Band-structure description of Mott insulators (NiO, MnO, FeO, CoO)

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Abstract. The unoccupied-states potential correction (USPC) in the local spin-density-functional (LSDF) formalism is proposed as a way to take correlation effects into account approximately. The method is based on using different potentials for the electrons in valence and conduction bands. When applied to antiferromagnetic transition-metal oxides (NiO, MnO, FeO, CoO), it solved the long-standing problem of reproducing the experimental values of the band gaps, which are underestimated in normal LSDF calculations. FeO and CoO become insulators, in contrast to the metallic ground state obtained in the usual LSDF calculations. Moreover, the calculated magnetic properties improved considerably due to introduction of the USPC. It is shown that band-structure calculations using the USPC provide a correct description of available data from spectral measurements (ultraviolet photoelectron spectroscopy, x-ray photoelectron spectroscopy, bremsstrahlung isochromate spectroscopy) for these compounds.

1. Introduction

Among the 3d-metal monoxides with the NaCl crystal structure, the compounds with metallic conductivity (TiO, VO) are easily distinguished from those with insulating properties and antiferromagnetic ordering (NiO, MnO, FeO, CoO). The latter are most interesting for solid-state theory in connection with the problem of the description of their electron structure and electronic and magnetic properties.

It is expected that oxygen 2p states are occupied, metal 4s states are empty and metal 3d states are partially occupied in these compounds. The last circumstance causes the main problem in explaining the insulating properties of these materials.

This contradiction is removed by use of Mott–Hubbard theory [1], which asserts that the strong intra-atomic d–d Coulomb interaction is much greater than the 3d bandwidth. As a result, a gap is formed between the filled and empty 3d states.

The existing discrepancies concerning the value of the Coulomb interaction and analysis of spectral data lead to ideas about an O 2p → 3d type gap in these compounds, which means a gap with charge transfer [2, 3]. The assumption of strong correlation effects, which are described in terms of configuration-interaction theory, is an essential condition for such a situation to occur [4, 5].

In spite of some success of one-electron spin-polarised band-structure calculations in describing the electron structure of 3d-metal magnetic monoxides [6], as a whole they do not reproduce band-gap values and underestimate values of local magnetic moments

(approximately 1.5 times for NiO). In connection with this, it is asserted that one-particle band-structure theory is not applicable to the analysis of electron structure and magnetic properties of compounds with strong electron–electron correlation. The last affirmation is very important in connection with the discovery of high-T_c oxide superconductors, which also belong to this class of compounds.

Owing to the above, an attempt to rehabilitate one-electron band-structure methods for the analysis of electron structure and magnetic properties of such materials is of exceptional interest. Earlier in [7] a method of taking correlation effects into account in the frame of the local spin-density-functional (LSDF) formalism was suggested by us. The method is based on the use of different potentials for the electrons in valence and conduction bands. The use of this method for calculation of electron structure and magnetic properties of La$_2$CuO$_4$ allowed us to obtain for the first time a stable anti-ferromagnetic solution with a spin magnetic moment $\mu_{Cu} = 0.38\,\mu_B$, a band gap of about 0.78 eV and a narrow peak in the density of states near the Fermi energy, the existence of which was predicted in many experimental works. In the same work, some preliminary results of using this method for the electron structure calculations of NiO are presented [7].

Complete data of self-consistent spin-polarised band-structure calculations for 3d-metal magnetic monoxides (MnO, FeO, CoO, NiO) with and without taking account of correlation effects are reported in the present paper. It was shown that calculations including the correlation effects give band-gap values and local magnetic moments that are in agreement with experimental data and provide the correct description of all available spectral measurements (ultraviolet photoelectron spectroscopy (UPS), x-ray photoelectron spectroscopy (XPS), bremsstrahlung isochromate spectroscopy (BIS), etc) for these compounds. It is very important that the ground-state calculations reproduce all spectral data without using the configuration-interaction theory as in [4, 5]. In our opinion, the approach suggested by us not only provides the rehabilitation of band-structure theory for the analysis of such materials, but also has important consequences for the interpretation of spectral data, and in particular shows the possibility of extracting information about the density-of-states distribution in the ground state of the system under investigation.

2. Method of calculation

It is necessary to point out that failure in the application of standard band-structure methods to the analysis of the electron structure of the given compounds stimulated activity in both model and LSDF calculations with account taken of correlation effects. First of all, work should be mentioned [8] in which model calculations of the electron structure of transition-metal oxides and halides were performed in the frame of the Anderson model using intra-atomic Coulomb integral values (U) and charge transfer energy (Δ) determined from spectral experiments.

Calculations of d$^8 \rightarrow$ d^9 and d$^8 \rightarrow$ d^7 excitation energies for NiO by the supercell method with a self-consistent account of charge redistribution around an atom having an excited shell were presented in [9]. The U and Δ parameters obtained were in agreement with experimental data, which indicates the possibility of determining in principle the parameters of the Anderson model in the LSDF approach.

The method of accounting for the correlation effects in band-structure calculations by introducing a self-interaction correction (SIC) was proposed in [10]. In the SIC method

the potential created by the charge density of the electron itself is subtracted from the total LSDF potential, which leads to lower energies of the occupied states. The SIC correction is not applied to the unoccupied states because they do not contribute to the electron density. As a result, the SIC method gives an increased energy difference between filled and empty states, in good agreement with experimental data (it was demonstrated for solid Ar in [10]). We have performed similar calculations for NiO. In this case the valence band, in contrast to Ar, is formed by states with different degrees of spatial localisation. Therefore, the SIC correction must have different values for p and d states and be greater for the latter due to their greater spatial localisation. Self-consistent band-structure calculations for NiO with the SIC for all states forming the occupied band gave a band gap increased to 4 eV, which agrees with the experimental value [2, 11]. However, in addition to this, a redistribution of states in the valence band took place, i.e. the d states of Ni fell below the O 2p states, which contradicts the photoemission data [2, 11]. This disagreement with experimental data calls for greater caution in the application of the SIC especially to transition-metal oxides.

