NATURE OF THE NiO ABSORPTION EDGE WITHIN A SPIN POLARIZED BAND SCHEME

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The NiO complex dielectric function has been calculated for a spin polarized band scheme applied to a D_{3d}^5 crystal structure. All band to band transitions have been allowed irrespective of the selection rules. The particular study of the d to d band transitions shows their existence and attributes the absorption edge to charge transfer between p ligand and d metal orbitals. Only one metal ion is implied in the onset transitions.

1. INTRODUCTION

THE NATURE of the NiO absorption edge has given rise to many interpretations based on theoretical and experimental arguments. The earliest explanation which actually is no longer favoured, assigned the absorption edge to $3d \rightarrow 4s$ orbital promotion transitions (Adler and Feinleib [1], Goodenough [2], Messick et al. [3]). For this purpose the existence of a $2p$ oxygen–$4s$ metal hybridization has been assumed to overcome the selection rules. Meanwhile energy level calculations performed by Johnson et al. [4] and by Messmer et al. [5] lead to consider $2p \rightarrow 4d$ charge transfer processes as the origin of the absorption edge. In fact high resolved photoemission and inverse photoemission measurements realised by Sawatzky and Allen [6] in the X-ray domain and by Hüfner et al. [7] in the UV domain indicate a charge transfer gap occurring between the ligand and the metal. These new measurements confirm previous X-ray and UV photoemission studies carried out by Kim [8]. Even if the charge transfer nature of the absorption edge is now widely accepted, the interpretation of the photoemission data does not reach unanimity. The diversity rests in the number of metal ions participating in the charge transfer mechanism.

Thus Sawatzky and Allen [6] comparing their results with the localized cluster calculation of Fujimori and Minami [9] identify the optical gap with $2d^8 \rightarrow d^8 L^{-1} + d^9$ type transitions. The same conclusion has been adopted by Merlin [10] in his comments on the electronic structure of NiO. Accordingly, their proposed transition process involves excitations between two different nickel ions. On the opposite Hüfner and Riesterer [11] by making comparison between NiO and NiS photoemission results support that the gap is ascribed to excitations of one nickel ion.

The one ion picture is also retained by Terakura et al. [12] for they pointed out that most of the available measurements are coherently explained in this sense.

Considering the theoretical situation, the local cluster approach better accounts for the photoemission results than does the actual spin polarized energy bands. This is mainly due to the fact that the local density formalism predicts too small a d gap: 0.3 eV by Terakura et al. [12], 0.4 eV by Belkhir and Hugel [13]. Nevertheless full adhesion to the cluster model forecasting a two metal ion process is frustrated because it is not in position to interpret the whole experimental data. So it seemed worth while to use the band theory results to get information about the absorption edge from another point of view.

The study of the complex dielectric function is a means to specify the onset excitations since it connects the band structure with the optical properties. Emphasis will be given to the d bands for the calculated electrical gap appears within their associated bands when the D_{3d}^5 crystal structure is taken into account. In the magnetic unit cell, the d electrons are issued from two metal atoms bearing opposite moments. The bands themselves are composed of a lower majority band (with five d electrons) and an upper minority band (with three d electrons). In the spin polarized band structure, the d majority band originates in the first metal atom and the d minority band comes from the second metal atom. It is clear that true d–d transitions cannot occur on selection rules grounds and that consequently the band theory excludes at the beginning the occurrence of two metal transition processes. However, d band transitions are likely to be present owing to the mixed character of the one electron crystal function. The considered d to d band transitions should permit to estimate their importance, either to rule them out or to keep them as

possible candidates for the absorption edge. Further they would give an insight in the gap excitation by inspecting the nature of the non-zero transition matrix elements.

In the second section the results of the band structure and the dielectric function are presented and discussed. The conclusion is drawn in the last section.

2. RESULTS AND DISCUSSIONS

In order to perform the optical properties, a recent spin polarized band structure [13] has been completed by adjoining the $4s$–$4p$ conduction bands. The valence and conduction band structure of NiO is presented in Fig. 1 together with the density of states. We recall that for the valence bands the majority and minority d bands overlap but that a gap of 0.4 eV is opened between the minority e_g and t_{2g} subbands. The Fermi level lies in the minority d subband gap. Another gap of 4.2 eV exists between the upper minority d band

Fig. 2. Contributions to the imaginary part of the complex dielectric function $\varepsilon_2(w)$ for NiO excepting the d to d band transitions.

and the $4s$–$4p$ conduction bands. The overall width of the $4s$–$4p$ band is about 11 eV.

The optical properties have been calculated for all possible types of band to band transitions disregarding the selection rules. For clarity the contribution to the dielectric function have been separated in two parts.

