Calculated optical curve for spin polarized MnO

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A spin polarized band structure has been used to calculate the dielectric function of MnO. It appears that d to d band transitions are at the origin of the absorption edge owing to the pd mixing. Like NiO, the onset excitations are of $p \rightarrow d$ charge transfer character. Only one metal ion is implied in the transfer process.

Introduction

Among the transition metal monoxides MnO sets the least problems when the electronic structure is described within the spin polarized band scheme. This is essentially the result of the atomic exchange which opens a consequent gap (2.2 eV, Belkhir and Hugel [1]) between the full majority and the empty minority d bands. Since the antiferromagnetic unit cell of D_{3d}^5 symmetry contains two metal ions, "majority" labels an electron in a metal ion with the spin parallel to the atomic moment, whereas "minority" labels an electron in a metal ion with the spin and atomic moment antiparallel. The presence of the forbidden band confirms the pre-eminence of the spin polarized approach with respect to the NaCl crystal structure where no d band separation can be induced by the crystal field (Mattheiss [2]). Concerning the optical properties, the absorption edge has been found around 3.8 eV (Iskenderov et al. [3], Hufmann et al. [4]) and the first maximum in the reflectance curves arises at 4.7 eV (Messick et al. [5], Ksendzov et al. [6]). Below the absorption edge the structures have been assigned to excitonic crystal field transitions between $3d$ states [3, 4]. Just above, Ksendzov et al. [6] concluded that transitions from the $3d$ bands to the conduction bands give rise to the singularities observed in the first part of the reflectance curve.

In contrast, the examination of the band structure conducts, on energy grounds, to consider transitions out of the majority d bands to the minority d bands as the most likely to generate the absorption edge. Pure d metal

intersite dipolar transitions cannot be envisaged because they are precluded by the selection rules. The remaining possibility is to ask if the mixing between p and d orbitals in the one electron crystal function is sufficient to give an observable manifestation in the dielectric function. The study of the dielectric function will serve to provide assignments for the structures which can be put in correspondence with the experimental spectrum.

Compared to NiO, MnO has received less experimental and theoretical attention. Despite the large amount of efforts devoted to NiO, the controversy about the interpretation of the onset energy in terms of one or two ions process is not settled (see for instance Merlin [7], Williams et al. [8]). It is only admitted that the onset mechanism corresponds to a $p \rightarrow d$ charge transfer excitation.

The purpose of our work is to take advantage of the information of the band results in order to furnish an independent interpretation of the optical spectra and to specify the nature of the absorption edge.