It is generally accepted that the LSDF approach correctly describes the characteristics of the ground state (charge and spin density), but gives a systematic error in the determination of the excitation energies. It leads to underestimated values of band gaps for the 3d-metal oxides under consideration. In general, the electrons of valence and conduction bands must be affected by potentials of different configurations, i.e. the conduction band electrons must be affected by the potential of a shell containing one electron more than that for the valence band electrons (see [12]). However, the standard LSDF approach requires the same potential for all electrons in both occupied and un-occupied parts of the band.

The use of the SIC allows us to decrease by one the number of electrons interacting with an electron in the valence band, thus providing different potentials for electrons in the valence and conduction bands. However, as mentioned above, the energies of different occupied states lower non-uniformly, which can lead to redistribution of the valence band states and hence to distortion of the ground-state results.

Using the method suggested by us [7], it is possible to obtain the required difference of potentials for the electrons of valence and conduction bands. However, in contrast to the SIC method, in this case the number of electrons acting on the electrons in occupied states remains unchanged, and the number of electrons with which an electron in the conduction band interacts is increased by one. As in the SIC method, the band gap between occupied and unoccupied states should be expected to increase; however, this would not be accompanied by any distortion of the ground-state characteristics, because the potential for valence band states does not change.

We named this method the 'unoccupied-states potential correction' (USPC). The scheme of the USPC method is as follows. Let $d^{n_{m\sigma}}_{m\sigma}$ be a d orbital with spin projection σ and orbital momentum projection m, where $n_{m\sigma}$ is its population in the ground state. The corresponding band is completely occupied if $n_{m\sigma} = 1$, and the potential obtained in the LSDF is the average potential that acts upon the electron on the given orbital. If $n_{m\sigma} = 0$, the corresponding band is empty and it is necessary to put an electron on the given orbital and to calculate the potential created by the charge and spin density corresponding to the excited configuration, thus obtaining the potential that affects the electron in this state.

It may happen that the band would be unoccupied but $n_{m\sigma} \neq 0$ because of hybrid-isation effects. In this case the $d^{n_{m\sigma}}_{m\sigma}$ configuration corresponds to the ground state, and $d^{1}_{m\sigma}$ to excited state. This can be interpreted as follows. The ground-state configuration

$d_{m\bar{o}}^{n_{m\sigma}}$ is realised with probability $n_{m\sigma}$ and the excited-state configuration $d_{m\sigma}^1$ with probability $(1 - n_{m\sigma})$ if the electron is on a $d_{m\sigma}$ orbital. Therefore, the average configuration from which the potential for the electron on a $d_{m\sigma}$ orbital is constructed will be $d_{m\bar{o}}^{n_{m\sigma}n_{m\sigma} + (1 - n_{m\sigma})}$.

Calculations were performed by the linearised muffin-tin orbitals method in the atomic sphere approximation (LMTO-ASA) [13], and the ratio of metal and non-metal sphere radii was chosen self-consistently in such a way that the atomic spheres were neutral. If, for the ground state of magnetic oxides, the configuration of metal atoms is $d^x(s, p)^{n-x}$, n being the number of valence electrons, then for the excited state it will be $d^{x+y}(s, p)^{n-x-y}$, with y being the d-orbital contribution to the wavefunction of the unoccupied band. In this approach, a change in d-shell charge is screened by changes in number of s and p electrons in the metallic atom sphere. For narrow-band materials (to which the oxides under consideration belong) one can distinguish sub-bands, corresponding to specific d orbitals. Therefore the potential will be orbital-dependent. For instance, in NiO (see figure 2) the valence band is formed by $t_{2g}^{\uparrow}$, $t_{2g}^{\downarrow}$ and $e_g^{\uparrow}$ states of Ni, and the conduction band by $e_g^{\downarrow}$ states. This means that the potential obtained for the ground-state configuration is used for all oxygen states and for all nickel states except $e_g^{\downarrow}$, and the potential of an excited configuration is taken only for the $e_g^{\downarrow}$ orbital.

In the LMTO-ASA method [13], the main system of equations can be written as follows:

$$\sum_{i'l'm'} [P_{ilm}(E)\delta_{ii'}\delta_{ll'}\delta_{mm'} - S_{lm,l'm'}^{ii'}(k)] \left(\frac{\mathrm{d}}{\mathrm{d}E}P_{i'l'm'}(E)\right)^{-1/2} B_{i'l'm'}(k) = 0. \tag{1}$$

Here $B_{ilm}(k)$ are LMTO expansion coefficients for Bloch functions (i is an atomic index, l an angular momentum index and m the angular momentum projection index), $S_{lm,l'm'}^{ii'}(k)$ is a structure matrix of the LMTO method and $P_{ilm}(E)$ is the LMTO potential function. The $S(k)$ matrix is determined only by the crystal structure and does not depend on the atomic potentials. The potential functions $P_{ilm}(E)$ depend only on the ith atom potential and are determined by the value of the logarithmic derivatives of the radial wavefunction on the surface of the atomic sphere for the angular momentum value l. If we are using the same potential for all orbitals of the ith atom, then $P_{ilm}(E)$ are independent of the index m and, for example, the same potential function corresponds to t_{2g} and e_g orbitals. But it is possible to use different potentials for different m values, as is done in our approach. This method of calculating potential functions corresponds to the introduction of an orbital-dependent potential, and the new Hamiltonian will be defined by equations (1). It was shown in [14] that equations (1) are equivalent to a secular equation of the form:

$$[H(k) - E]B(k) = 0 \tag{2}$$

with energy-independent Hamiltonian matrix $H(k)$.

