

Soft-x-ray-absorption studies of the location of extra charges induced by substitution in controlled-valence materials

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We present high-resolution $2p$ x-ray-absorption spectra from $3d$ transition metals M in three series of pseudobinary and pseudoternary oxides. We show how the detailed shape of the multiplet within the spectra can be used to determine the valence of the M ions. The spectra of the early-transition-metal compounds show dramatic changes as a function of substitution due to changes in the M $3d$ occupancy, indicating that the extra holes or electrons are located predominantly at the $3d$ -metal sites. This contrasts strongly with the behavior of the spectra of late-transition-metal compounds, for which the extra charges induced by substitution go to oxygen states.

I. INTRODUCTION

It has long been known that pseudobinary and pseudoternary transition-metal oxides like $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ can be produced with wide concentration ranges, and that these materials show interesting changes in physical properties as a function of composition.¹⁻³ It was generally assumed that replacement of metal ions by other ions with a different valency (e.g., La^{III} by Sr^{II} in $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$) would lead to changes in the transition-metal electronic configuration, and it is for this reason that we write of *controlled valence* (see, e.g., Ref. 4). However, such an ionic model is naive and particularly the advent of high- T_c superconductors has generated the need for more precise information on the changes in electronic structure as a function of substitution.

One of the questions which must be answered is *on which site do the extra electrons or holes reside when substitutions are made?* For this question, soft-x-ray-absorption spectroscopy (XAS) is an ideal tool because of its site- and symmetry-selective character.⁵ This potential has been illustrated by numerous XAS and electron-energy-loss-spectroscopy studies of high- T_c superconductors (see, e.g., Refs. 6 and 7) and late- $3d$ -transition-metals (M) oxides.⁸ Here we extend these studies to early- $3d$ -transition-metal oxides.

In this study we present high-resolution $2p$ x-ray-absorption spectra from $3d$ transition metals in $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ and $\text{Li}_x\text{Zn}_{1-x}\text{V}_2\text{O}_4$ as well as $\text{Li}_x\text{Ni}_{1-x}\text{O}$. The need for high resolution arises because the lifetime broadening of the M $2p$ levels is less than 0.2 eV for Ti and only 0.4 eV for Ni.⁹ Because of the dipole selection rule the spectra are dominated by the $2p \rightarrow 3d$ channel, transitions of the form $2p \rightarrow 4s$ are much weaker and contribute to the background observed at higher energies. In the $2p^5 3d^{n+1}$ final states of these materials, both the Coulomb and exchange interactions between the $2p$ core hole and the $3d$ electrons, as well as the $2p$ - $3d$ - $3d$ multiplet interactions are large by comparison with the dispersion of the $3d$ bands. This leads to strong multiplet effects in the spectra, but the peak shapes are characteristic of the ground-state configuration and the crystal-field strength and symmetry.^{10,11} Thus, by comparing the spectra with atomic-multiplet calculations projected in the appropriate crystal field it is possible to determine the valency of the M ions.^{10,11} The calculation cannot predict the absolute energy position of the multiplet because it does not take proper account of relaxation and screening effects.^{10,11} In the present case the energy scales of the calculated spectra were off by 2–3 eV and the multiplets were shifted by hand to get the best agreement with the experiment. The shift required was not significantly different for ions of different valency.

II. EXPERIMENTAL DETAILS

The Ti and V spectra were taken at BESSY with the SX700/II monochromator of the Freie Universität Berlin.¹² The resolving power $E/\Delta E$ of this monochromator was always higher than 5000. The instrumental resolution ΔE (full width at half maximum) was better than 90 meV at the Ti edges (at 450 eV) and 100 meV at the V edges (at 510 eV). The Ni spectra were taken at LURE with the double-crystal monochromator installed at the SA-21 beam line. The energy resolution ΔE of this monochromator at the Ni edge was approximately 0.4 eV. All the spectra reported here were collected using the total electron yield mode in a vacuum better than 5×10^{-10} Torr.

