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d-d transfer in transition-metal monoxides and dihalides

E. J. Ojala and K. Terakura
Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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It is pointed out that some qualitative differences exist in the upper *d*-band edge of the observed uv photoemission spectra among the insulating transition-metal monoxides (TMO's) and dihalides (TMH's), MnO, NiO, $MnCl_2$, and $NiCl_2$. On the basis of band-structure calculations, we interpret this fact as a manifestation of the significance of the *d-d* hopping in TMO's. In relation to this, we predict that photoemission and inverse photoemission spectra will show significant changes for TMO's as the measuring temperature crosses the Néel temperature, but virtually no change for TMH's.

I. INTRODUCTION

Recently, many features of the x-ray photoemission (XPS) and bremsstrahlung isochromat (BIS) (Refs. 1 and 2) and uv photoemission spectra (UPS) (Ref. 3) of NiO were successfully interpreted by local cluster calculations including configuration interactions.[4] These calculations include hybridization between anion *p* and cation *d* states and the *d-d* Coulomb interaction *U*. Kübler and Williams also gave a coherent interpretation of these experiments based on band-structure calculations using the local-spin-density-functional (LSDF) formalism for a supercell of Mg_7NiO_8.[5] Among the arguments in the latter work, the point related most closely to the present paper is the following: By adding (subtracting) one *d* electron per unit cell and keeping charge neutrality by introducing a uniform charge background, they obtained an upward (downward) shift of unoccupied (occupied) *d* levels by about 2 eV with respect to the ground-state *d* band. Thereby, their effective *U* of 4 eV, which includes the effects of oxygen-*p*-state polarization, explains the observed separation between the d^8L peak of XPS and the d^9 peak of BIS.[1,2] With these new experiments and theories taken together, we admit that localized holes and electrons participate in the processes of XPS, UPS, and BIS as far as the *d*-state part of the spectra of NiO is concerned. On the other hand, significance of the *d-d* hopping in transition-metal monoxides (TMO's) is also clear, for example, from the relatively high Néel temperature T_N and from the variation of the lattice constant[6] across the TMO series. The purpose of this paper is to show another piece of evidence of *d-d* hopping derived from photoemission spectra, particularly at $T > T_N$.

Looking at the UPS spectra of TMO's by Eastman and Freeouf[7] and of transition-metal dihalides (TMH's) by Kakizaki *et al.*,[8,9] we notice some interesting features at the upper *d*-band edge. In Fig. 1 the small-binding-energy parts of the spectra are shown for NiO, MnO, $NiCl_2$, and $MnCl_2$. All other spectra except that of MnO exhibit sharp upper edges. The edge in the MnO spectrum is clearly more rounded. We will discuss this material dependence of the spectral shape on the basis of electronic structure calculations, and we conclude that the behavior is reasonable and, in fact, is an indication of considerable *d-d* hopping in TMO's.

In the following, the results of the electronic structure calculations from our earlier works[10–12] will be referred to for the TMO's, but new calculations were carried out for TMH's in nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AF) states by the augmented-spherical-wave (ASW) method[13] with the LSDF formalism. The lattice parameters for TMH's are taken to be the same as those used by Antoci and Mihich[14,15] in their calculations for nonmagnetic TMH's. Their results for the intersecting-sphere model are very similar to ours for