Results

Figure 1 presents the spin polarized valence and conduction bands of MnO obtained by extending a previous work [1] to the $4s$ and $4p$ metal functions. As mentionned in the introduction, the significant feature is the presence of the 2.2 eV d gap containing the Fermi level. The p and d band organisation is in qualitative agreement with the antiferromagnetic structure calculations of Wilson [9], Andersen et al. [10], and Terakura et al. [11]. The difference between the various spin polarized bands lies in the width of the d gap and in the additional splitting of the majority and minority d bands into e_g and t_{2g} subbands. While the calculated structures exhibit comparable band profiles, there is less in common with the experimental electronic structure of [6]. The major points of divergence are the very broad forbidden bandwidth (4.7 eV) and the fact that the $3d$ minority band
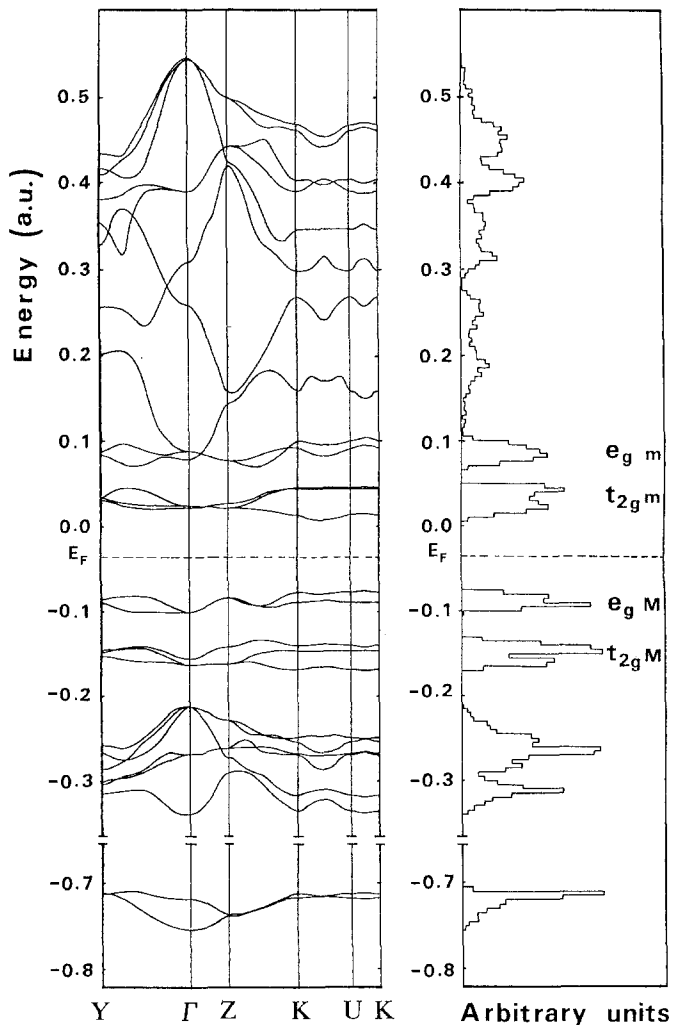
Fig. 1. Spin polarized valence and conduction band structure of MnO together with the density of states. The predominant symmetry character of the $3d$ bands are indicated. M and m refer respectively to the majority and minority d subbands

merges in the $4s-4p$ conduction band. The discrepancy between the calculated and experimental structure will have implications in the identification of the optical structures.

The comparison between the spin polarized D_{3d}^5 (this work) and NaCl symmetry density of states [12] shows that the energy interval ranging from the top of the $2p$ oxygen band to the bottom of the $4s-4p$ conduction bands is the same in both structures (about 8 eV). On the other hand the d bands are completely upset under the influence of the magnetic exchange potential and the D_{3d}^5 crystal structure [1]. These modifications go in the right way as they recover the insulating nature of MnO.

The complex dielectric function $\varepsilon_2(w)$ has been performed without taking care of the selection rules. Figure 2 displays separately all the considered band to band transitions. As in the spin polarized band scheme each majority and minority d band separates further into an e_g and t_{2g} subband [1], four structures would be expected from the d to d band transitions. In fact, only two manifestations are recorded: one shoulder at 3.2 eV and a significant peak at 4.7 eV. The d density of states maxima being on our energy scale at -0.15, -0.095, 0.025 and 0.08 a.u., one concludes that the d band transitions become effective only between the e_gM and the $t_{2g}m$ and e_gm subbands. The symbols M and m stand for "majority" and "minority". Since in both experimental reflectance spectra, Messick et al. [5] and Ksendzov et al. [6], the first maximum appears at about 4.7 eV, our present study allows to infer that the e_gM and e_gm subbands are implied in the onset excitations.