The problem of the non-orthogonality of the unoccupied states with the occupied ones appears when one uses different potentials for these states. But this is not the case in the Hamiltonian construction procedure suggested by us. Different potentials were used in calculations of potential parameters for different *basis orbitals*, but not for the resulting bands. The Hamiltonian matrix was constructed from the calculated potential parameters and structure constants, and all states, for both occupied and unoccupied bands, were eigenstates of the same Hamiltonian and hence were orthogonal to each other. To exclude possible misunderstanding, one must distinguish clearly between the unoccupied band and the basis orbital that gives the major contribution to that band.
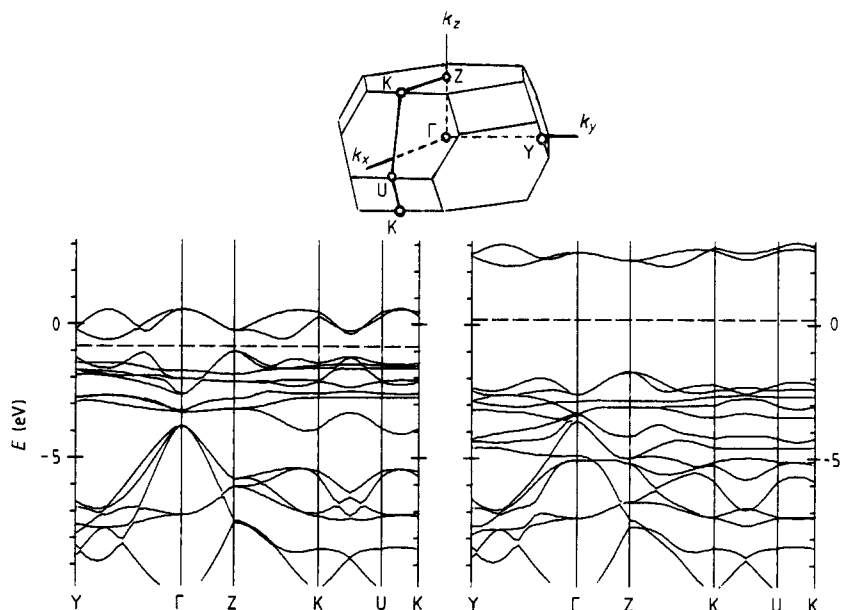
Figure 1. First Brillouin zone and $E(k)$ curves for antiferromagnetic (AF2) NiO. The Fermi level E_F is shown by a broken line. The right-hand side shows the results of calculations with the unoccupied-states potential correction (computation 2) and the left-hand side the results without this correction (computation 1).

3. Results and discussion

The results of band-structure calculations for NiO, MnO, FeO and CoO are presented in figures 1–8: dispersion curves $E(k)$, total density-of-electron-states curves $N(E)$ and e_g- and t_{2g}-state distributions with different spin projections are shown. The curves represent the results obtained in calculations: without (computation 1) and with (computation 2) the USPC. The calculated values of the band gaps and local magnetic moments for magnetic oxides are given later in tables 1 and 2.

It is necessary to point out that the use of the standard self-consistent spin-polarised method, when applied to the oxides mentioned above, gives energy bands with metallic conductivity for FeO and CoO and energy bands that are underestimated in comparison with the experimental data values of the band gap for MnO and NiO. In this respect, the results obtained are fully identical to those formerly published in [6].

The use of the USPC leads to essential reconstruction of the electron structure of magnetic oxides. First of all, a gap appears in all oxides, which naturally corresponds to their insulating properties. The application of the USPC resulted not only in the appearance of gaps with width close to the experimental one (see table 1), but also in drastic reduction of the hybridisation between $e_g^{\downarrow}$ d states and oxygen p states. This leads to a smaller contribution of d electrons with 'spin down' to the occupied bands and, respectively, to increased spin magnetic moments on metal atoms (e.g. on Ni in NiO, the moment increased from $1.11\mu_B$ to $1.63\mu_B$, which is considerably closer to the experimentally observed values $1.64\mu_B$ [15] and $1.77\mu_B$ [16]).