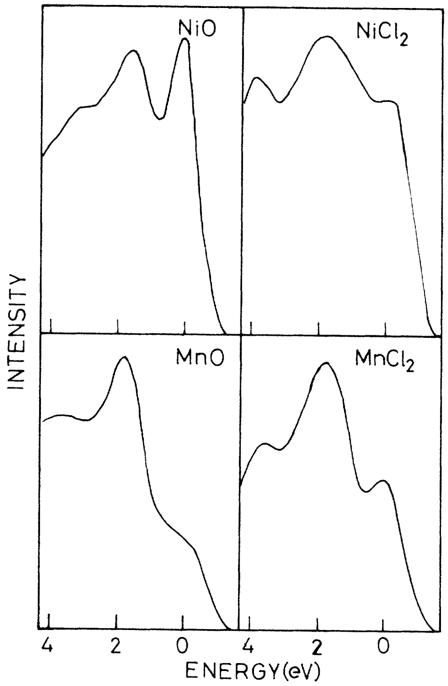

FIG. 1. The upper part of the UPS spectra of NiO and MnO (Ref. 7) and of $NiCl_2$ and $MnCl_2$ (Ref. 8) taken at a photon energy of 30 eV. The energy zero is taken at the top of the uppermost structure.

NM states, except for the difference that our anion p to cation d energy separation is smaller than theirs by about 1 eV.[16]

In Sec. II we present detailed discussions of the qualitative difference between the shape of the upper d-band edge in the UPS spectrum of MnO and that of some other transition-metal compounds (NiO, $NiCl_2$, and $MnCl_2$). Section III is devoted to a brief discussion of the anion p to cation d energy separation in relation to the effective-U effect, both below and above T_N. Concluding remarks will be made in Sec. IV.

II. SPECTRAL SHAPE OF UPPER-d-BAND EDGE OF UPS

If we take the main lines of the UPS spectra of TMO's and TMH's to be only ligand-field levels broadened due to instrumental and lifetime smearing effects, the very broad shape of the MnO spectrum at the upper-d-band edge (Fig. 1) seems puzzling, especially because the lifetime broadening should be very small around that energy. We will give an interpretation of this material dependence of the spectral shape by using the band-structure calculations for some different magnetic orderings.

Before presenting a detailed discussion, we will comment on our reason for doing this sort of analysis of the UPS or XPS spectra of insulating transition-metal compounds by using the band calculations based on the LSDF formalism. Let us take NiO as an example. Our band calculation for the ground state predicts only a 1 eV bandwidth for both the t_{2g} and e_g states.[12] For such a narrow-band case, the d-d Coulomb correlation effect and also the polaronic effect due to the polarization of oxygen p states will make d holes, created in the process of photoemission, fairly localized. One can say that the localized picture is supported by the narrow bandwidth obtained by the band calculations. Another important aspect is that, in NiO, both the ligand-field splitting and the exchange splitting are about 1 eV,[12] so that the e_g band of majority spin overlaps the t_{2g} band of minority spin. Therefore, the ratio of the weights of the topmost peak (e_g states of majority spin and t_{2g} states of minority spin) and the second peak (t_{2g} states of majority spin) is about 5:3, being close to the value observed by XPS. Except for the problem of the oxygen p to nickel d energy separation, our band density of states (DOS) corresponds well with the experimentally decomposed contributions in the UPS spectra.[7] (The satellite problem is beyond the scope of this paper.) For MnO in the ground-state magnetic ordering, the localization problem is just the same as in NiO. As for the level scheme, ligand-field theory predicts only two levels separated by $10Dq$,[7] which correspond to our t_{2g} and e_g bands. Again, the discrepancies between UPS (or XPS) spectra and our band DOS are concerned with the O p to Mn d energy separation and satellites. Such is also the case even for FeO and CoO, which will not be discussed here. (See Fig. 2 of Ref. 7 and Figs. 8 and 9 of Ref. 12.) The arguments in the above imply that the band-structure calculation can be a good guide for interpreting the UPS and XPS spectra even for insulating transition-metal compounds.

Returning to the main theme of this section, we first point out two crucial factors for understanding the material dependence of the spectral shape. The first one is the temperature T at which the measurements have been carried out with respect to T_N: for MnO $T > T_N$ (122 K), for NiO $T < T_N$ (523 K), for $MnCl_2$ $T > T_N$ (2 K), and for $NiCl_2$ $T > T_N$ (52 K). (To our knowledge, no data have been taken for MnO or any of the materials considered here both below and above T_N.) It will become clear that the difference in the relative magnitude of T and T_N is responsible for the difference in the upper-d-band edge shapes of MnO and NiO. This behavior is a consequence of the change in the d-d hopping associated with the change in the magnetic ordering. The second factor, the crystal structure, will then explain why the edge of the UPS spectra of TMH's is sharper than that of MnO, although all spectra were measured at $T > T_N$. The two factors will be described in detail in the rest of this section.