The samples were polycrystalline pellets prepared by successive cycles of grinding, pressing, and heating in appropriate atmospheres; further details are published elsewhere.¹³ With the exception of some La-rich $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ samples discussed in the text below, no secondary phases were observed in the x-ray diffraction spectra taken to study the homogeneity of the samples. In order to avoid possible oxygen losses during the baking in vacuum the samples were introduced to the analysis chamber by means of a fast-entry-lock system. In addition, the samples were scraped *in situ* with a diamond file to remove surface contamination.

III. RESULTS AND DISCUSSION

The Ti 2*p* spectra of $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ as a function of Sr content are shown in Fig. 1. As throughout this paper, the spectra have been normalized to the maximum peak heights, because absolute normalization of photoyield XAS spectra is not possible. As one replaces Sr by La in $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ the spectra start to show dramatic changes related to a growing Ti^{III} component. To prove this point the spectra for $x=1$ and 0 are compared to theoretical calculations for Ti^{IV} and Ti^{III} in octahedral symmetry.^{10,11} The crystal-field parameter, $10Dq$, was chosen to give the best agreement with the experiment.^{10,11} The spectrum of the parent compound SrTiO_3 corresponds exactly to ground state Ti^{IV} in octahedral symmetry with $10Dq=1.8$ eV. This is somewhat surprising as one would expect covalency effects to play some role here. For the compound LaTiO_3 , where Ti is nominally present as Ti^{III} , the theory gives no explanation for the sharp peak at 457 eV and the shoulder at 462.5 eV. These peaks are in fact due to 5–10% of impurity phases, including TiO_2 , which were found in these materials by x-ray diffraction analysis after the measurements (it is known that La-rich samples are difficult to prepare and to keep pure). However, the rest of the spectrum agrees rather well with the theory for Ti^{III} in octahedral symmetry with $10Dq=1.5$ eV. In conclusion the changes observed in the spectra are related to an increase in the Ti 3*d* occupancy indicating that most of the extra electrons provided by La reside at the Ti site.

The nominal valence of V in ZnV_2O_4 is 3.0 and this increases to 3.5 in LiV_2O_4 . The V 2*p* absorption spectra of $\text{Li}_x\text{Zn}_{1-x}\text{V}_2\text{O}_4$, shown in Fig. 2, bear out this description

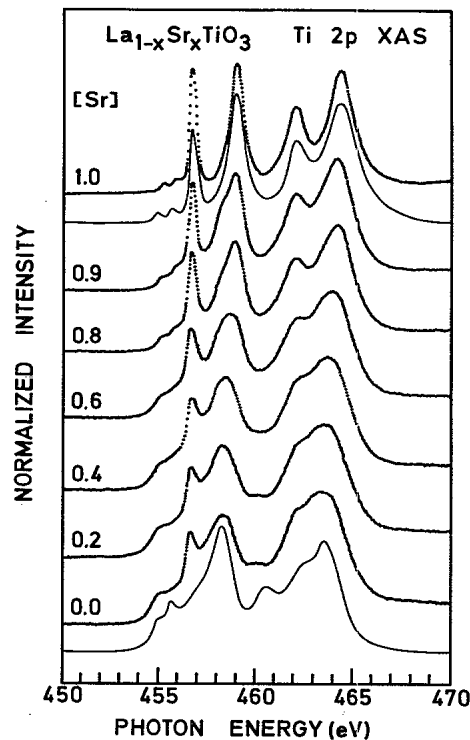


FIG. 1. Ti 2*p* x-ray-absorption spectra of $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ as a function of Sr content. Dots: experimental spectra; solid line: theoretical simulations.