The existence of such d to d transitions, where the e_gM crystal functions are mainly issued from the metal plus d orbitals, and the e_gm functions from the metal minus d orbitals does by no means signify the occurrence of a two metal process. As a matter of fact, the one electron crystal function is expanded in the LCAO model over all the valence and conduction orbitals. The corresponding $d-d$ dipolar matrix elements become non-zero due to the predominence of the mixed orbital matrix elements $\langle pPd_M \rangle$ and $\langle pPd_m \rangle$, p and d refer to the atomic oxygen and metal orbitals located on different crystal sites; P represents the momentum. Two kinds of transitions are possible: p to d_m or d_M to p excitations with the first orbital belonging to the e_gM and the second to the e_gm subbands. The evaluation of the $\langle pV(\text{metal})d_m \rangle$ (-0.03 a.u.) and the $\langle pV(\text{oxygen})d_M \rangle$
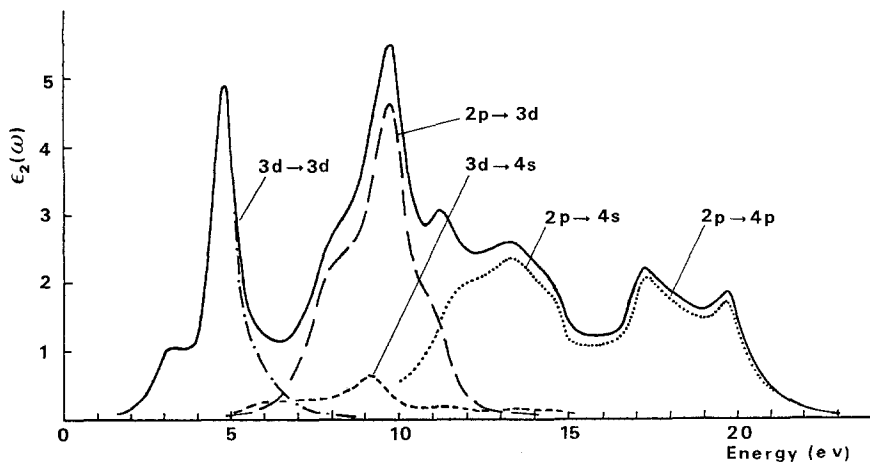

Fig. 2. Imaginary part of the complex dielectric functions $\varepsilon_2(w)$ for MnO together with the various band-to-band transitions
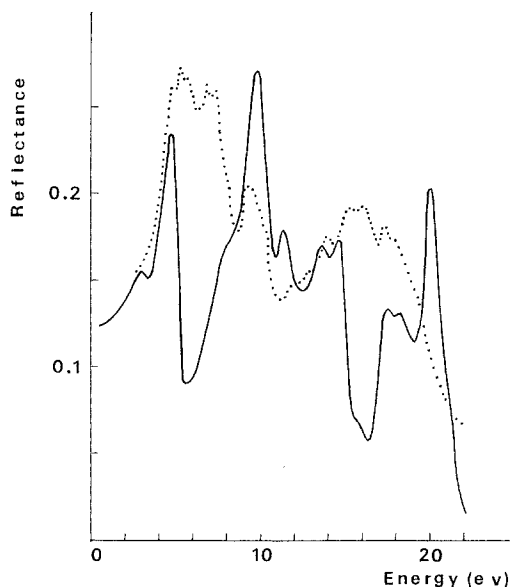
Fig. 3. Calculated reflectance spectrum (full line) compared with the experimental results [6] (dotted line)

$(-0.02$ a.u.) potential integrals connected respectively to the first and second channel permits to retain the $p \to d$ excitations as the predominant process for the onset procedure. These excitations correspond without ambiguity to a charge transfer mechanism restricted to one metal ion.

The interpretation of the absorption edge in terms of $3d-4s$ band to band transitions is not supported by our present study. The $3d \to 4s$ contributions are too faint to afford a detectable manifestation in the optical curve. This is not surprising for selection rule reasons and also because the overlap is better realised with the first than with the second neighbour orbitals.

The second prominent peak in the dielectric function is the result of transitions out of the $2p$ oxygen bands to the $3d$ empty minority subbands. It occurs at 9.7 eV and as for the d band transitions involves the e_g subband, the t_{2g} subband giving no clear contributions to $\varepsilon_2(w)$. This structure is related to the maximum in the reflectance curve (Fig. 3) appearing at 9 eV and termed as $2p \to 3d$ excitations. The structures ranging from 12 to 20 eV are attributed like the analysis of Ksendzov et al. [6] to transition happening between the $2p$ oxygen valence and the $4s-4p$ metal conduction bands. The double peak at 13.6 and 14.5 eV is due to $2p \to 4s$ transitions and the peaks at 17.4 eV, 18.2 eV and 20 eV to $2p \to 4p$ transitions.