Let us recall that a stable magnetic solution for NiO had been obtained in [6] only for antiferromagnetic AF2 structure, but for antiferromagnetic AF1 and ferromagnetic
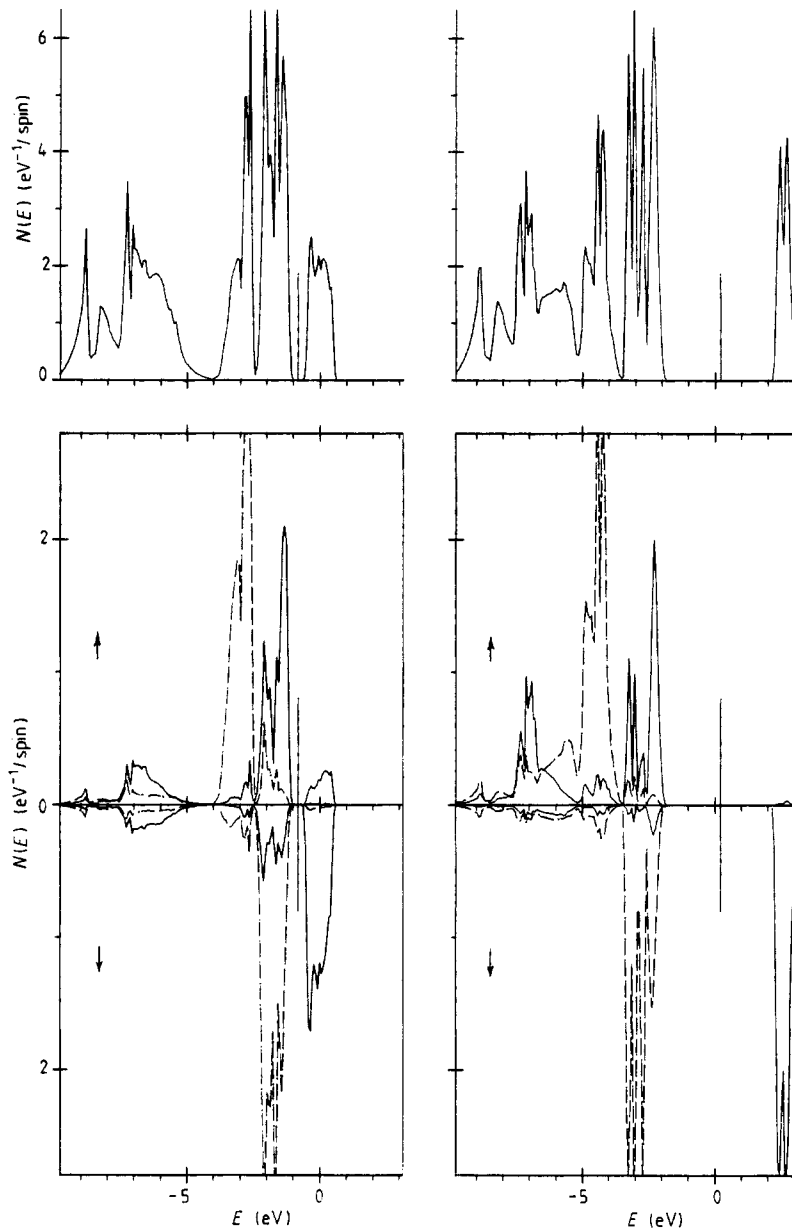
Figure 2. Total (upper pair) and partial densities (lower pair) of states for Ni d orbitals in NiO. The full (broken) curves denote e_g (t_{2g}) contributions. The arrows denote 'spin-up' and 'spin-down' states. The Fermi level (vertical lines) was placed in the middle of the energy gap. The right-hand side corresponds to the calculations with the unoccupied-states potential correction (computation 2) and the left-hand side to calculations without this correction (computation 1).

structures, the values of the Ni magnetic moment were zero, which indicates the itinerant nature of the magnetic moment in this compound. We obtained the same results in our calculations without the USPC. Self-consistent band-structure calculations for NiO with
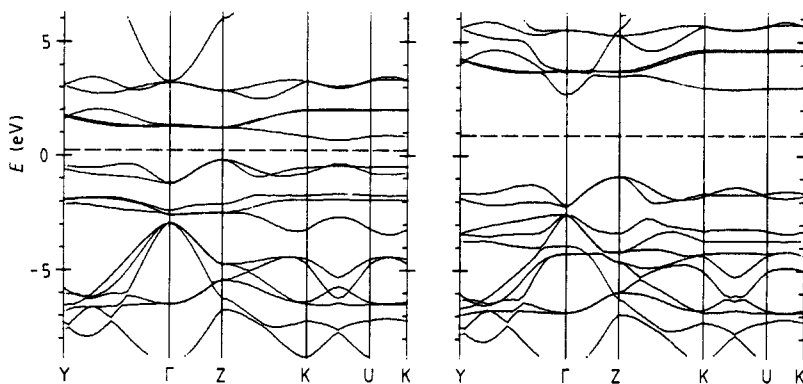
Figure 3. $E(k)$ curves for MnO. The notations are the same as in figure 1.

ferromagnetic structure were performed by us with the USPC and a stable magnetic solution with magnetic moment 1.7 μ_B was obtained. This result agrees with the localised nature of magnetic moments in NiO.

Consider, now, the general structure of energy bands of magnetic 3d-metal oxides obtained in the present calculations. Oxygen 2s states form the lowest energy band (not shown in figures 1–8), separated from the O 2p band by a gap of about 8–9 eV width. The use of the USPC does not change the energy position of this band (at $E = -20$ eV in the energy scale adopted in figures 1–8) nor its structure. An O 2p band in all oxides, according to computation 1, is separated by a gap from higher-lying $t_{2g}^\uparrow$ states. The USPC slightly modifies the structure of the O 2p band, giving no shift in its centre of gravity. Its top is raised to higher energies. The $t_{2g}^\uparrow$ band hits in the same energy region as the top of the O 2p band (because of an increase in magnetic moment resulting in an increase in energy splitting of 'spin-up' and 'spin-down' d states), which leads to mixing of O 2p and $t_{2g}^\uparrow$ states. The energy of the $e_g^\uparrow$ band is lowered on average by 1 eV in computation 2, as compared to computation 1. In the regions of partly occupied and unoccupied states, the order of the d bands remains the same: $t_{2g}^\downarrow$ and $e_g^\downarrow$. It is necessary to point out that the $e_g^\downarrow$ band overlaps with the 4s–4p band. Inclusion of the USPC leads to an increase in the energy of the unoccupied $t_{2g}^\downarrow$ and $e_g^\downarrow$ bands on average by 2–3 eV.

On the whole, the energy band structures of all the oxides considered (figures 1–8) are similar with respect to the shape of the total and partial density-of-states curves.

Concluding this section, let us discuss the origin of the band gap in magnetic oxides on the basis of our calculated band structures. The ratios of atomic sphere radii obtained from the electroneutrality condition were equal to $R_{Me}/R_O \simeq 1.5$–1.6. If the presence of Me^{2+} and O^{2-} ions is assumed (usually the ratio of ionic radii is equal to 0.5), such a distribution of charge density in atomic spheres corresponds to partial inclusion of the oxygen-ion charge density in metal atomic spheres and its approximation by s and p electrons of the metal. Consequently, a decrease in the s- and p-electron number with increasing occupancy of d orbitals in an excited state can be interpreted as the result of transfer of electrons from oxygen ions to the metal d shell. This corresponds to a $d^n \rightarrow d^{n+1}L$ transition or 2p $\rightarrow$ 3d transition, i.e. to a transition with charge transfer.