TMO's crystallize in the NaCl structure. It was shown[12] that the electronic structure of TMO's is very sensitive to the magnetic ordering. MnO in the FM or AF I configuration has a wide e_g band,[12] similar to the NM case, due to the large d-d hopping in the NaCl structure. In NiO the situation is fairly subtle; even the atomic magnetic moment in FM and AF I states is on the verge of being or not being stable.[6,12] (In the AF I configuration, the magnetization varies in the [100] direction.) The ground-state antiferromagnetic ordering (AF II) shown in Fig. 2, in which the magnetization varies in the [111] direction, has the special property of coupling oppositely magnetized cation atoms via intermediating oxygen p orbitals. Thus the d-d hopping of $dd\sigma$ type between the second-nearest-neighbor cations, which is the dominant d-d hopping in TMO's, is effectively reduced to make the e_g band very narrow. This special aspect of the AF II configuration is responsible also for producing a gap in both MnO and NiO in band theory.[12]

TMH's, $MnCl_2$ and $NiCl_2$ (and also $NiBr_2$), crystallize in the rhombohedral $CdCl_2$ structure. This crystal structure can be obtained from the NaCl structure by removing every other metal layer in the [111] direction. Doing this in Fig. 2 and then reversing the spins of every other (111) metal layer, the ground-state magnetic ordering (AF) is realized. The actual magnetic structure of $MnCl_2$ is believed to be more complicated than that described above,[17] but that is not important in the present context. What is important here is that the $dd\sigma$ interaction mediated by the anion, which in TMO's makes the e_g band fairly broad in the NM, FM and AF I states, is completely absent in TMH's. Therefore, the e_g band of TMH's is expected to be very narrow irrespective of the magnetic orderings.

With the above qualitative consideration, we discuss in more detail the results of the electronic structure calculations for TMH's by comparing and contrasting them with those for TMO's.[12] One may notice that even the calculation for the NM state shows the clear-cut and qualitatively important difference between the band structures of TMH's and TMO's. As shown by Mattheiss,[18] the t_{2g} and e_g bands in NM TMO's with the NaCl structure will

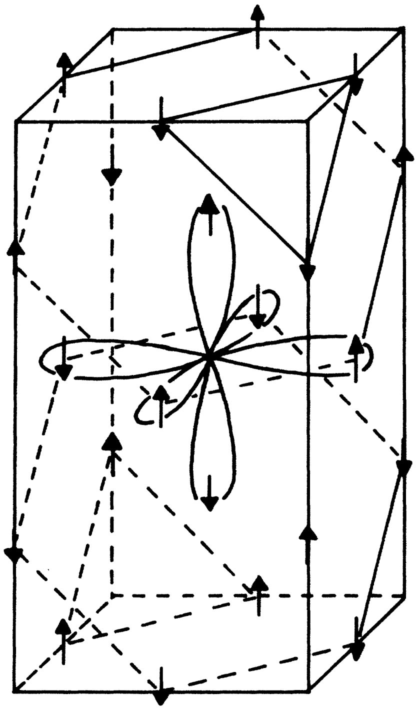

FIG. 2. Antiferromagnetic ground-state ordering of the second kind (AF II) of NiO and MnO. Metal sublattice and p orbitals at the central oxygen site are shown. Oxygen p orbitals couple different magnetic sublattices in this ordering. The $CdCl_2$ crystal structure can be generated by removing every other metal layer in [111] direction. The antiferromagnetic ground-state configuration of $NiCl_2$ and $MnCl_2$ is then obtained by reversing the spins of every other metal layer and replacing oxygen atoms by chlorine atoms.

