The two-band model of the LaCoO$_3$ semiconductor-metal transition: a spectroscopic evaluation

The two-band model of the LaCoO₃ semiconductor–metal transition: a spectroscopic evaluation

G Thornton†, I W Owen†§ and G P Diakun‡

† Interdisciplinary Research Centre in Surface Science and Department of Chemistry, University of Manchester, Manchester M13 9PL, UK
‡ SERC Daresbury Laboratory, Warrington WA4 4AD, UK

Abstract. Co K-edge near-edge x-ray absorption spectra are reported for RECoO₃ (RE = Y, Ho, Gd, Nd) at 300 K and for LaCoO₃ in the temperature range ($140 \leqslant T \leqslant 830$ K). The pre-edge structure associated with Co 1s → 3d excitation is found to be comparable for all the cobaltates at room temperature, consistent with the proposed similarity of their electronic structure. For LaCoO₃, temperature-dependent changes are observed in the pre-edge structure. These data, when compared with previously published UV photoelectron spectra and calculated density of states, are found to be consistent with a proposed model for the higher-order semiconductor-to-metal transition of LaCoO₃ which involves increased σ^*–π^* band overlap with temperature.

1. Introduction

Transition metal ternary oxides form a group of materials with a wide variety of physical properties, these being dictated to a large extent by the nature of the d electrons in the oxide. The discovery of high-T_c superconductors has given additional impetus to work aimed at providing a more complete understanding of the nd electronic structure of transition metal oxides. Until recently, the rare earth cobaltates (RECoO₃) were thought to represent a unique subset of this group which exhibited a first-order localized-to-itinerant 3d-electron phase transition [1]. This entropy-driven phase change was thought to trigger a semiconductor-to-metal transition in the cobaltates without an accompanying modification to their distorted perovskite structures.

Our re-evaluation of the structural and electronic properties of the cobaltates using neutron diffraction, electrical conductivity and differential thermal analysis measurements produced very different conclusions [2–4]. Our latest work [4] points to a general model for the cobaltes involving a gradual thermally activated population of a delocalized σ^* 3d band (using the symmetry labels defined by Goodenough [1, 5]). This band along with other major bonding interactions arises from orbital overlap within and between the CoO₆ slightly distorted octahedra [4]. Population of the σ^* band leads to the

§ Present address: VSW Scientific Instruments Ltd, Warwick Road South, Old Trafford, Manchester M16 0JT, UK.

higher-order transition between a lower-temperature semiconducting state and a higher-temperature metallic state in the cobaltates over the approximate temperature ranges La: 385–570 K; Nd: 400–590 K; Gd: 490–770 K; Ho: 540–795 K and Y: 575–850 K [4].

Three related models of the transition are consistent with the structural and conductivity data [3, 4], differing only in the extent to which electron correlation effects are assumed to be present. In the simplest model, correlation effects are taken to be relatively small, i.e. $U < W$ where U and W are the d–d Coulomb repulsion energy and d-band width, respectively. In this case the transition would involve a thermal population of the highly antibonding unoccupied σ^* band from the occupied π^* band, resulting in an increase in the Co–O bond length. In turn, this would stabilize the σ^* band relative to π^*, making the $\sigma^* \rightarrow \pi^*$ excitation easier. This model is analogous to the electronic/ structural feedback mechanism deduced for the semiconductor-to-metal transition of Ti_2O_3 [1, 5, 6]. Two related models can be constructed in which the effect of correlation is increased sufficiently to localize the π^* band and to localize the σ^* band in the semiconducting state. Such a discriminating effect of correlation is possible because $W_{\pi^*(t_{2g})} < W_{\sigma^*(e_g)}$. In the itinerant σ^*, localized π^* model the transition mechanism is basically the same as the two-band model described above, except that in the metallic phase the t_{2g} levels would lie within the σ^* band. In the second modified model, the semiconducting phase would consist of localized $\sigma^*(e_g^0)$ and $\pi^*(t_{2g}^6)$ orbitals, the metallic phase being that described for the itinerant σ^*, localized π^* model.

In this paper we attempt to distinguish between these qualitative models of the RECoO$_3$ electronic structure using spectroscopic data. We combine Co K-edge x-ray absorption spectra which probe the unoccupied conduction band states with previously published UV photoelectron spectroscopy (UPS) data on the occupied states [7]. The results are found to be consistent with the weak-correlation two-band model.

