Nonlocal Screening Effects in 2*p* X-Ray Photoemission Spectroscopy Core-Level Line Shapes of Transition Metal Compounds

M. A. van Veenendaal and G. A. Sawatzky

Laboratory of Applied and Solid State Physics, Materials Science Centre, University of Groningen, Nijenborgh 4,
9747 AG Groningen, The Netherlands

(Received 23 December 1992)

We show that the 2*p* core-level line shapes of transition metal (TM) compounds are strongly influenced by the presence of more TM ions. Using calculations of clusters, involving more than one TM ion we explain the double period main line of the Ni 2*p* spectrum of NiO as well as the difference in line shape compared with Ni impurities in MgO and show the sensitivity of the line shape in NiO to surrounding defects. This intersite charge transfer screening also explains the wide asymmetric shape of the main line of the Cu 2*p* spectrum of CuO and the high-T_c compounds.

PACS numbers: 71.10.+x, 71.28.+d, 79.60.−i

X-ray photoemission spectroscopy (XPS) core-level line shapes have played an important role [1,2] in the study of transition metal compounds. However, some important aspects are still not understood. First of all there are unexplained structures in core-level spectra, like the large width of the main line of CuO and the high-T_c compounds [3–5] and the doubly peaked structure of the main line of the Ni 2*p* XPS spectrum of NiO, which cannot be explained by present day methods. Connected with this is the strong dependence of the Ni 2*p* line shape on surface treatment [6,7], demonstrating the importance of core-level line shapes in the study of defects. The second point concerns the use of 2*p* XPS in the evaluation of model Hamiltonian parameters, which leads consistently to low estimations of the charge transfer energy, in the nickel dihalides [1] and especially for the high-T_c compounds [3,4]. In this paper we will show that these discrepancies can be explained by going beyond the Anderson impurity limit and also demonstrate the sensitivity of the line shape to neighboring defects. Although we restrict ourselves here to the description of core-level XPS we believe that the inclusion of more transition metal atoms is important for various kinds of spectroscopy and that the use of single site approximations, like in the Anderson impurity approximation or the small cluster approaches, to describe the electronic structure has severe shortcomings.

For transition metal compounds and the high-T_c superconductors the creation of a core hole in 2*p* XPS is accompanied by a strong Coulomb repulsion with the holes in the localized 3*d* orbitals. The lowest energy state will then be of the form $\underline{2p}3d^{n+1}\underline{X}$, whereas the ground state is of predominantly $3d^n$ character (here $\underline{2p}$ and $\underline{X}$ refer to a core hole and a valence band hole, respectively). In most calculations $\underline{X}$ refers to a hole in the ligand band, e.g., O 2*p* in NiO, because most calculations are limited to a single transition metal ion, as an impurity or surrounded only by ligand atoms in a cluster. The lowest energy valence hole would correspond to the top of the valence band and additional structure of the main line can arise because of the valence ligand band structure. However, in recent valence band studies it has been shown that the lowest energy electron removal states are not of solely ligand character but are part of "bound states," intimately coupled to transition metal *d* holes. Examples are the $^2E\ d^8\underline{L}$ state in NiO [8] or the local $d^9\underline{L}$ singlet [9] in CuO, often referred to as the Zhang-Rice singlet [10]. These states are similar to the so-called multiple charge impurity states in semiconductors, described by Haldane and Anderson [11]. Such states, which can be 0.5 eV above the top of the ligand valence band, can only be included in calculations of transition metal line shapes in systems with more than one transition metal ion. As examples of how this effect can change the core-level spectrum we will discuss the Ni 2*p* XPS spectrum of NiO, and also briefly discuss the results for CuO.

For the clusters used in this paper a reduced basis set of the e_g orbitals and the σ-bonding O 2*p* orbitals has been used. The model Hamiltonian for the various clusters takes into account the hybridization between nearest neighbor Ni 3*d* and O 2*p* orbitals, with t_{pd} proportional to $(pd\sigma)$, and between nearest neighbor O 2*p* orbitals, with $|t_{pp}|=\frac{1}{2}[(pp\pi)-(pp\sigma)]$, in terms of Slater-Koster integrals [12], and includes a Coulomb interaction between two holes on the same nickel atom, with $U_{dd}(^3A_2)=A-8B$ in terms of Racah parameters and an on site core hole 3*d* electron interaction Q. The parameters are given in Table I. The multiplet effects for the $2p^53d^n$ configurations have been neglected. Exact diagonalization methods are used to determine the ground state and core hole spectral line shape.

