ORIGIN OF THE d BAND SEPARATION FOR THE TRANSITION METAL MONOXIDES

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The LCAO method based on localised functions has been applied to the transition metal oxides in their antiferromagnetic ordering. A gap is systematically opened in the d band for the semiconducting and insulating compounds MnO, FeO, CoO and NiO. It is shown that, in contrast to the NaCl structure, the pd covalency is responsible for the band separation when the D_{3d}^5 space group is considered.

INTRODUCTION

THE SPIN polarized energy band model applied to the transition metal oxides (especially MnO and NiO) in their antiferromagnetic ground state proved the merit of the band approach in the understanding of their electrical properties. Wilson [1] through an APW procedure was the first to predict the insulating nature of MnO and NiO within their low temperature moment ordering. More particularly he obtained a gap between the majority e_g–t_{2g} bands for MnO, while for NiO the gap is between the minority e_g–t_{2g} bands. For the preceding author the d band separation occurs ever since the crystal-field splitting becomes sufficiently large and the e_g and t_{2g} bands sufficiently narrow. Another contribution made by Anderson et al. [2] in the atomic sphere approximation scheme is, besides the band structure, the reproduction of the observed equilibrium lattice constant for the series CaO through NiO. More recently Terakura et al. [3], using the augmented spherical wave method, showed that the band structure is very sensitive to the magnetic configuration. In particular they concluded that for MnO and NiO the observed antiferromagnetic state is crucial for the insulating behaviour of these solids. In the case of MnO a large exchange splitting of the Mn d bands is required but not sufficient. In fact, among different magnetic arrangements, only the experimental antiferromagnetic structure leads to a gap. The reason given by Terakura and coworkers is that, going from the theoretical ferromagnetic to the real antiferromagnetic case, the energy separation between the majority and minority d bands increases at the same time as the overlapping subbands become narrow. The same terms cannot be applied to NiO because the reduced exchange produces the majority and minority d bands to overlap. But NiO turns out to be a semiconductor

within the band picture of Terakura et al. [3] for the e_g and t_{2g} subbands are split in the minority d band.

This short presentation of the available spin-polarized results shows the ability of the band theory to describe adequately the electronic structure. While the situation of MnO having five d electrons is quite clear as the dominant term is the size of the atomic exchange splitting, the situation of NiO bearing eight d electrons is not settled. For this latter compound the subband separation derives from another factor.

Presently the purpose is to investigate more precisely the origin of the $3d$ gap appearance within an antiferromagnetic ground state LCAO procedure. The LCAO method is well adapted for this preoccupation for it allows us to identify easily the overlap and potential integrals which influence the gap. Our contribution appeals essentially to group theoretical considerations by comparing the results of the chemical NaCl structure of these oxides with the ones of the D_{3d}^5 spacial group to be considered when the magnetic ordering is taken into account.

In the second section the results are presented and discussed. The conclusion appears in the last section. Let us close our introduction by pointing out that a full and extensive survey of the experimental and theoretical situation for these compounds has recently been reviewed by Brandow [4].

RESULTS

The band structure method based on well defined localized orbitals proposed by Hugel et al. [5] has been extended to the spin polarized case and applied to the antiferromagnetic ground state of MnO and NiO. The localized spin polarized orbitals have been obtained through the resolution of a set of coupled Schrödinger equations with local Hamiltonians in a self-consistent
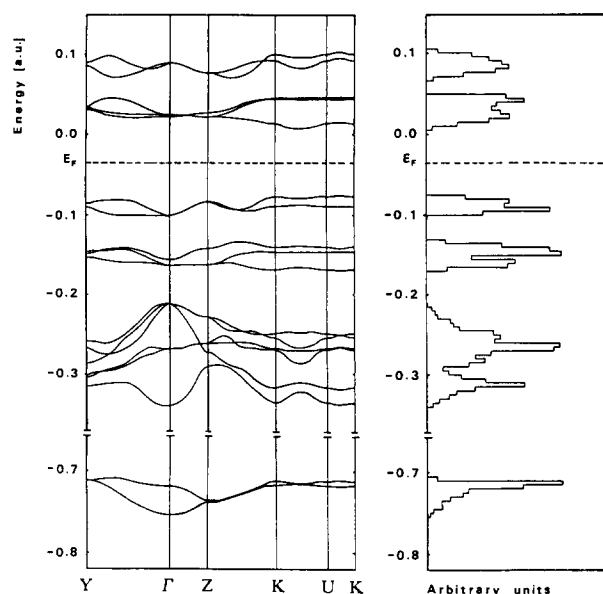
Fig. 1. Spin polarized band structure of MnO, together with the density of states. The Fermi level appears in broken line. The rhombohedral Brillouin zone has been labelled following Slater [7].

