EDCs after subtraction of background and multiplication by the photoionization cross-section, and the difference spectra, at 20 and 110 K, respectively.

Since the intrinsic magnetic moment of LaCoO$_3$ is almost zero at 20 K [6, 7], it is expected that the difference spectrum at 20 K reflects the Co 3d state in the LS state. The difference spectrum at 20 K shown in figure 5(a) exhibits an intense peak at 2 eV and a small hump at 6 eV in the VB region. It should be noted that the peak positions of 2 and 6 eV in the difference spectrum do not agree with those of the peaks in the original EDCs or with those in the XP spectra [7, 10] where the photoionization cross-section of Co 3d is larger than that for the present excitation energies. This will be discussed later. Concerning the satellite, there are two peaks at 10 and 12 eV, which were also identified in the previous XP spectra [7, 10].

It is observed in figure 5 that the difference spectrum changes systematically with increasing temperature, although the change in EDCs is not as clear (figure 1). The area intensities of the difference spectra in figure 5(a)–(d) are set equal. By raising the sample temperature, the onset of the peak at 2 eV shifts to higher binding energies, while the onset of the original EDCs does not show such a large shift (figure 2). The loss of the spectral weight at the top of VB is compensated partly by the increase around 6 eV. Saitoh *et al* [7] obtained a difference spectrum at 80 K similar to the spectrum in figure 5(c). Their spectrum also shows the gap between the onsets of the EDC and of the difference spectrum. In their spectrum, the peak near 2 eV is a little lower in binding energy and narrower on the high-energy side than ours. We obtained a difference spectrum which resembles closely that shown in [7] when neglecting the photon-energy dependence of the ionization cross-section of non-resonant components. In the satellite, the peak at 10 eV becomes higher than that at 12 eV with increasing temperature.

The observed temperature dependence of the difference spectrum is not caused by the effect of charging up, because the peaks of EDCs are not shifted, as seen in figure 1. Further, it is not due to any degradation of the sample surface because (i) the dirty peak is not observed, (ii) the binding-energy region where the spectral weight changes by heating is different from the region affected by oxygen adsorption [14], and (iii) the 20 K spectrum was reproduced well after a set of heating experiments. We have also examined difference spectra, which are made *without* subtracting background due to secondary electrons and/or *without* taking account of the photoionization cross-section of non-resonant components. The intensity distribution of difference spectra thus obtained deviated from those shown in figure 5; however, we found similar temperature dependence: spectral weight near the Fermi level transferred to higher binding energies and the change in the relative intensity of the two peaks in the satellite. Thus the temperature dependence of the difference spectrum reflects the change in the electronic structure of LaCoO$_3$ associated with the low-temperature magnetic transition.

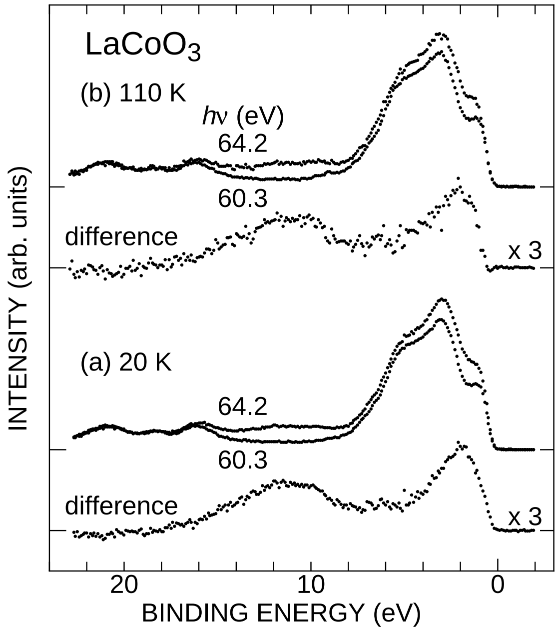

Figure 4. Energy distribution curves of LaCoO$_3$ measured at on- (64.2 eV) and off- (60.3 eV) resonance and difference spectra between these curves at (a) 20 K and (b) 110 K.

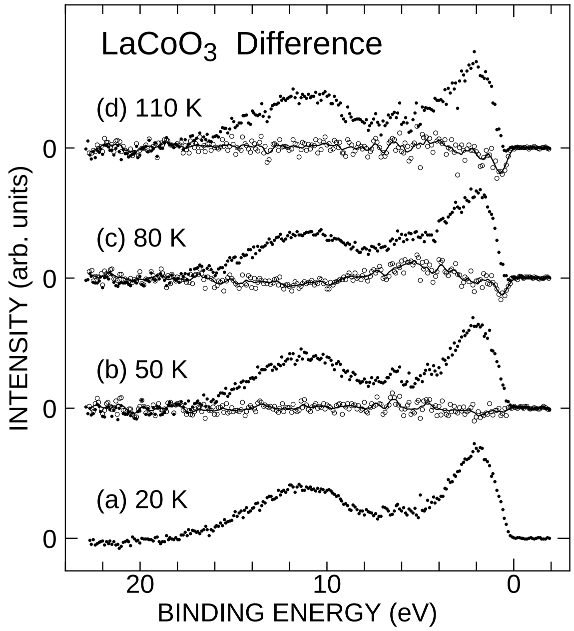

Figure 5. Difference spectra (dots) of LaCoO$_3$ at (a) 20 K, (b) 50 K, (c) 80 K and (d) 110 K. Area intensities of these spectra are set equal. Open circles in (b)–(d) are differences from the difference spectrum at 20 K. Solid curves are guides to the eye.