The $e_g^2(^3A_2)$ ground state of NiO can be written as $\alpha|d^8\rangle+\beta|d^9\underline{L}\rangle+\gamma|d^{10}\underline{L}^2\rangle$. Figure 1 shows the Ni 2*p* spectrum for a NiO$_6$ cluster, as shown in the inset of Fig. 1. As explained above the lowest final state of the spectrum has mainly $3d^9\underline{L}$ character [1]. The finite overlap of the frozen ground state with the core electron removed with the unscreened final state of mainly $3d^8$ character leads to the satellite structure at high binding energies.

TABLE I. Summary of the parameters used in the calculation of the Ni $2p$ and Cu $2p$ spectra. All energies are in eV.

	Ni $2p$	Cu $2p$
Δ	5.5	3.5
Racah A	6.6	6.5
B	0.13	0.15
C	0.60	0.53
$pd\sigma$	1.3	1.5
$pp\sigma$	−0.55	−1.0
$pp\pi$	0.15	0.3
U_{pp}	⋯	6.0
Q	8.0	7.7

The peak in the center has predominantly $3d^{10}\underline{L}^2$ character.

The major discrepancy with experiment, shown in Fig. 2(a), in this explanation is the absence of the well known doubly peaked structure of the main line, for which a large number of explanations have been proposed. In an Anderson impurity like model it could be a result of $3d^{10}\underline{L}^2$ states [12] or $2p^5 3d^9$ multiplet splitting [13]. However when one accepts such an explanation it is difficult to explain that the extra peak is not present for a Ni impurity in MgO [14], where the Ni atom is in a similar octahedral oxygen surrounding. Other explanations assume that the extra peak indicates the presence of various Ni sites as a result of defects usually interpreted as Ni^{3+} ions [15]. This would also explain the strong dependence of the Ni $2p$ spectrum on surface treatment. However, ion sputtering shows an increase of the high binding energy shoulder. This is rather surprising since McKay and Henrich [6] clearly showed that ion sputtering leads to an oxygen deficient surface and therefore a reduction of the Ni valency would be expected.

To study the effects of more Ni atoms we have looked at a Ni_7O_{36} cluster (see the inset in the upper half of Fig. 2). However, inclusion of all valence holes for this cluster would lead to a fourteen particle problem. In order to reduce the size of the calculation the holes of the NiO_6 clusters have been frozen onto the Ni atom, except for the central Ni atom which also contains the core hole. To compensate for the energy increase, resulting from the switching off of the hybridization for these holes, the energy of a single hole in an e_g orbital has been adjusted in such a way that the energy required to add a hole to a NiO_6 cluster with two frozen holes is equivalent to the energy needed to add a hole to a normal NiO_6 cluster with two holes. To ascertain the validity of this approach a calculation for a Ni_2O_{11} cluster using this approximation has been compared with a Ni_2O_{11} calculation with four holes. The agreement between the two calculations is very good.

The Ni $2p$ spectrum for the Ni_7O_{36} cluster is shown in Fig. 2(b). The most important feature of this calculation is the appearance of the extra peak at the high binding energy side of the main line, which is a result of a screening process by an electron that does not come from the

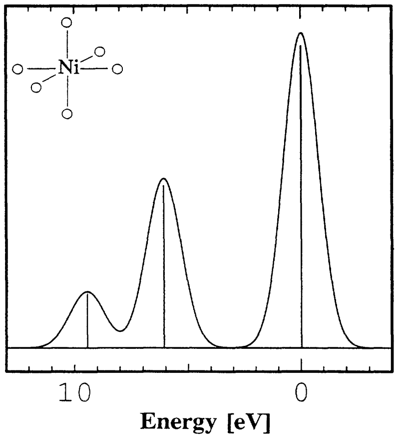

FIG. 1. The Ni $2p$ spectrum calculated for a NiO_6 cluster; see inset.

