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Study of the electronic structure of $NiCl_2$, $CoCl_2$, $FeCl_2$, and $MnCl_2$ by the intersecting-spheres model

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The self-consistent band structure of the layer crystals $NiCl_2$, $CoCl_2$, $FeCl_2$, and $MnCl_2$ has been calculated by the intersecting-spheres model, using both the Slater and the Gáspár-Kohn-Sham approximation of the exchange potential. The results of these calculations, when compared with the experimental data and with previous results obtained for $MgCl_2$, provide a rough and qualitative but reasonable interpretation of the various x-ray and optical spectra of these materials.

INTRODUCTION

We have recently calculated the band structure of $MgCl_2$ using the intersecting-spheres model,[1] and those computations have allowed us to provide a rough, but seemingly correct interpretation of the x-ray spectra of that crystal. That work allowed us to estimate how accurate a description of the excitation spectra of $MgCl_2$ is provided by our rigid-band model (we remember that within the local-density formalism there is no sound theoretical reason for finding a close correspondence between calculated gaps and observed transition energies). In particular, we have noticed that the forbidden gap Δ of $MgCl_2$, as it results from the band calculation, is severely underestimated when the Slater or the Gâspâr-Kohn-Sham approximation of the exchange potential is used, since $\Delta = 5.5$ eV in the Slater case and 4.3 eV when the Gâspâr-Kohn-Sham exchange is used, while the experimental value[2] inferred[1] from the K-absorption and -emission spectra is $\Delta \simeq 7.5$ eV. While the identification of the gap between the halogen p levels and the metal s conduction band is unambiguous for $MgCl_2$, this is not the case for $NiCl_2$ and for the other materials investigated in the present work. For these crystals the identification is in fact complicated by the simultaneous presence of the empty s and d levels of the transition-metal ion. We have therefore reconsidered the problem, already investigated by us,[3] avoiding drawing conclusions from quantitative agreements between calculated gaps and observed structures which may be fortuitous; we have tried instead to learn something from qualitative facts, such as the behavior of corresponding levels in different compounds having the same crystal structure.

In the present work we have therefore comparatively investigated the electronic structures of $NiCl_2$, $CoCl_2$, $FeCl_2$, and $MnCl_2$. The first part of this article provides a description of the band structures of the above-mentioned crystals; the second part is devoted to a comparison of the calculated band structure with the experimental x-ray, optical, and photoemission spectra published in the literature. This comparison is maintained within the limits of qualitative considerations, but nevertheless, it enables us to provide a coherent interpretation of the main features of the spectra.

BAND STRUCTURE OF $NiCl_2$, $CoCl_2$, $FeCl_2$, AND $MnCl_2$

All the self-consistent band structures reported in this paper were calculated using the intersecting-spheres model.[4,5] This model, which can be applied both to molecules and to crystalline solids, has been described in detail in the articles cited above, to which the interested reader is referred. All the calculations were performed using the frozen-core approximation and simply neglecting the core Bloch sums in the secular equations. This procedure, which previous calculations[3] have shown to be highly accurate, is very simple to perform and makes the introduction of more complicated pseudopotential schemes practically unnecessary. We have found also that for the ionic compounds studied in the present work the contribution to the potential within a given atomic cell due to the neighboring ones can be simply approximated through a constant Madelung term, provided that errors in the relative position of the bands as large as 0.5 eV and errors in the charge content of the atomic cells no larger than 0.1 electrons can be tolerated. Since we knew that the use of the present calculations could not be rigorously quantitative, we have adopted the above-mentioned simplification, which reduces to less than half the time required for the computations.