4. Comparison with experiment

The results of a comparison of experimental values of band gaps and local magnetic moments with those obtained in the given calculations for magnetic oxides are presented
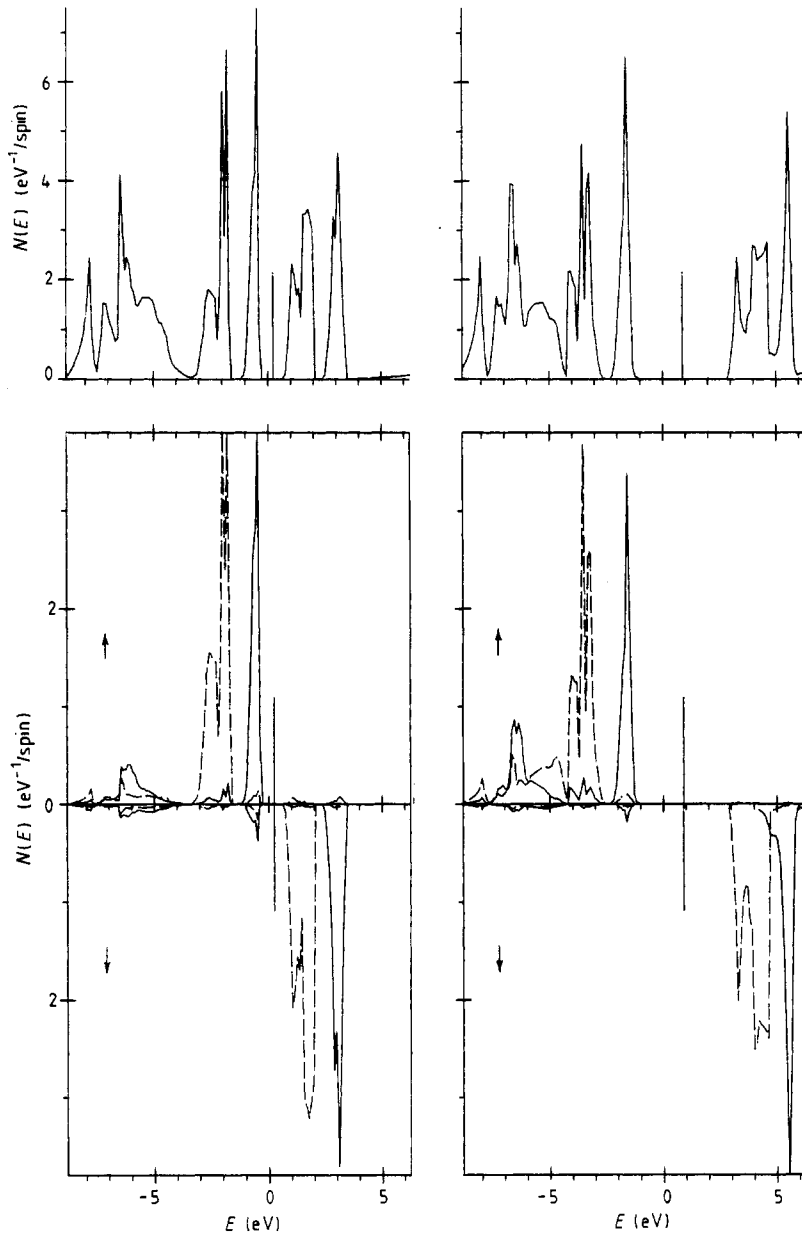
Figure 4. Total and partial densities of states for MnO. The notations are the same as in figure 2.

in tables 1 and 2. Also listed for the sake of comparison are data obtained in [6]. Analysis of these results leads to the conclusion that the suggested USPC method gives an opportunity to obtain for the first time good enough agreement with experiment within the frame of the LSDF approach. It is interesting also to compare the results obtained with data from spectroscopic experiments. To date, only MnO [22] and NiO [2, 11, 23] have been investigated fully. FeO has been examined less thoroughly [24], mostly
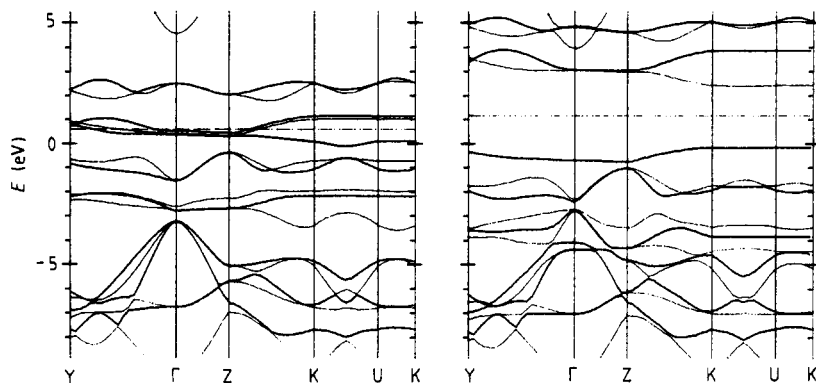
Figure 5. $E(k)$ curves for FeO. The notations are the same as in figure 1.

Table 1. Energy gaps (eV).

	MnO	FeO	CoO	NiO
Without USPC	0.82	0	0	0.41
With USPC	3.59	2.50	2.66	3.90
Experiment	3.6–3.8 [17, 18]	–	≃3 [19, 20]	4.0 [11], 4.3 [2]

because of difficulties in growing non-defect single crystals. We know only earlier papers for CoO [25, 26].