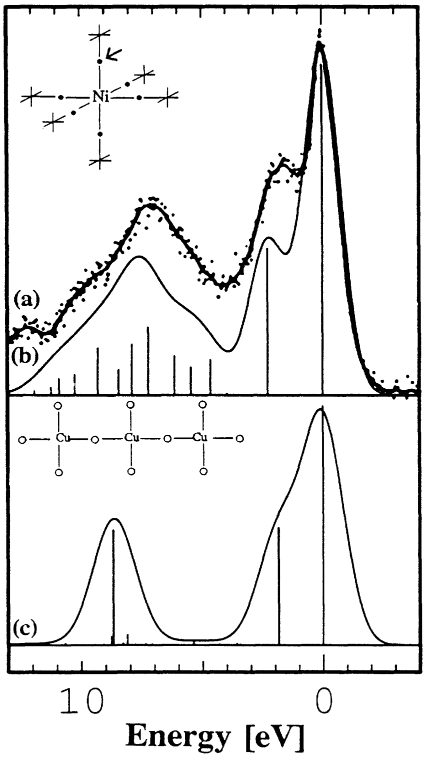

FIG. 2. (a) Experimental Ni $2p^{3/2}$ spectrum of a NiO single crystal, reproduced from Ref. [7]. (b) The Ni $2p$ spectrum calculated for a Ni_7O_{36} cluster. The inset shows this cluster which consists of a Ni atom octahedrically surrounded by six NiO_6 clusters (shown only schematically) on which the holes have been frozen onto the Ni atom, as described in the text. (c) The Cu $2p$ spectrum calculated for a Cu_3O_{10} cluster (see inset) with three holes.

oxygen orbitals around the Ni atom with the core hole, but from a neighboring NiO_6 unit. The NiO_6 unit with the core hole then has a local configuration which has mainly $2\underline{p}3d^9$ character. The extra hole on a neighboring NiO_6 unit without the core hole couples antiferromagnetically to the two other holes, forming a local ^2E symmetry state around that center [8]. Since NiO is a charge transfer insulator extra valence holes reside primarily on the oxygen orbitals around the Ni site, as is clearly confirmed by the O 1s XAS absorption data [16] of $Li_xNi_{1-x}O$.

There is also a clear change in the satellite structure. This should be attributed to the small satellite structure resulting from the intersite charge transfer screening and the larger width of the $3d^{10}\underline{L}^2$ states due to oxygen banding effects. The spectrum shows good agreement with data for high quality single crystals, shown in Fig. 2(a), reproduced from a paper by Neumann and co-workers [7], which also shows a relatively small high binding energy side feature. *Therefore we propose that the doubly peaked main line is intrinsic for bulk NiO* and not a result of defects, but, as we will show below, its intensity can be strongly affected by defects.

These strong nonlocal effects also play a major role for the Cu 2p spectrum of CuO and the high-T_c compounds [17]. The Cu atoms in these compounds are in an approximate square planar symmetry. For this calculation a Cu_3O_{10} cluster (see the inset in the lower half of Fig. 2) with a reduced basis set of $d_{x^2-y^2}$ and σ-bonding O 2p orbitals has been used. The Hamiltonian is similar to that of the nickel cluster, except for the inclusion of a Coulomb interaction on the oxygen orbitals U_{pp}; see Table I. This has been done to use exactly the same parameter set as Eskes and Sawatzky [18] although U_{pp} has little effect on the Cu 2p spectrum.

The calculation for three holes, i.e., one per CuO_4 unit, is shown in Fig. 2(c). It turns out that for formally divalent Cu atoms the nonlocal screening is even energetically more favorable than the local screening. This is a result of the large stabilization energy of the two hole Zhang-Rice singlet [9,10]. The main line has two contributions: The lowest final state is a result of the intersite charge transfer screening leading to a $2\underline{p}3d^{10}$ configuration for the CuO_4 unit with the core hole and a Zhang-Rice singlet on a neighboring CuO_4 unit. The peak at higher binding energies corresponds to the usual assignment for the Anderson impurity limit, i.e., a configuration with mainly $2\underline{p}3d^{10}\underline{L}$ character. The satellite is of predominantly $2\underline{p}3d^9$ character. Thus inclusion of more Cu atoms clearly explains the wide asymmetric shape of the main line. Furthermore it also removes the discrepancy between parameters obtained from Cu 2p core-level spectroscopy compared to valence band spectroscopy. Especially in the study of high-T_c materials by Cu 2p XPS this has often led to low estimations of the value of the charge transfer energy. In all calculations, also for Ni 2p, parameters have been used that are also applicable for the interpretation of valence band spectra [8,18]. For the high-T_c compounds the parameters are also compatible with values obtained from constrained LDA calculations [19,20].