The atomiclike functions used to build the Bloch sums were generated, as is usual for the intersecting-spheres model, by solving the self-consistent atomic problem with the outer boundary condition of vanishing functions imposed not at infinity but at a finite radius. The value of this radius was chosen to be $R=5.7$ a.u. for all the atoms, as was done in previous calculations.[1] Discarding the core states, which only contribute a fixed-charge-density distribution, we have built Bloch sums using the atomiclike orbitals $4s$, $5s$, $4p$, $5p$, $3d$, $4d$, $4f$ for the transition-metal atom and the orbitals $3s$, $4s$, $3p$, $4p$, $3d$, $4d$, $4f$ for the Cl atom. This choice considers orbitals of different azimuthal quantum number that lie in energy below a common upper limit, set at 30 eV above the position of the Cl $3p$ levels. This way of selecting the basis functions was tested by us in the case of alkali halides[6] and the actual setting of the limit was chosen to ensure that the estimated truncation errors were less than 0.5 eV even for levels lying 1 Ry above the bottom of the conduction bands. Previous calculations[3] performed by us for $NiCl_2$ did not include the f orbitals which proved to be essential[6] to reach a satisfactory convergence for the high-lying conduction levels.

All the crystals considered here have the structure of $MgCl_2$. Since this structure and the associated Brillouin zone, which is shown in Fig. 1, are described in Refs. 1 and 3, we do not describe them here. We remember only that the lattice constant of these crystals was assumed[7] to be $a=11.584$ a.u. for $NiCl_2$, $a=11.641$ a.u. for $CoCl_2$, and $a=11.717$ a.u. for both $FeCl_2$ and $MnCl_2$. For all the crystals considered here the thickness of the interstitial spline regions was chosen to be $d=0.8$ a.u., as previously done.[1,3] The crystal potential was expanded in spherical harmonics retaining terms up to $l=4$.

The resulting band structures are shown in Figs. 2–6, which display the energy levels along a path in the irreducible segment of the Brillouin zone which can easily be traced in Fig. 1. Figures 2 and 3 display the band structure of $NiCl_2$ calculated with the Gáspár-Kohn-Sham ($\alpha=\frac{2}{3}$) and with the Slater ($\alpha=1$) approximation, respectively. When these figures are compared with the band structure of $MgCl_2$, shown in Figs. 2 and 3 of Ref. 1, we note a striking similarity between the two results, both for the valence p levels and for the conduction levels above the Γ_1^+ minimum. Obviously, the band structure of $NiCl_2$ displays, in addition, five narrow bands originating from the metal $3d$ levels. These bands lie in the gap between the halogen p levels and the Γ_1^+ conduction minimum, and they can be divided into two groups of three and two as a consequence of the near-octahedral symmetry occurring around the transition-metal site; in the case of $NiCl_2$ they are partly filled with eight electrons. The only relevant effect of the presence of these d levels on the overall band structure seems, however, to be a downward shift of the Γ_3^+, Z_3^+, L_2^+, F_2^+, and upper F_1^+ valence levels; the eigenvectors corresponding to these levels

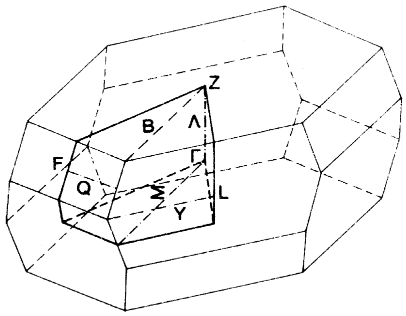

FIG. 1. Brillouin zone for the crystals studied in this paper. The symmetry points Γ, Z, L, F and the symmetry lines Σ, Λ, Y, Q, B (dash dotted) are shown. The heavy lines delimit the irreducible segment.