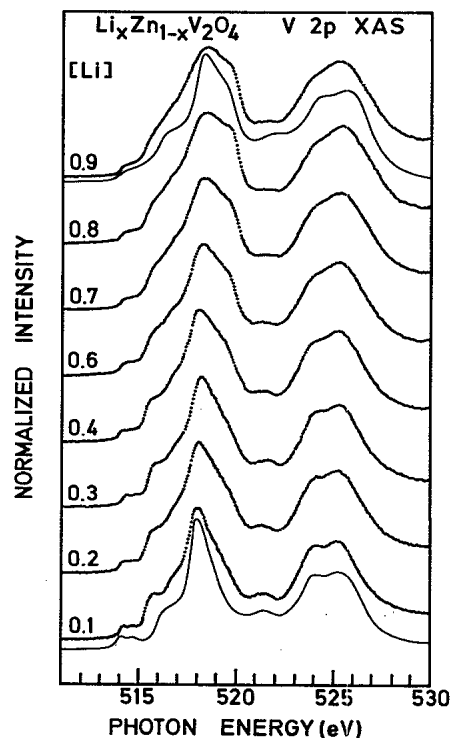


FIG. 2. V 2*p* x-ray-absorption spectra of $\text{Li}_x\text{Zn}_{1-x}\text{V}_2\text{O}_4$ as a function of Li content. Dots: experimental spectra; solid line: theoretical simulations.

to a surprising degree. In the Zn-rich samples (pure ZnV_2O_4 was not available to us) the observed spectra resemble the theoretical calculation for V^{III} ($3d^2$) in an octahedral symmetry with $10Dq = 1.5$ eV. As Zn^{II} is substituted by Li^{I} , the V spectra broaden and shift to higher energy, as expected if the extra holes reside on the V sites. However, the spectrum of LiV_2O_4 cannot be accurately simulated by a mixture of V^{III} and V^{IV} (with $10Dq = 2.4$ eV) as shown in Fig. 2.

There are three possible explanations for the discrepancies observed here, of which we reject the first two. The first is the breakdown of octahedral symmetry at the V site due to random substitution of Zn by Li in the second sphere. We have looked for such effects in noncubic perovskites and we could not find them. The second explanation is that the extra holes also have considerable weight on the oxygen sites. This can be simulated by decreasing the weight of the V^{IV} component in the theoretical spectrum. Such simulations are not better than the one shown in Fig. 2; therefore we reject this explanation also. The third class of explanations involve the hopping of the extra hole on the V site. If the holes are mobile (conductivity measurements show that they are, but on a different time scale), then the spectrum need not be the simple sum of the V^{III} and V^{IV} components.

In sharp contrast to the spectra of the Ti and V controlled-valence materials, the spectra of late transition-metal oxides exhibit only weak changes upon substitution, as illustrated for $\text{Li}_x\text{Ni}_{1-x}\text{O}$ in Fig. 3. Here the minor changes and the extra broadening can be attributed to an increase in covalency, changes in the crystal field, and the presence of additional screening channels.

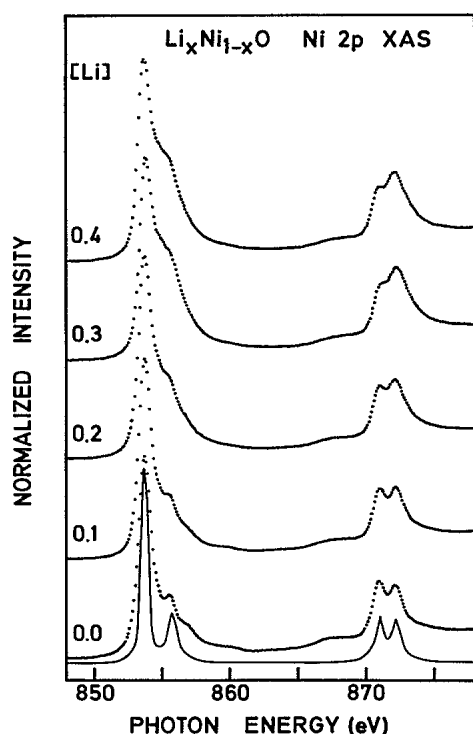


FIG. 3. Ni 2p x-ray-absorption spectra of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ as a function of Li content. Dots: experimental spectra; solid line: theoretical simulations.