manner. The local crystal potential is the result of the superposition of individual ionic potentials expressed in term of a local exchange-correlation potential appropriate to treat the magnetic materials. The analytical form of von Barth and Hedin [6] derived from the local density theory has been adopted.

The basis functions are the $2s$ and $2p$ α (spin up) and β (spin down) orbitals of the oxygen and the $3d$ α and β orbitals for the metal ions. According to the spin dependence of the exchange potential the localized majority spin metal orbitals are always lower in energy and different than the minority spin ones. But as for the α metal ion the α (majority) and β (minority) atomic like functions are respectively identical to the β (majority) and α (minority) atomic like functions for the β metal ion, the α and β spin polarized energy bands look the same. As a result, the band structure is doubly degenerate with the majority bands below the minority bands.

The band structure of MnO and NiO are presented respectively in Fig. 1 and 2 together with their density of states. For MnO one observes a gap of 2.2 eV between the majority and minority d bands which contains the Fermi level. Further each d band divides into two subbands, e_g and t_{2g}, the majority band showing a gap of 0.7 eV while the minority band opens only a gap of 0.4 eV. Nevertheless the intra atomic exchange giving rise to the gap between the filled majority and the empty minority d bands suffices to explain the insulating nature of MnO. In the case of
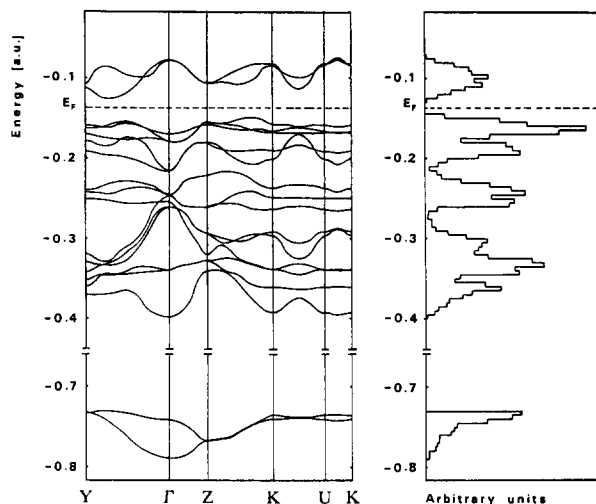

Fig. 2. Spin polarized band structure of NiO together with the density of states. The Fermi level appears in broken line. The rhombohedral Brillouin zone has been labelled following Slater [7].

NiO the majority and minority d bands overlap due to the reduction of the intra atomic exchange. Additionally the oxygen $2p$ band extends over the lower part of the majority d band. The separation between the majority e_g and t_{2g} subbands disappears but the subband gap (0.4 eV) persists in the minority d band allowing us to recover the semiconducting behaviour of NiO, the Fermi level lying in the minority subband gap. Only the majority d subband gap is observed in MnO by Wilson, the non-existence of the minority subband separation being due to the mixture of the d and $4s$ states. The magnitude of our bandwidths for MnO and NiO and the ones of Terakura *et al.* are comparable. The difference appears in the density of states with a larger d peak separation in our results.