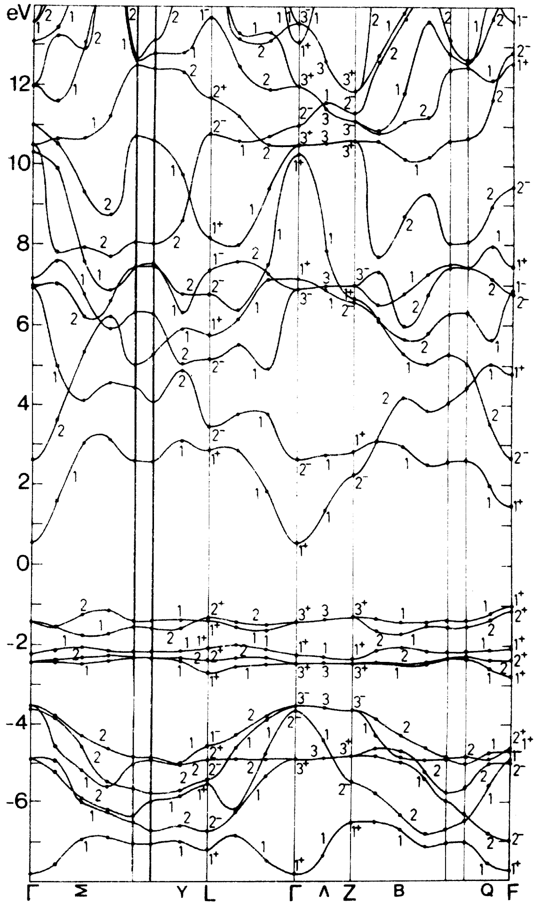

FIG. 2. Band structure of $NiCl_2$ along a path connecting and including the symmetry lines shown in Fig. 1. The Gáspár-Kohn-Sham ($\alpha=\frac{2}{3}$) approximation for the exchange potential was used.

contain, in fact, a sizable contribution coming from the metal $3d$ orbitals. Owing to the strong similarity existing between the band structures of $MgCl_2$ and of $NiCl_2$, the analysis of the wave functions of the conduction levels reported in Table II of Ref. 1 is also valid for $NiCl_2$, provided that the heading "Ni" is substituted for "Mg" and 4 is substituted for 3 in the labels of the metal orbitals. For $NiCl_2$ the width of the p valence region is $W = 4.3$ eV when $\alpha = \frac{2}{3}$ and $W = 3.2$ eV when $\alpha = 1$. The gap between the valence Γ_3^- level and the Γ_1^+ conduction minimum has a width $\Delta = 4.1$ eV when $\alpha = \frac{2}{3}$, while $\Delta = 5.9$ eV when $\alpha = 1$. These values are very similar to those obtained for $MgCl_2$, using the approximation of the self-consistent potential adopted in the present work. We note that when $\alpha = 1$ the d levels lie closer to the top of the p valence band than when $\alpha = \frac{2}{3}$. We note further that, as it occurred for $MgCl_2$, even for $NiCl_2$ a region with a low density of states can be predicted to occur between 7 and 10 eV above the bottom of the conduction band.

In Figs. 4, 5, and 6, respectively, the band structures of $CoCl_2$, $FeCl_2$ and $MnCl_2$ are reported. The upper part of each of these figures displays the Gâspâr-Kohn-Sham result, while the bands calculated with the Slater approximation are shown in the lower part. In these figures we have not reported the high-lying conduction bands—they are so similar to those occurring for $NiCl_2$ that it is useless to show them individually. Looking instead for the differences we find that while the $\Gamma_3^- \rightarrow \Gamma_1^+$ gap widens slightly (0.4 eV) when going from $NiCl_2$ to $MnCl_2$, the whole d region moves upward considerably. In the case of the Slater approximation it goes from a location in near contact with the p valence bands to a position in the middle of the $\Gamma_3^- \rightarrow \Gamma_1^+$ gap; when $\alpha = \frac{2}{3}$ the d region is located in $NiCl_2$ in the lower half of the gap, while in $MnCl_2$ it reaches the conduction Γ_1^+ level. While shifting, the d bands also undergo deforma-