The first contribution presented in Fig. 2 concerns the transitions out of the $2p$ oxygen band to the minority $3d$ band and the $4s$–$4p$ bands. The general features are comparable with the structures observed for the same type of transitions in the NaCl band calculations excepting the $2p$–$3d$ structure which from 4.8 eV in NaCl is shifted to 6.2 eV as a consequence of the spin polarization. The $2p \rightarrow 4s$ structure arises at 13.7 eV (12.6 in NaCl) and the $2p \rightarrow 4p$ structures arise at 19.3 and 20.5 eV (17 and 19.8 in NaCl). The correspondence between the NaCl and spin polarized peaks yields evidence that the one electron picture based on the local density formalism correctly describes the $2p$ and $4s$–$4p$ energy bands. The band approach provides also an assignment to the experimental peaks which do not enter in the calculated cluster diagram. The structures exhibited at 13.5 and 17.3 eV in the measured valence band [6] have been termed as $4s$ and $4p$ peaks following our energy band calculations [13]. These calculated and experimental peaks are in satisfactory accordance with the experimental structures shown by Powell and Spicer [15] at 13, 13.8 and 17.5 eV. Unfortunately the proposed assignment cannot be taken as definitive because the structure around 13.8 eV has received a $3d \rightarrow 4s$ identification by McKay and Henrich [16].

The second contribution displayed on Fig. 3 is devoted to the properly d band transitions. The
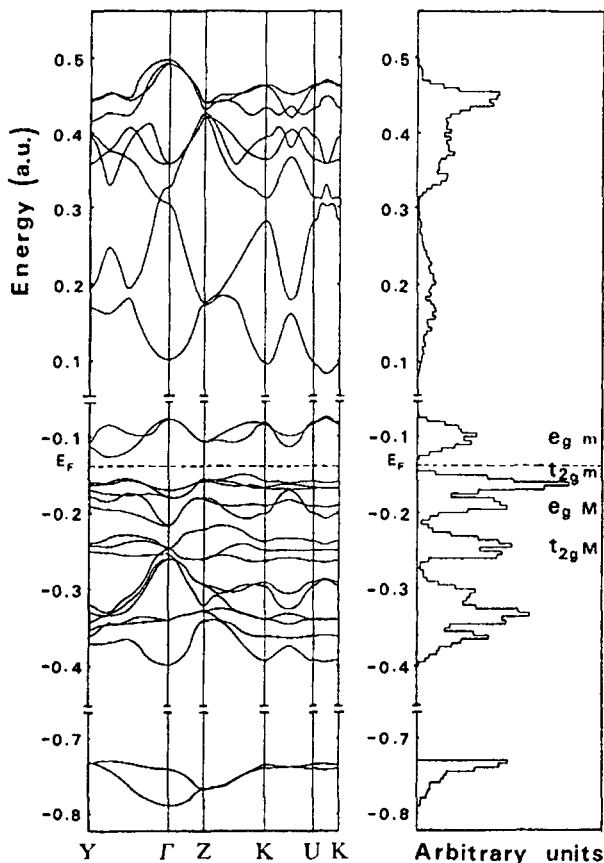

Fig. 1. Spin polarized valence and conduction band structure of NiO together with the density of states. The rhombohedral Brillouin zone has been labelled following Slater [14]. The predominant character of the majority (M) and minority (m) d subbands are indicated.
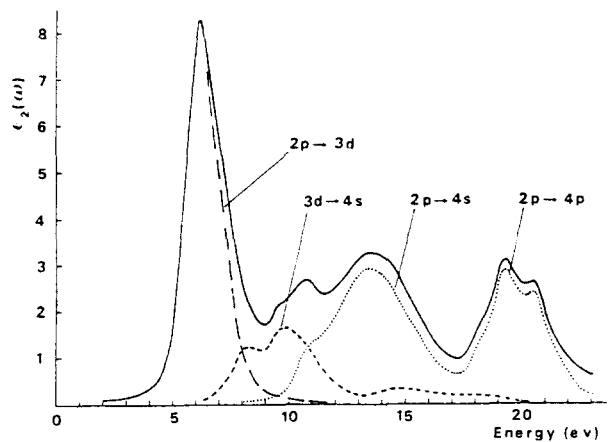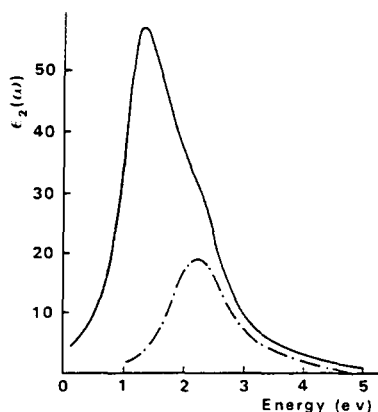
Fig. 3. Contributions to the imaginary part of the complex dielectric function $\varepsilon_2(w)$ for NiO given by the d to d band transitions. The discontinuous line indicates the transitions between the majority and the minority d bands.

noticeable fact is that one prominent peak emerges due to transitions taking place between the minority t_{2g}–e_g subbands. The intensity of that structure makes it reasonable to designate it as responsible for the absorption edge although the energy does not correspond to the well known onset energy (3.8 eV [15]). The minority d bands being generated by d orbitals belonging mainly to one of the metal atom, the observed d transitions imply an intra site process. The presence of a strongly p–d mixing was exposed in [13] conducts then to admit charge transfer type excitations.