MnO. The results of angle-dependent UPS for two polarisations, $\alpha = 80°$ and $\alpha = 45°$, and of UPS with varied excitation energy (30–80 eV) have been published recently in [22]. Unfortunately, BIS measurements for MnO are absent; therefore, in this case the occupied part of the energy bands can be compared with experiment only on a relative energy scale (for comparison with experiment, the results of computation 2 with the USPC were taken). According to experimental UPS spectra, the separation between the centres of gravity of $e_g^\uparrow$ and $t_{2g}^\uparrow$ occupied bands is about 1.8 eV, which is close to the calculated value ($\simeq 1.6$ eV). The bottom of the O 2p band is separated from the top of the $e_g^\uparrow$ band, according to experiment, by $\simeq 8$ eV, which practically coincides with the theoretical estimates. We have pointed out that taking into account the USPC results in the $e_g^\uparrow$ band falling by approximately 1.0 eV. Just such an energy shift was artificially assigned to the theoretical bands obtained in [6] for good agreement with experimental data [22] (see figure 1 in [22]). In our case, this shift was found as a result of self-consistent calculations without the introduction of any correction, allowing for relaxation effects.

According to angle-dependent UPS data [22], no noticeable dispersion of 3d states was observed for MnO throughout the Brillouin zone. This conclusion on the whole correlates with the $E(k)$ curves presented in figure 3. Appreciable dispersion of O 2p states in the Brillouin zone is revealed in both calculations and experiment.

The conclusion that the shape of the main spectrum has an antiresonance character near the excitation threshold energy (2p–3d) was made from analysis of resonance UPS data for MnO [22]. This suggested that a configuration $3d^5L$ appears in the final state of the photoemission process, the latter thus being a 2p–3d transition. As mentioned above,
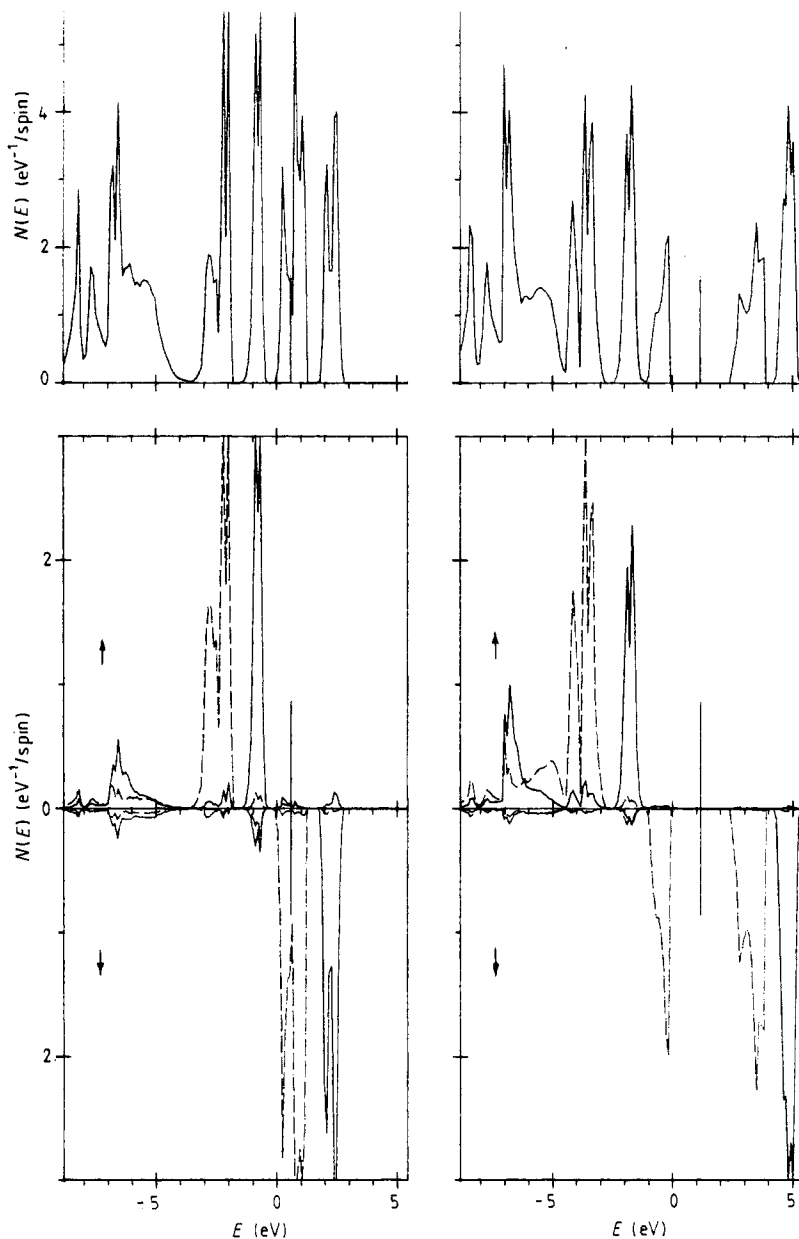
Figure 6. Total and partial densities of states for FeO. The notations are the same as in figure 2.

a similar conclusion about the insulating gap origin was also made from theoretical calculations.

NiO. A full set of spectroscopic data are available for this compound, including UPS with varied excitation energy [2], BIS [2, 11] and angle-dependent UPS [23]. Note first of all that the band-gap value, determined from UPS and BIS ($\Delta E \simeq 4.0$–4.3 eV), is in full
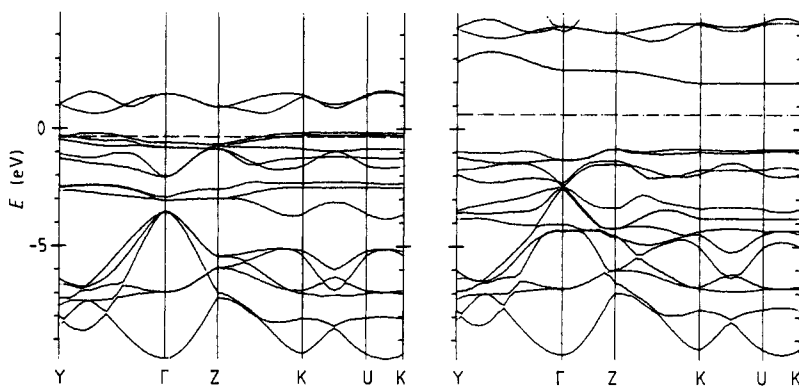
Figure 7. $E(k)$ curves for CoO. The notations are the same as in figure 1.