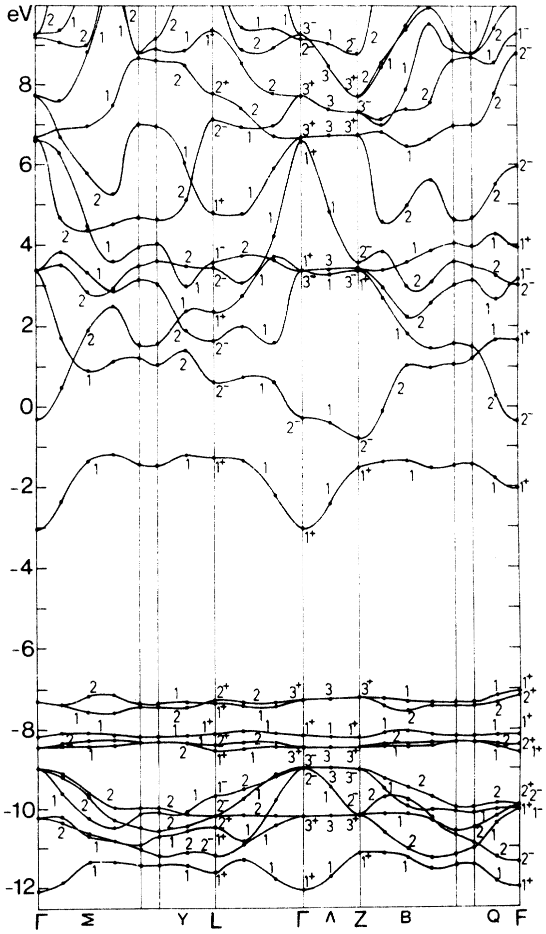

FIG. 3. Band structure of $NiCl_2$ along the path adopted in Fig. 2. The Slater approximation ($\alpha = 1$) for the exchange potential was used.

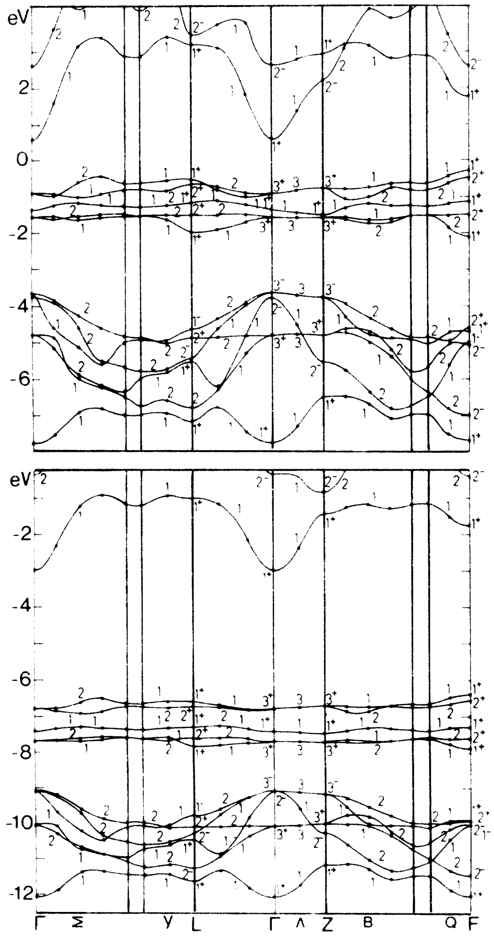

FIG. 4. Band structure of $CoCl_2$. The upper and lower parts display the result for $\alpha = \frac{2}{3}$ and 1, respectively.

tions that are not negligible; an indicative average value for the overall shift of the d bands relative to the Γ_3^- valence level is 2 eV both for $\alpha=1$ and for $\alpha=\frac{2}{3}$. When the d bands shift upward the Γ_3^+, Z_3^+, L_2^+, F_2^+, and upper F_1^+ valence levels follow them somewhat, tending to the position which they assume in MgCl_2. The proximity of the highest F_1^+ and L_1^+ d levels seems also to influence the F_1^+ and L_1^+ conduction levels, which shift upward 0.5 eV relative to the Γ_1^+ bottom conduction level when we go from NiCl_2 to MnCl_2.