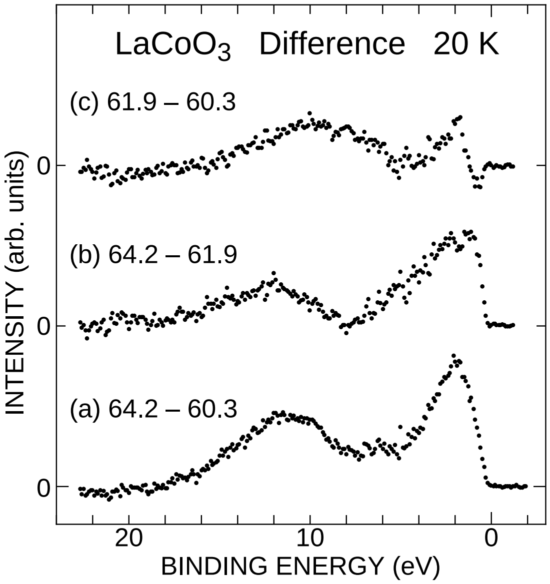

Figure 6. Difference spectra of $LaCoO_3$ at 20 K made by different choices of photon energies at on- and off-resonances. (a) On, 64.2 eV and off, 60.3 eV; (b) on, 64.2 eV and off, 61.9 eV; and (c) on, 61.9 eV and off, 60.3 eV.

Saitoh *et al* have calculated the Co 3d photoemission spectra for LS ($^1A_1$), IS ($^3T_1$) and HS ($^5T_2$) initial states using a full-multiplet configuration-interaction cluster model [7]. We compare the present difference spectra with their calculation. The difference spectrum at 20 K (figure 5(a)) agrees qualitatively with the calculated spectrum for the LS state. The calculation also shows two peaks in the VB region: intense and weak ones near the top and bottom, respectively. These peaks have been located at 1 and ~5 eV in the calculated LS spectrum, so as to reproduce the XP spectrum [7]. The peak energies are somewhat lower than those observed in figure 5(a). The calculation predicts, in addition, a single-peak satellite around 12.5 eV for the LS state, while two peaks are seen for the satellite in figure 5(a).

With increasing temperature, the IS [7–9] or HS [4–6] states are gradually populated following the magnetic transition around 90 K. According to the theoretical calculation by Saitoh *et al* [7], it is expected that the peak intensity near the top of VB decreases while the intensity around the bottom increases, and that the peak at ~10 eV develops when either the IS or the HS state is mixed into the initial state. This is also consistent with the present results, except for the observed loss of the spectral weight near the Fermi level.

As described above, the difference spectra agree qualitatively with the calculated spectra, but disagree in detail. This may be understood by taking account of an effect of Co 3d–O 2p mixing on the resonant photoemission process. Such an effect has been known for other transition-metal compounds, for example, CuO [11]. According to the theoretical calculations [7–10], the Co 3d and O 2p states of $LaCoO_3$ are strongly hybridized. The degree of hybridization for initial orbitals varies from orbital to orbital. Depending on the nature of the wavefunction of the initial orbitals, either constructive or destructive interference between direct 3d emission and an autoionization process takes place [11], and then the photoemission intensity at each binding energy shows different resonance behaviour. This may be responsible for the disagreement of the peak positions in the EDC and the difference spectrum.

The photoexcited state is inseparable in the resonant photoemission process, and thus the nature of the state is also important. Figures 6(a)–(c) show the difference spectra at 20 K made of three different sets of *on*- and *off*-resonance EDCs. The overall shape of the difference spectrum does depend on the selection of photon energies for on- and off-resonance, i.e., on the photoexcited intermediate state. The spectrum in figure 6(a) is the same as that which appears in figure 5(a). In figure 6(b) the peak near the top of VB is now located at ∼1 eV, and the satellite consists of an intense peak around 12 eV and a small hump at 10 eV. The difference spectrum in figure 6(b) is in better agreement with the calculated LS spectrum than that in figure 6(a). On the other hand, the spectrum in figure 6(c) agrees less well with the calculation and shows *negative* enhancement near the Fermi level. Such negative enhancement or destructive interference may be responsible for the apparent gap between the onsets of EDC and of the difference spectrum (figures 2 and 5). Unfortunately we have no prescription for a proper choice of on- and off-resonance energies to obtain the 3d spectrum of $LaCoO_3$. The situation will be better in the Co 2p→3d photoabsorption region because the Co $2p_{3/2}$ and $2p_{1/2}$ absorption bands are well resolved, in contrast to the 3p absorption [10].

4. Summary

Co 3p–3d resonant photoemission spectra have been measured to study the Co 3d electronic state in $LaCoO_3$ in the temperature range 20–110 K. The energy distribution curves do not change significantly in the measured temperature range. However, the difference spectrum shows systematic change with increasing temperature, corresponding to the spin-state transition around 90 K. By raising the sample temperature from 20 to 110 K, the Co 3d spectral weight near the Fermi level is lost and transferred to higher binding energies, and the relative intensity of the peaks in the satellite is changed. The results obtained agree qualitatively with the Co 3d spectra calculated using a cluster model by Saitoh *et al* [7]. However, it should be considered carefully that both initial and photoexcited intermediate states are involved in the resonant photoemission process, when comparing the experimental results with theoretical calculations and examining the models for the low-temperature magnetic transition of $LaCoO_3$.

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