A more detailed analysis is pursued by examining the transition matrix elements. The optical absorption refers to one electron crystal functions developed in the LCAO scheme over all the valence and conduction electron orbitals. More specifically, the d crystal functions show particular weight for the $2p$ oxygen orbitals as has been checked on the partial density of states. The dipolar matrix elements between d crystal functions become then effective thanks to the orbital transition elements $\langle p|P|d \rangle$ where p and d stand for localized atomic orbitals and where P represents the impulsion. The latter term describes indeed a charge transfer mechanism and the absorption edge should satisfy both channels: d–p excitations with d belonging to the full t_{2g} and p to the empty e_g minority d subbands or p–d excitations with the inverted process. The resort to the first-neighbour potential integrals will permit to appraise the strength of each channel. The magnitude of the $\langle pV(\text{metal})d \rangle$ potential integral (-1.06 eV) which is about twice the value of the $\langle pV(\text{oxygen})d \rangle$ integral points out the predominance of the $p \rightarrow d$ charge transfer onset excitations.

Transitions between the majority and minority d bands also happen but their manifestation coming out

close to the main peak is occulted. Nevertheless a similar p–d charge transfer figure applies in that case.

The conceptual difference which exists between the cluster approach and the band structure formalism will now be underlined for it influences directly the interpretation of the d–d transitions. The cluster model proposed by Fujimori and Minami [9] and used by Sawatzky and Allen [6] for the NiO electronic valence structure locates from the onset the electrons of sites and deals with intercluster transitions for the non-excitonic processes. The cluster description incorporates local interactions the most important of which are the Coulomb interactions defined in the conventional manner as the energy U required to remove a d electron from one site to another one. The magnitude of U is obtained from a fit over the measured spectrum and asks for a value about 7–9 eV [6]. Within this context the first ionization peak has been ascribed to transitions of charge transfer type between two nickel sites. However that assignment is subjected to the lack of consensus about the U values. Indeed the experimental and theoretical estimations of U, reported in the review paper of Brandow [17], range over a wide interval going from 1 eV to about 16 eV. Although the cluster model finds a satisfactory agreement with the experimental results, the recent suggested low values of U (1–3 eV [12, 16]), if confirmed, are susceptible to modify the two ions interpretation.

In contrast to the electron confinement inherent in the cluster model, the electronic states are presently described by the band theory where the electrons are not attached to a particular site, but are allowed to move over the whole crystal volume. Besides, all the interactions included in the LCAO matrix elements are numerically calculated from the crystal potential and wave functions. The band structure derived from the local density approximation is not able to predict the observed optical gap but for all that does not invalidate the one site picture. The reason is that an improvement of the theoretical gap would only act on the stuctures depending upon the d bands. More, all the spin polarized band structures comprising a gap in the minority d band, like the one of Terakura et al. [12] for example, will conduct to a one ion analysis since the density of states shows a similar organisation.

Finally, the cluster model is constrained by its essence to consider intersite d–d transitions, while the approach in terms of delocalized states discriminates the transitions with respect to the selection rules on one hand and with respect to the strength of the dipolar matrix elements on the other. The resulting one site picture issued from our band structure distinguishes furthermore from the two sites one by its parameter free determination.

3. CONCLUSION

The reality of the *d* band transitions established in the present work is no more than a consequence of the *pd* covalency. The large admixture of the *p* orbitals in the one electron *d* crystal function finds its origin in the D_{3d}^5 crystal symmetry and relaxes the imposed selection rules. As a result the existence of the *d* band transitions modifies a first conclusion based on an NaCl band structure calculation [18], where the onset energy was attributed to the excitations between the $2p$ oxygen and the $3d$ metal bands. These transitions still occur but at higher energies than in the NaCl symmetry as the overall *d* bands have been enlarged and split by the exchange potential. What remains unchanged is the characterisation of the absorption edge in terms of *pd* interatomic charge transfer.

The spin polarized band structure results propose an answer to the dilemma caused by the interpretation of the absorption edge relative to the one or two metal ions picture. Within the dipolar approximation the lowest band to band energies in NiO correspond to the minority $t_{2g}-e_g$ subbands excitations. As such, they generate the absorption edge although presently their energies are not in agreement with the experimental values. In spite of that restriction, these transitions reveal to give the most significant contribution to the dielectric function and involve undoubtly only one metal ion. Thus the theoretical approach confirms the conclusion adopted by the authors who privileged the one ion picture. Nevertheless further work has to be undertaken to evaluate the possibility of enhancing the separation between the *d* minority subbands.

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