In order to explain the behavior of the d bands relative to the other levels we remember that they are partially filled and that the filling decreases in steps of one electron when we go along the series NiCl_2, CoCl_2, FeCl_2, MnCl_2. It is reasonable to expect a shift of the d levels of atomic origin, and we have verified its existence by performing atomic calculations. We have found that the atomic d levels, calculated with the Slater-exchange approximation, shift upward about 3 eV when going from Ni to Mn. The crystalline environment modifies the numerical value of the shift without essentially altering the atomic trend. A similar shift of the d levels may be noticed also in the calculated band structures[8] of FeO, CoO, and NiO, although in that case the mixing of p and d levels seems to be more important than in the present case.

COMPARISON WITH EXPERIMENT

We have shown previously that, if the d levels are not considered, a striking similarity exists between the calculated band structure of NiCl_2, CoCl_2, FeCl_2, MnCl_2, and the occurring for MgCl_2. It is reasonable, then, to expect such a likeness to occur even for the experimental data. This is indeed the case for, e.g., the x-ray K-absorption and -emission spectra.[9] If the K-absorption curves reported in Fig. 1 of Ref. 9 are compared with the spectrum of MgCl_2 shown in Fig. 1

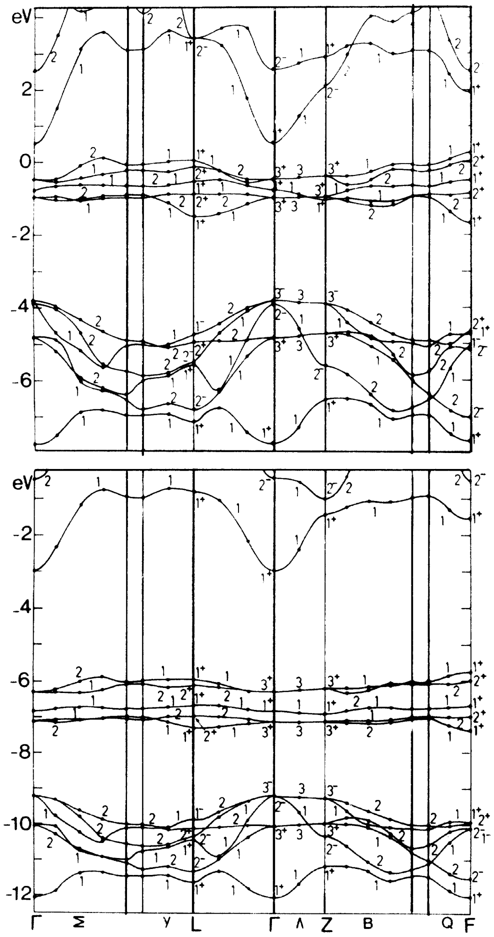

FIG. 5. Band structure of FeCl_2. The upper and lower parts display the results for $\alpha=\frac{2}{3}$ and 1, respectively.

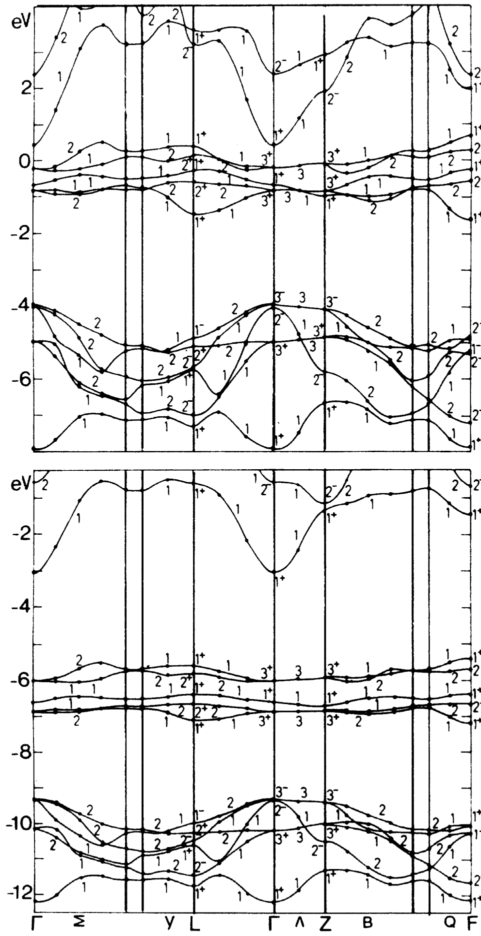

FIG. 6. Band structure of MnCl_2. The upper and lower parts display the results for $\alpha=\frac{2}{3}$ and 1, respectively.