2. Experimental details

Co K-edge near-edge structure measurements employed a channel cut Si(220) monochromator on station 7.4 at the SRS, Daresbury Laboratory. At the Co K edge (7710 eV), the monochromator resolution is less than 1 eV. The absorption coefficient was measured in the transmission mode in ~0.3 eV steps, using ion chambers to monitor the incident and transmitted x-ray beam intensity. LaCoO$_3$ measurements employed a combined vacuum furnace/liquid nitrogen cryostat; the remaining cobaltates were measured at room temperature with the samples mounted on double-sided tape.

The cobaltate samples were those used in previously reported neutron diffraction and electrical conductivity measurements [4]. Full details of sample preparation and characterization are given in [4]. For the absorption measurements the samples were diluted with boron nitride. To ensure that the LaCoO$_3$ elevated temperature (470, 670, 830 K) measurements were not affected by sample reduction, an x-ray diffraction study was carried out under similar temperature/vacuum conditions. Only lattice-expansion-derived changes were observed in the diffraction patterns up to the highest temperature measured (770 K).

3. Results and discussion

The near-edge Co K-edge spectra of the cobaltates shown in figure 1 confirm our earlier suggestion [4] that the electronic structure is qualitatively independent of the rare
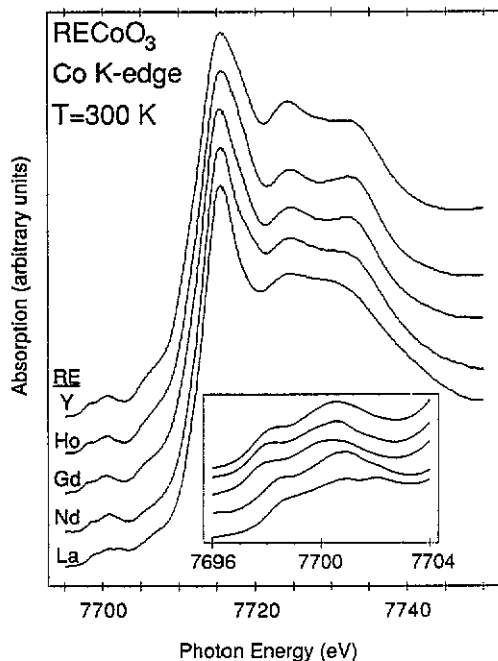
Figure 1. Co K-edge x-ray absorption spectra of RECoO₃ (RE = Y, Ho, Gd, Nd, La) at 300 K. The inset shows an expanded view of the pre-edge region.
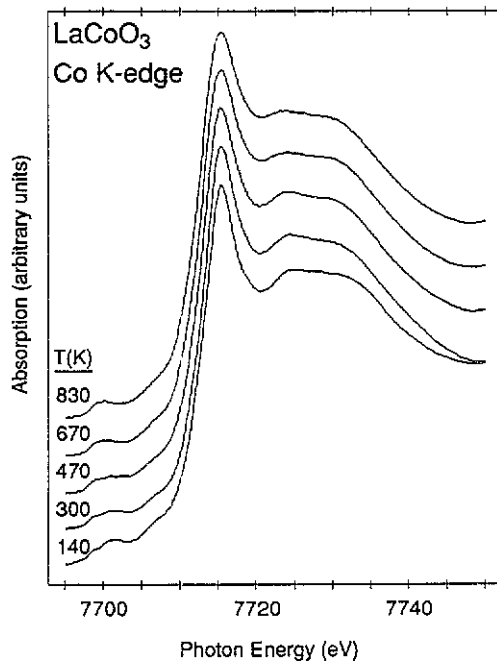
Figure 2. Co K-edge x-ray absorption spectra of LaCoO₃ as a function of temperature.

earth cation. This is indicated by the similar pre-edge structure observed in the region $7696 \leqslant h\nu \leqslant 7704$ eV which arises from Co $1s \rightarrow 3d$ conduction band excitation. Although such transitions are disallowed in the dipole approximation, a finite transition probability comes from both p-state mixing and the quadrupole term [8, 9]. Since structure at higher photon energies mainly reflects multiple-scattering resonances in the continuum [8], the trend observed along the La to Y series will arise from a combination of factors. These include the decreasing (increasing) RE–O (Co–O) bond distance [4] and the differing contributions of RE orbitals to conduction bands well above the Fermi level [10].