Discussion

One observes that the gap deduced from the spin polarized band structures is systematically smaller than the experimental absorption edge (2.2 eV versus 3.8 eV [3, 13]). This discrepancy between the experimental and theoretical point of view is simply explained by considering the way in which the intrinsic gap has been defined.

The location of the characteristic features associated with the onset excitations serves in the experimental approach to assign the value of the gap. In contrast, the filling of the energy levels becomes the relevant criterion used in the band scheme. Thus our spin polarized calculation gives rise to a forbidden energy interval of 2.2 eV separating the upper occupied from the lower empty band states. Now, the study of the calculated spectrum shows that the lowest energy excitations occurring between the $t_{2g}M$ and $e_g m$ bands produce only a shoulder at 3.2 eV. In return, the transitions becoming effective between the $e_g M$ and $e_g m$ bands exhibit a steep absorption behaviour and generate the maximum at 4.7 eV. If one admit to qualify the intrinsic gap as being due to the preceding transitions, one would find a value of 3.9 eV, close to the experimental result. The value corresponds to the energy difference between the $e_g M$ and $e_g m$ density of states and is the result of the spin polarized treatment applied to MnO. For MnO the theoretical gap is in agreement with the experimental value, ever since the classical band occupation is forsaken on behalf of the representative absorption edge transitions. But as our description appeals to band states, the usual gap definition has been adopted.

The difficulty encountered in the theoretical estimation of the MnO optical gap is related to the presence of the d electrons. The problem, which is still open to discussions, is to know if they are to be considered in terms of localized or itinerant states. Up to now the experimental results dealing with the d electrons have exclusively been fitted within a confined ionic model. This predominancy has become widely accepted because the extended picture actually fails to account for the crystal field absorption peaks of the Mn^{2+} ion. The present density of states provides only one structure on this side of the absorption edge whereas five structures are experimentally observed. However, the d electrons, even described by localized orbitals, are subjected to the periodicity conditions which imply to work with Bloch states. An experimental contribution in favour with the itinerant property is given by the recent photoconductivity measurements performed by Mochizuki [13]. The author concludes that the photoconductivities associated with the crystal field excitations are inconsistent with the Frenkel excitonic model. Instead, the intervention of a promotion mechanism has been suggested, the role of which is to produce carriers both in the oxygen $2p$ and the metal $4s$ bands. Our description based upon delocalized states is not in contradiction with the proposed deductions. Furthermore the requirements imposed by the experimental data can easily be satisfied since the electronic d states present some mixing with essentially the p oxygen orbitals. The theoretical spectrum (Fig. 2) shows that the electron and hole conduction can be realized respectively through $3d \to 3d$ and $2p \to 3d$ transitions. Finally, the first experimental questioning about the excitonic model has to be confirmed and further work is necessary in order to estimate under what conditions the itinerant aspect can deal with the structures attributed to the crystal field.

Conclusion

The spin polarized band structure proposes an identification of some of the main structures arising in the reflectance curve (Fig. 3). One exception affects the absence of the highest structure in the observed doublet at 4.7 and 7.1 eV. The delocalized approach reproduces the homologous of the experimental peaks emerging at 4.7 and 9.5 eV but are termed differently with regard to the experimental interpretation. The second exception is the presence of the dip around 16 eV in the calculated curve which has no equivalent in the experimental spectrum. Even if some structures between 12 and 20 eV find their counterpart in the measured reflectance, only a partial correspondence can be fulfilled with the actual band model.

The study shows that the absorption edge is similar to that of NiO and consists of a $p-d$ charge transfer mechanism. The energy of such transitions is associated with the normally forbidden d band excitations. The relative small dispersion of the d bands seems to credit a weak pd mixing and an essentially atomic character for the one electron crystal functions. In fact the pd covalency is as important as in the NaCl type symmetry so that presently the narrowness of the d bands is the result of the D_{3d}^5 space group. The nature of the transitions susceptible to become effective is governed by the strength of the crossed orbital dipolar matrix elements appearing in the expansion of the band-to-band matrix elements. This is a supplementary aspect of the itinerant LCAO picture which illustrates the ability to discriminate the orbitals taking part in the transitions.

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