of Ref. 2 we find that the structures labeled C, D, and E are common features of all the spectra, for which even a rough quantitative agreement exists. For what concerns the A and B structures shown in Fig. 1 of Ref. 9 we note that while B lies at a nearly fixed energy in the various spectra, the structure A shifts about 3 eV towards higher energies when we go from $NiCl_2$ to $MnCl_2$. It is reasonable, then, to associate the structure B with a transition involving the F_1^+ conduction level, as was done[1] for the structure A of $MgCl_2$, which lies at the same energy (we remember that the K transition having the Γ_1^+ level as final state is not allowed for radiation incident normally to the plane of the layers). The shifting structure labeled A in Fig. 1 of Ref. 9 can then be identified with K transitions involving the empty metal $3d$ levels as final states.

For what concerns the other structures visible in the K-absorption spectra it seems hazardous to try an identification; we note only that in all the spectra a sharp minimum of the intensity of absorption is found about 8 eV above the B structure. This minimum has a theoretical counterpart in the dip of the density of states which an inspection of the bands allows predicting between 7 and 10 eV above the bottom Γ_1^+ conduction level. Finally, we note the apparent agreement between the Gâspâr-Kohn-Sham result for the p valence band width and the experimental K-emission data which seems to suggest that the occupied d levels contribute slightly to the emission curves, their presence being revealed only by the long high-energy tail.

The interpretation of the K-absorption data allows us to undertake the more difficult task of understanding the $Cl^- L_{2,3}$ spectra.[10] Also, in this case we have a high-energy part of the absorption curves, above say 204 eV, which does not change much when we go from $NiCl_2$ to $MnCl_2$, and which is roughly reminiscent of the spectrum[10] occurring for $MgCl_2$. The low-energy part of the curves displays instead dramatic changes when we go along the series of the four compounds. The identification of corresponding structures is complicated by the doubling produced by the spin-orbit splitting of the Cl $2p$ level. It is, however, possible to identify the shifting doublet A, clearly visible in the spectra of $NiCl_2$ and $CoCl_2$ (see Fig. 7 of Ref. 10), with transitions arriving at the empty d levels. The fixed B doublet can instead be attributed to excitons connected with the bottom Γ_1^+ of the conduction bands. We note that the B doublet lies at the same energy as the A doublet in the spectrum of $MgCl_2$, for which the association with the above mentioned Γ_1^+ level has already been proposed.[1] The structure called D in the spectra of the transition metal halides can consequently be associated with an exciton resonance connected with the F_1^+ level. We note further that even in the $Cl^- L_{2,3}$ spectra we find a minimum of absorption about 7 eV above the B doublet which can be associated with the already mentioned dip in the theoretical density of states.

For what concerns the interpretation of the low-energy part of the spectra of $FeCl_2$ and $MnCl_2$ we are confronted with a rather interesting situation. In fact, if the d levels get close to the conduction-band continuum or become degenerate with it near to the Γ_1^+ bottom, as is suggested by the calculated band structures and by the K-absorption data of $FeCl_2$ and $MnCl_2$, we must expect that both the propagating s states and the localized d levels will contribute to the formation of core excitons. The two competing mechanisms can give rise to interference phenomena, causing a strong dependence of the height and shape of the excitonic peaks on the relative position of the bands. Such a situation indeed seems to occur in the lower part of the spectra of $FeCl_2$ and $MnCl_2$, which cannot be interpreted with an additive one-electron scheme.