Temperature-dependent spectra of LaCoO₃ are shown in figure 2. Here the principal modification to the spectra is a change in shape of the pre-edge region, which figure 3 shows in detail. Overall, as the temperature is raised there is an apparent shift of intensity towards lower photon energy, i.e. towards the Fermi level, E_F. Both static (lattice expansion) and dynamic (increased lattice vibration) structural modifications are candidates for a source of this effect unrelated to the LaCoO₃ phase transition. The former will alter the average Co absorber potential and the latter will give rise to some broadening. In addition, both can induce a redistribution of spectral intensity by modifying the mixing of other orbitals with Co 3d. However, none of these effects is expected to be significant by comparison with the changes observed in figure 3. This was confirmed by the observation of relatively small changes in Ti K-edge (4966 eV) absorption spectra of SrTiO₃ over the temperature range $300 \leqslant T \leqslant 800$ K. SrTiO₃ is a
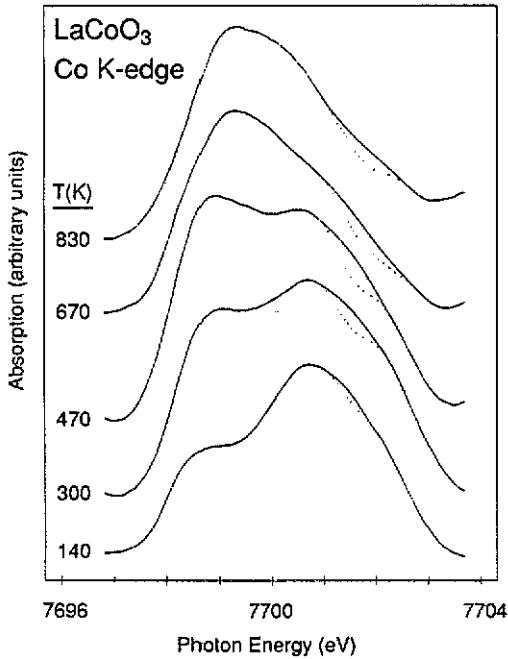
Figure 3. The pre-edge region of figure 2, after background subtraction and correction for an incompletely normalized monochromator glitch present in all spectra (the broken curve represents the uncorrected data).
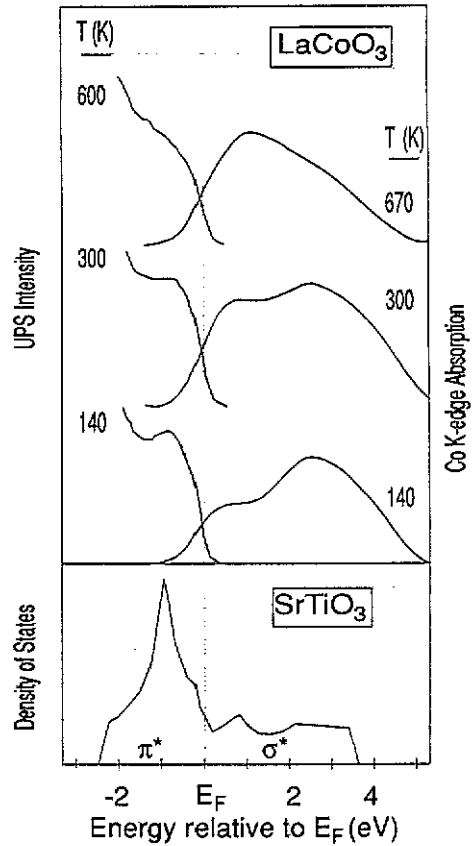
Figure 4. The upper part contains figure 3 spectra on the right and LaCoO$_3$ UPS spectra from [7] on the left. The lower part shows the theoretical conduction band density of states for SrTiO$_3$ [10]. Details of the alignment procedure are described in the text.

cubic perovskite with a similar coefficient of expansion to LaCoO$_3$ [11]. We take this to indicate that the temperature dependence of spectra recorded at $T \geqslant 300$ K in figure 3 is derived from modifications to the electronic structure associated with the LaCoO$_3$ semiconductor–metal transition.

In order to relate the figure 3 spectra to the electronic structure we employ a calculated density of states (DOS) for SrTiO$_3$ [10] in the absence, to our knowledge, of results for LaCoO$_3$. This is justified by the expected similarity of the theoretical one-electron band structures [10]. We also make use of temperature-dependent UV photo-electron spectroscopy (UPS) measurements of LaCoO$_3$ [7], which probe the occupied density of mainly Co 3d states near E_F. These are shown in figure 4, along with our x-ray absorption spectroscopy (XAS) data. The two sets of spectra were aligned at the nominal E_F positions in the 600 K (UPS) and 670 K (XAS) data; the bottom of the calculated σ^* density of states was also aligned at this energy.