We shall now show that unlike to the NaCl structure, the D_{3d}^5 rhombohedral structure generates a gap in the $3d$ bands whose origin is due to the covalency between the $2p$ oxygen and $3d$ metal functions. In the NaCl structure the pd covalency plays a negative role for Mattheiss [8] established that the separation between the average energies of the t_{2g} and e_g subbands, defined as the crystal field effect, increases at the same time as their width, thus preventing the band gap formation. The importance of these pd interactions has been stressed in a previous study, Hugel and Carabatos [9], where it was found that the crystal field separation was made up of an ionic term and a three times larger covalent term.

Presently the d energy levels at the center of the Brillouin zone no longer separate in a two fold degenerate Γ_{12} (-0.184 a.u.) and a three fold degenerate Γ_{25}, (-0.202 a.u.) level but in one Γ_1 (-0.170 a.u.) and

two Γ_5 (-0.077 a.u., -0.179 a.u.) twofold degenerate levels.

The notable difference told by the group theory is that the basis Γ_1 and Γ_5 functions are not pure *d* functions as for Γ_{12} and Γ_{25}, but a combination of *p* and *d* orbitals. The hybridization shifts the energies such as the upper Γ_1–Γ_5 separation reaches 2.5 eV when the Γ_{12}–Γ_{25}, separation limits to 0.5 eV in NiO. The gap obtention is then ensured by smaller energy bands than in the NaCl structure. This stems from the fact that among the metal–metal interactions expressed in the rhombohedral axis system, the ddσ interactions are absent in the d_{yz} and d_{zx} matrix elements. More it has been verified that putting the two center *pd* integrals equal to zero the gap vanishes in the *d* band. Shortening arbitrarily the *pd* integrals until fifty percent of their initial values, the gap persists. This indicates that its existence is not fortuitous and that essentially the *pd* interactions contribute.

Another interesting simulation is the suppression of the exchange by equalizing the minority and majority orbital energies together with their two center integrals. For NiO the overall band profiles remain the same except a reduction of the 3*d* minority gap to about 0.2 eV. For MnO however, the *d* band organisation is completely changed as the majority and minority *d* bands imbricate like in NiO with nevertheless the maintenance of a small 3*d* minority gap (0.1 eV). The above numerical test shows that the exchange is neither the prime cause of the electrical gap apparition in NiO, on the opposite to MnO, nor responsible of the 3*d* subband formation even if it participates.

CONCLUSION

The role of the *pd* orbital coupling, of great importance in both the rocksalt and magnetic structures because it acts prominently on the *d* band scheme, leads to a satisfactory issue only when care is taken of the magnetic ordering. It is the magnetic lattice which gives rise to the 3*d* gap for it favours the *pd* hybridization and conducts to small dispersive bands. In particular the *pd* mixing enhances the separation of the energy levels belonging to each subband over all the points of the Brillouin zone, including the center. On the other hand, the classical ligand field theory which partially removes the degeneracy of the atomic *d* levels by the octahedral surrounding, is not able to explain by itself the gap creation. The initial energy difference between the split *d* localized orbitals is not consequent enough (0.25 eV) to avoid the overlap when these levels enlarge in the crystal. In agreement with the analysis of Mattheiss [8] the present work enables us to conclude that the D_{3d}^5 symmetry is responsible for the *d* subband gap formation which thus appears systematically for MnO through NiO.

The FeO and CoO transition metal oxides will present similar band structures. The general trend when one goes from MnO to NiO in the transition metal series will be the decrease of the gap between the majority and minority *d* bands owing to the reduction of the intra atomic exchange. Unfortunately a difficulty is then encountered with FeO and CoO. The Fermi level lying in the minority t_{2g} band, the electrical properties cannot be explained. As for MnO and NiO the spin polarized model leads to a consequent improvement, it is thought that further progress can be accomplished by sticking closer to the experimental evidence. CoO [10] presenting a large orbital moment one has to introduce the spin orbit coupling and deal with spinor functions. This study will be devoted to a future work.

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