But the comparison with theory ($10Dq = 1.5$ eV) in Fig. 3 shows clearly that the Ni ions remain essentially *divalent*. Thus the charge imbalance has to be compensated by the O ions; this was nicely illustrated by Kuiper *et al.*⁸ analyzing the preedge structure in the O 1s absorption spectra. Thus, in this case, we could say that it is the valence of the oxygen which is being *controlled*.

Now we want to address the following question: *are the extra holes compensated by vacancies in the lattice?* Charge compensation by vacancies in the lattice can be important for some systems and for low doping concentration. However, for high doping concentrations charge compensation by vacancies cannot be attained without extensive crystallographic changes. In the present case the composition of the samples is changed over large ranges and the presence of an important amount of vacancies can be ruled out based on the x-ray diffraction evidence.

We have not attempted to make a quantitative determination of the number of extra holes or electrons as a function of doping level. An attempt based on a direct comparison between theory and experiment would only work if the compounds were completely ionic. But it is well known that the bonding in these materials has a partially covalent character, and even worse for the present purpose, the covalency changes across the series. Although it is possible to predict a trend in the covalent contribution to the bonding in the series a quantitative determination is beyond the scope of the present paper. More work will be done in the future to determine the relative ionic-covalent character of the bonding and to make a quantitative estimation of the number of extra charges in these materials.

The results we have presented here illustrate the capability of soft XAS at the 3d transition-metal $L_{2,3}$ edges to identify the sites of extra electrons or holes in controlled-valence materials. This capability depends on improvements in monochromator resolution made possible only in the last two years. It is also to some extent unexpected because the extent to which multiplet interactions and crystal-field effects dominate the form of the spectra has only recently been fully recognized (see, e.g., Refs. 10 and 11). As mentioned above, this is because the size of the $2p$ - $3d$ - $3d$ interactions is large by comparison with the dispersional widths of the individual 3d bands. For these oxides the dispersion of the 3d bands may be derived from the widths of peaks in O 1s XAS spectra, and is often only of the order of 1 eV,¹⁴ while the multiplet interactions spread the $L_{2,3}$ spectra over a range of 5–10 eV.

The recent results obtained with XAS indicate that in general the extra holes or electrons in *controlled-valence materials* reside predominantly in the M 3d bands for Ti and V, but in the O 2p bands for Cu and Ni.^{6–8} Mn and Co oxides should be considered as intermediate cases with extra charges of mixed character due to particularly important covalency effects.^{15,16} There is an apparent division between the transition-metal elements to the left and right of the Periodic Table. However, we think it is time to note another possible correlation based on the much older concept of oxidation-reduction (redox) poten-

tials.¹⁷ Basically strong oxidizing agents have a highly positive redox potential for the reaction $M^{n+} \rightarrow M^{(n+1)+} + e^-$. Ni^{III} or Cu^{III} are very strong oxidizing agents and it is not surprising that the extra holes in controlled-valence compounds of Ni^{II} and Cu^{II} do not reside on the Ni or Cu. By comparison, V^{IV} is a much weaker oxidizing agent, so in the solid the V^{III} ions can easily accommodate an extra hole. However, the redox potential does not take into account correctly solid-state effects like hybridization and the Madelung potential. Therefore, it cannot be applied directly to a particular case unless the redox potentials are available for the specific material. Nevertheless, the tendency in the redox potential is the same as in the charge transfer parameter Δ used in model calculations.^{18,19} This fact allows one to predict general trends and provides an additional source of information which can be used for comparison purposes. It would also be interesting to study controlled-valence materials with more strongly oxidizing agents like Cr^{VI} or even Mn^{VII} and also with unstable valencies like Cr^V or Mn^{VI}.

IV. SUMMARY AND CONCLUSIONS

In summary we have studied, by means of XAS, the valency of first-row transitional metals in pseudobinary

and pseudoternary oxides as a function of substitution. In this respect, the $M 2p$ spectra proved to be a very useful tool due to their high sensitivity to the ground-state configuration combined with the well-known site- and symmetry-selective character of XAS. We found that in the early-transition-metal oxides the extra holes or electrons provided by substitution reside primarily on the M site, in sharp contrast with the behavior of the late-transition-metal where the valency of the M ions does not change.

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