The $M_{2,3}$ absorption spectra[11] are rather difficult to understand, since the starting levels lie at a different energy in each of the four compounds. It seems, however, reasonable to attribute the strongest peak in the spectra of $FeCl_2$ and $CoCl_2$, and the peak labeled H in the spectrum of $NiCl_2$, reported in Fig. 6 of Ref. 11, to a transition associated with the bottom of the conduction bands Γ_1^+. In this way we preserve the evenness of the shift of the metal $3p$ levels, as suggested by the atomic calculations. The structure labeled H in the spectra of $CoCl_2$ and $FeCl_2$ should instead be associated with the d levels. This is all that can be said with the help of the calculated band structures. Obviously the spectra contain much more information which cannot be understood with a one-electron scheme.

The most intriguing of the unexplained features of the $M_{2,3}$ spectra is the complete absence of any structure in the low-energy side of the H peak in $NiCl_2$. According to the band calculations and also to the experimental K and $L_{2,3}$ spectra, sharp and well-separated structure associated with the d levels should be present there.

For what concerns the fundamental absorption spectra[12] it is reasonable to interpret the fixed D structures in Fig. 2 of Ref. 12 as excitons associated with the $\Gamma_3^- \rightarrow \Gamma_1^+$ interband gap. Its width should therefore be about 8.5 eV, a value which is much larger than that predicted, even with the Slater approximation. It was this discrepancy which led us to a wrong identification of the fundamental gap in a previous work[3] concerning $NiCl_2$, $NiBr_2$, $CrCl_3$, and $CrBr_3$.

The shifting structure B in Fig. 2 of Ref. 12, which in the spectrum of $MnCl_2$ finally merges into the D structure, is evidently associated with the empty d levels and confirms the overall picture provided by the band calculations. We observe, however, that both the additional structures which are present in the low-energy part of the spectra and the interesting details of the merging of the D and B structures cannot be understood with a one-electron approach. We note further that a shallow minimum is visible in the fundamental absorption spectra of $NiCl_2$, $CoCl_2$, and $FeCl_2$ about 7.5 eV above the D structures, in correspondence with the theoretically predicted dip.

Finally, for what concerns the photoemission data[13] we confirm the interpretation of the spectrum of $NiCl_2$ previously given[3] by us, and observe that the distance between the structures labeled A and D in Fig. 1 of Ref. 13, which presumably mark the top of the occupied d levels and the bottom of the p valence bands, respectively, is 2 eV larger in $MnCl_2$ than in $NiCl_2$. This behavior is roughly consistent with the results of the band calculations but, again, a detailed analysis of the observed multiplet structure is beyond the possibilities of a one-electron formalism.

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[1] S. Antoci and L. Mihich, Solid State Commun. 31, 861 (1979).

[2] C. Sugiura, Phys. Rev. B 9, 2679 (1974).

[3] S. Antoci and L. Mihich, Phys. Rev. B 18, 5768 (1978).

[4] S. Antoci and L. Mihich, J. Chem. Phys. 64, 1422 (1976); S. Antoci, J. Chem. Phys. 65, 253 (1976).

[5] S. Antoci and L. Mihich, Solid State Commun. 22, 783 (1977); S. Antoci and L. Mihich, Phys. Rev. B 17, 1859 (1978).

[6] S. Antoci and L. Mihich, Phys. Rev. B 21, 3383 (1980).

[7] R. W. G. Wyckoff, *Crystal Structure* (Interscience, New York, 1964).

[8] A. B. Kunz and G. T. Surratt, Solid State Commun. 25, 9 (1978).

[9] C. Sugiura, J. Phys. Soc. Jpn. 33, 455 (1972).

[10] S. Sato *et al.*, J. Phys. Soc. Jpn. 30, 459 (1971).

[11] S. Nakai *et al.*, Phys. Rev. B 9, 1870 (1974).

[12] T. Ishii *et al.*, Solid State Commun. 13, 281 (1973); Y. Sakisaka, T. Ishii, and T. Sagawa, J. Phys. Soc. Jpn. 36, 1365 (1974).

[13] T. Ishii *et al.*, Phys. Rev. B 12, 4320 (1975).