Now that we have found that the presence of other transition metal atoms can have a large effect on the 2p XPS spectra of pure compounds we look at the effect of changes in the surroundings on the balance between the local and the intersite screening. First of all it can make a large difference whether the Ni atom is in the bulk or at the surface. These effects can be simulated by studying a Ni_6O_{30} cluster, as shown in the inset of Fig. 3(a). Contrary to what one might expect the removal of a NiO_6 cluster does not lead to a decrease of the feature due to the intersite screening, but to a relative increase; see Fig. 3(a). This is a result of the fact that the cluster with the core hole also goes from a sixfold to a fivefold coordination, which is energetically less favorable. The removal of an oxygen atom from the Ni_7O_{36} cluster (see the arrow in the upper half of Fig. 2) enables us to study the effect of an oxygen deficiency. As is clear from the dotted line in Fig. 3(a) the increase of the nonlocal contribution to the main line is even enhanced compared to the calculation of the surface.

Second, since in both the local as well as the intersite screening a hole moves onto the ligand orbitals, hybridization is essential to stabilize the hole addition on a

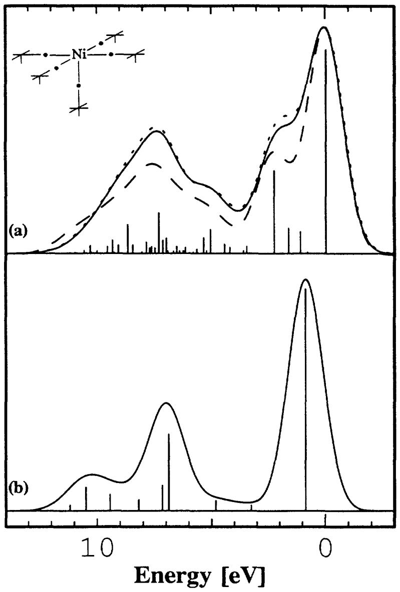

FIG. 3. (a) The solid line shows the Ni 2p spectrum for a Ni_6O_{30} cluster (surface); see inset. The dotted line shows the calculation for an oxygen defect. The same cluster was used as in the inset of Fig. 2(a), but with the oxygen atom indicated by the arrow removed. For comparison the dashed line shows the calculation for the Ni_7O_{36} cluster. The poles belong to the surface calculation. (b) Calculation of the Ni 2p spectrum for a Ni impurity in MgO, as explained in the text.

neighboring cluster relative to the mainly $\underline{2p}3d^{n+1}\underline{L}$ state of the local screening. For example if the neighboring sites of the Ni atom, where the core hole is created, are not occupied by Ni atoms but, e.g., Mg atoms, like in $Ni_xMg_{1-x}O$, there is a much smaller benefit due to hybridization compared to NiO as a result of the absence of *d* orbitals in the valence band region. This can be simulated in the Ni_7O_{36} cluster by raising the *d* orbital energies on the sites other than the Ni atom where the core hole is created (leaving the oxygen orbitals unchanged). As one can see from Fig. 3(b) the doubly peaked structure has completely disappeared. Thus we see that for an isolated Ni atom the Anderson impurity limit is valid in stark contrast with NiO.

A third possibility which influences the balance between local and intersite screening is the valency of neighboring atoms. This is especially important for doped systems like the high-T_c compounds. Removing an electron from a site which already had an extra hole would lead to a state which is at high energy. Using a Cu_3O_{10} cluster [17] it is found that hole doping leads to a preference of the local screening with respect to the intersite screening. An extreme case of this is the formally trivalent compound $NaCuO_2$, where the screening is completely accomplished by electrons from the surrounding ligands.

In conclusion we have shown that the presence of more transition metal atoms can severely influence the shape of the 2*p* photoemission spectra. It turns out that there is a competition between screening electrons coming from the surrounding ligands and electrons coming from ligands around a neighboring transition metal ion. These effects explain the double peaked main line of NiO and the broad asymmetric main line of CuO and the high-T_c compounds. These effects depend strongly on the nature of the surrounding atoms and also on their valency. We also find that the Anderson impurity limit is again restored for a Ni impurity in MgO. Therefore for a large number of compounds the Anderson impurity limit is not the right starting point for the interpretation of the transition metal 2*p* core-level photoemission spectra.

Although we have only described core-level spectroscopy we believe that the influence of different screening channels is also important for other kinds of spectroscopy. Most obvious is x-ray emission spectroscopy where the intermediate level (after emission of the core hole) is equivalent to the final state in Cu 2*p* XPS. But also valence band spectroscopy leads to Coulomb interactions of a size comparable to that of the core hole repulsion in 2*p* XPS. The neglect of nonlocal screening effects and the influence of other transition metal atoms could therefore result in an inadequate description of the electronic structure.

This work was financially supported by the Nederlandse Stichting voor Fundamenteel Onderzoek der Materie (FOM) and the Stichting Scheikundig Onderzoek in Nederland (SON), both financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

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