Table 2. Local magnetic moments (μ_B).

	MnO	FeO	CoO	NiO
Terakura *et al* [6]	4.45	3.43	2.35	1.09
Without USPC	4.47	3.42	2.29	1.05
With USPC	4.74	3.72	2.70	1.68
Experiment	4.79 [16]	–	3.35 [21]	1.64 [15], 1.77 [16]

agreement, with the calculated one ($\Delta E = 3.9$ eV). The UPS, measured at $E = 66$ eV (figure 9), is most convenient for comparison with calculated bands. In this case both O 2p and Ni 3d states are clearly revealed owing to a favourable relation between the photoionisation cross sections. In the experimental spectrum five peaks are clearly distinguished (A, B, C, D, E). Two high-energy (D, E) peaks have mainly 3d character, and two others (B, C) are of mixed (Ni 3d–O 2p) or purely O 2p character (figure 9). It is typical that a structure similar to that described above is also observed in the density of states. Moreover, the energy separation of the peaks and their genesis are in satisfactory agreement.

It is important that, as with MnO, the experimental spectrum can be interpreted on the basis of calculations performed for the ground state without the use of ideas about many configurational interactions.

FeO. UPS spectra measured with variation of excitation energy (35–120 eV) [24] were chosen for comparison with experiment. Like NiO, five overlapping sub-bands are distinguishable in this case (see figure 2 in [24] for $E = 55$ eV), which can be identified with the maxima on the $N(E)$ curve presented in figure 6.

CoO. UPS data obtained at $E = 30$ and 1486 eV have been reported in [25, 26]. The general structure of experimental UPS for CoO and FeO, as shown in [25], is very similar. We have noted above the similarity of the energy band structures of these compounds (see figures 5 and 7). This means that the conclusions about correspondence between experimental and theoretical spectra that were made for FeO are applicable also for CoO.
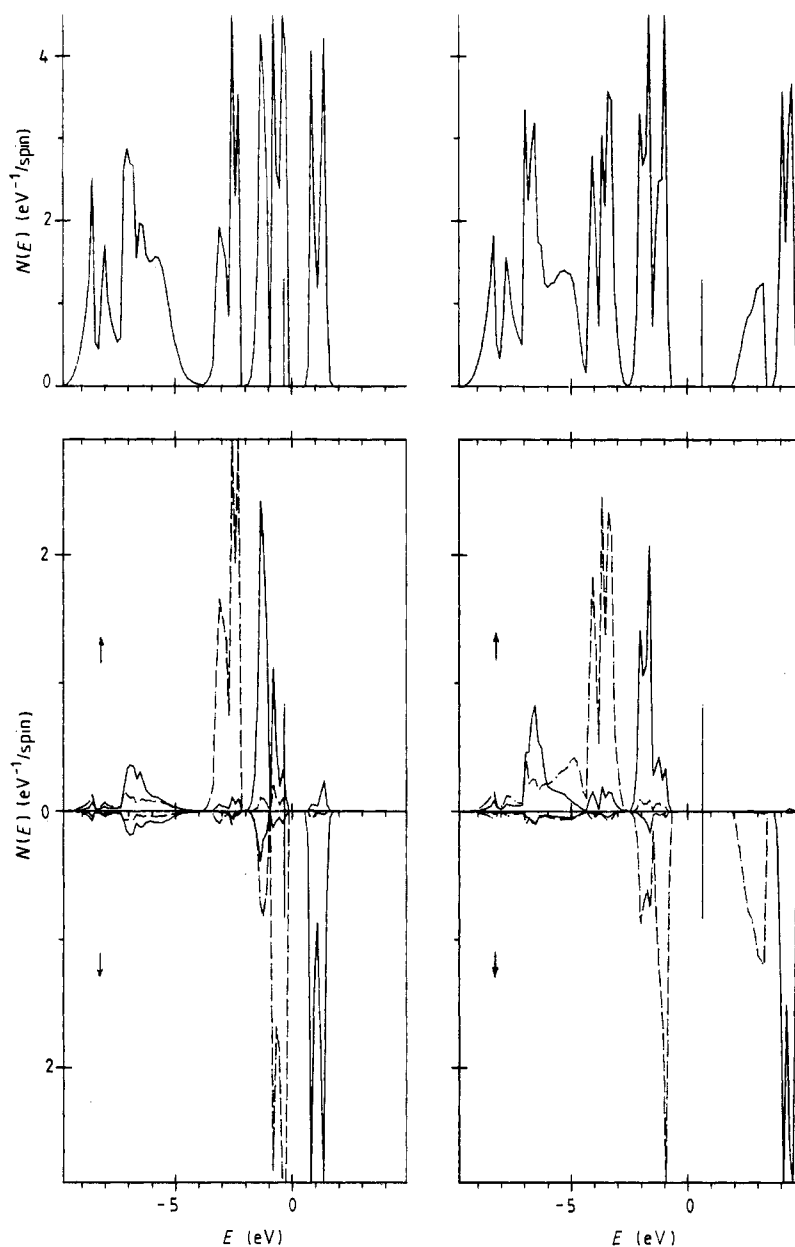
Figure 8. Total and partial densities of states for CoO. The notations are the same as in figure 2.