The region of the calculated DOS shown in figure 4 contains most of the 3d-orbital contribution to the band structure, which can be separated into π^* (t$_{2g}$ overlap) and σ^*

(e_g overlap) components. In $SrTiO_3$ there is a small ($\sim$0.1 eV) overlap between these components, both of which are unoccupied and are accessible by XAS. XAS measurements by Balzarotti *et al* [12] found reasonable agreement between the Ti K-edge pre-edge structure of $SrTiO_3$ and the calculated DOS. In the low-temperature semiconducting state of $LaCoO_3$ the π^* and σ^* components will be separated by a small gap. The six d electrons of $LaCoO_3$ fill the π^* component, and this region of the DOS can be accessed by UPS. Hence, we could interpret the 140 K data in figure 4 as simply reflecting the one-electron DOS of the occupied π^* bands (UPS) and unoccupied σ^* bands (XAS). The similarity in the position of features in the spectra and calculated DOS is certainly consistent with this interpretation.

On the basis of this simple one-electron band structure model of $LaCoO_3$ we expect the UPS and XAS spectra recorded above the higher-order transition to reflect an overlap of the π^* and σ^* bands. To picture the resultant DOS in a very qualitative fashion, we can consider sliding the π^* and σ^* components shown in figure 4 over one another. This would have the effect of transferring intensity from the occupied DOS (UPS) to the region of the unoccupied DOS just above E_F, and is consistent with the difference between the upper two sets of experimental data in figure 4. Providing an explanation for the difference between the lower two sets of experimental data in figure 4 is less straight-forward in this model. However, it could have a similar origin, since 300 K is at the low-temperature edge of the transition [4]. This view is supported by the apparent similarity of the 140 K XAS spectrum with a spectrum recorded at 60 K [13].

We now turn to the alternative models of the $LaCoO_3$ semiconductor–metal transition and first consider the effect of a correlation-localized $\pi^*(t_{2g}^6)$ band. The fact that a single 3d-derived feature is observed in the UPS spectrum at 140 K is not inconsistent with this picture since it would represent ionization of a filled narrow band. Whether its binding energy is consistent with this model is less clear. The assignment of the UPS spectra of the transition metal monoxides MnO, CoO and NiO is still controversial [13–15], although it is generally agreed that the valence band satellites correspond to unscreened d^{n-1} final states. On this basis, the $LaCoO_3$ UPS feature at around 7 eV binding energy [7] arises from unscreened d^5 final states. The valence band 3d-ionization-derived features near E_F in the monoxide UPS spectra have been ascribed to final states screened by either O 2p (charge transfer) [14, 15] or 3d [16] electrons, depending on the degree of correlation invoked. On the basis of a correlation-localized t_{2g}^6 ground state (with some O 2p mixing) for $LaCoO_3$, the 3d-derived feature seen in figure 4 must represent a d^5 O $2p^{-1}$ final state. Since the position of this state is dependent on U as well as the relative energies of Co 3d and O 2p one-electron orbitals [15], its position at the energy expected from the one-electron DOS would be accidental.

In this itinerant σ^*, localized π^* model, at higher temperatures we expect to see evidence of additional final states in the XAS spectra analogous to those observed in the XAS spectrum of VO_2 above the semiconductor–metal transition [9]. This has as its origin the effect of a core hole on vacant localized electronic states near E_F; in $LaCoO_3$ such states would be generated by transfer of electrons from the narrow π^* band into the σ^* band. Although we cannot rule out the presence of such states in the higher-temperature spectra of figure 3, there is no obvious evidence for their contribution to the spectra.

In the second modified model of the $LaCoO_3$ transition, the low-temperature cor-relation-localized $\sigma^*(e_g^0)$ and $\pi^*(t_{2g}^6)$ bands transform in the metallic phase to collective σ^*, localized π^* bands. In this picture, we expect final state structure in the low-temperature XAS spectra corresponding to a variety of final states involving O 2p and Co

3d t_{2g} hole states. This would be analogous to structure identified in the $L_{2,3}$ edge spectra of NiO [17]. In addition, the XAS final state effects described above for the itinerant σ^*, localized π^* model will be modified in the transition region by the presence of a narrow σ^* band. However, reliably predicting the combined influence of these processes is made difficult by the dipole-disallowed nature of the XAS spectra.

4. Conclusions

In this study we have used temperature-dependent x-ray absorption spectra of $LaCoO_3$ in conjunction with previously published UPS results [7] to assess models of the higher-order semiconductor–metal transition. Although strong correlation effects cannot be entirely ruled out, there is no reason to invoke their presence, the data being consistent with a one-electron DOS picture of the electronic structure. This leads us to propose an itinerant electron model of the transition in which the full π^* and empty σ^* bands in the semiconducting state overlap in the metallic state.

Acknowledgments

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