While the increase of the energy gaps follows naturally from our potential corrections, which raise the unoccupied states on the energy scale relative to the occupied states, the improvement of the calculated magnetic parameters was rather surprising (table 2). Magnetic moment values increase by $(0.3–0.6)\mu_B$ as a result of including the USPC. Moreover, the magnetic solution for NiO now exists independently of the type of
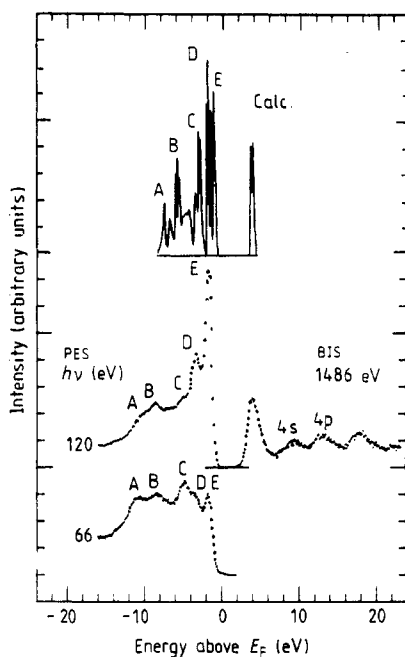
Figure 9. The calculated total densities of states (computation 2) and the experimental spectra [2] for NiO.

magnetic structure, which confirms the localised nature of the Ni magnetic moment. The cause of these changes is the raising of energy of the unoccupied 'spin-down' d orbitals, which leads to decreasing p–d hybridisation for the 'spin-down' electrons. As a result, the contribution of d $^\downarrow$ orbitals to the occupied part of the valence band decreases and the magnitude of the magnetic moment becomes closer to the integer ionic value.

It is commonly recognised that, although the LSDF calculations can give wrong excitation energies, the ground-state characteristics, such as total energy, charge and spin electron densities, must be described correctly. Our results show that the correction to the potential of the unoccupied states can significantly improve the ground-state characteristics. We believe that correct determination of the p–d energy difference is important not only for excitation energies but also for the correct description of the p–d hybridisation and, hence, of the values of magnetic moments and exchange inter-action parameters.

For MnO and NiO, the changes in the electron structure arising from the USPC are quantitative, since energy gaps also existed in the calculations without the correction (although for NiO the energy-gap value has increased more than 10 times). But for CoO and FeO the electron structure changes drastically, having transformed from metallic to insulating type. In figures 5 and 7 three $t_{2g}^{\downarrow}$ bands crossing the Fermi level split due to the USPC into occupied and empty bands, and one empty band for CoO and two for FeO move up in the energy scale.

For NiO and MnO the calculated magnetic moment values are close to the exper-imental data (see table 2), while for CoO the experimental value is $0.65\mu_{B}$ greater than the calculated one. It is known that there is unquenched orbital angular momentum in CoO. For its estimation it is necessary to calculate the contribution of different d orbitals to the occupied bands. The standard LSDF gives three degenerate $t_{2g}^{\downarrow}$ orbitals, of which

any three independent linear combinations can be used. The USPC removes this degeneracy and raises the energy of the empty states. But which linear combinations of t_{2g} orbitals correspond to empty or occupied states remains uncertain. Following the analysis in [6] we accept that for CoO the occupied bands will be formed by an xy orbital and a linear combination of xz and yz orbitals, which corresponds to an orbital angular momentum projection $m = +1$, and the empty band corresponds to the combination with $m = -1$. As a result, the orbital angular momentum value for a Co atom will be 1. In reality this value can be less than 1 due to the not purely t_{2g} origin of the bands in question.

It is interesting to compare our approach with the Anderson impurity model calculation of McMahan *et al* [27]. The main problem in both cases was to take into account different d configurations of the metal atom with different energies in contrast to the one-electron LSDF calculations with an average d configuration and average energy of d orbitals. In [27] only the model parameters were calculated in the LSDF and the correlation effects were treated directly in the impurity approximation. In our approach, different d configurations are related to different d spin-orbitals. (This is possible only when each unoccupied band is formed mainly by a certain d spin-orbital.) After that the degeneracy in the energy of d orbitals is removed and the usual band-structure calculations are performed. We think that our approach can be considered as a rather simple and natural realisation of the idea of 'lower and upper Hubbard bands' in the frame of band-structure calculations.

We present here the results of the application of our approach to four transition-metal compounds. (The results of calculations for La_2CuO_4 are presented in [7].) One can ask what would be found if this approach were applied to solids with a different type of electronic structure such as a transition metal, an insulator and a semiconductor? The simplest case is an insulator, for which the valence and conduction bands are formed by different orbitals, but here the problem of the correct description of the excited shell screening can appear. In a semiconductor both bands are formed by the same orbitals and one must take as a basis set the Wannier-type functions and not the atomic-like LMTO orbitals. As for metals and compounds with a metallic type of electronic structure, the main question is as follows. Are the correlation effects strong enough to produce a gap between the occupied and unoccupied bands? if this is not the case, then our approach cannot be applied because it is necessary to have a totally unoccupied band corresponding to the certain orbital for our method.

5. Conclusions

In the present paper we suggest a method to take account approximately of correlation effects in electronic structure calculations for narrow-band transition-metal compounds. The core of the method is the unoccupied-states potential correction. The application of this method to the electronic structure calculations for the antiferromagnetic 3d-metal monoxides NiO, MnO, FeO and CoO not only gave for all these compounds an insulating type of band structure with correct band gaps, but also significantly improved the values of their magnetic parameters. We believe that one-electron methods of band-structure calculations based on the local spin-density-functional approach, after rather simple modifications, can be applied to systems with strong electron correlations.

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