always overlap, however strong the p-d hybridization is. This overlap mainly stems from the strong d-d hopping, which makes the e_g band very wide. In contrast, in TMH's with the $CdCl_2$ structure the t_{2g} and e_g bands split even in the NM state, the e_g band being very narrow.[14,15] This is just what we anticipated from the crystal structure of TMH's. It is thus evident that magnetic ordering does not play a significant role in producing a band gap at the Fermi level in TMH's. They have a band gap even in the FM state, simply because the exchange splitting is larger than the d-band width in $MnCl_2$ and it is larger than the e_g-band width in $NiCl_2$ (also $NiBr_2$). Due to the weak intersublattice coupling in the $CdCl_2$ structure, the DOS's of FM and AF states exhibit only minute differences and the DOS's for both of the majority and minority spin states look very similar to the NM DOS. It should be noted, however, that despite its weakness, the intersublattice coupling causes a small lowering of the e_g band in the AF configuration, thus stabilizing it (lower total energy) against the FM configuration just as in the TMO cases.[12]

Based on these arguments, we have the following qualitative correspondences between the electronic structures of TMO's and TMH's: TMO's in the AF II configuration without intersublattice coupling [see Figs. 4(b) and 6(b) in Ref. 12] correspond to TMH's in the AF configuration and TMO's in the AF II correspond to TMH's in the FM configuration. TMO's in FM and AF I configurations have no correspondence among TMH's. These features imply an important difference between TMO's and TMH's when modeling the paramagnetic state, $T > T_N$, by complete spin disorder. Simply, the paramagnetic DOS can be taken as some average of the DOS's obtained for different magnetic orderings or at least it should reflect the main features of them. It is clearly so in MnO. The DOS obtained from coherent-potential-approximation (CPA) calculations on MnO (Ref. 10) exhibits a smaller (larger) insulating gap and broader (narrower) e_g band compared to the DOS in the AF II (FM and AF I) configuration. This is mainly a consequence of the increased (decreased) d-d hopping in complete spin disorder compared to that in AF II (FM and AF I) ordering. The width of the t_{2g} band which mainly comes from the direct first-nearest-neighbor d-d interaction remains almost unchanged in all cases.

We will show that the above discussion together with the DOS's of TMO's (Refs. 10 and 12) and of TMH's leads to a natural explanation for the upper edges of the experimental UPS spectra shown in Fig. 1. To focus on the edge problem, only the occupied part of the DOS's will be shown, the position of the unoccupied bands of TMH's being nearly the same as shown previously for TMO's.[12] We show in Fig. 3 the most relevant DOS's to

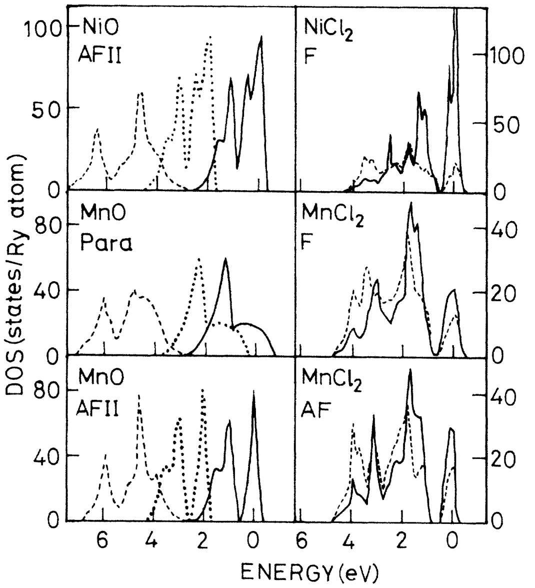

FIG. 3. Occupied part of the calculated densities of states for NiO, MnO, $NiCl_2$, and $MnCl_2$. Upper two panels show the most relevant DOS to be compared with the experimental data in Fig. 1. Lower panel gives a prediction for the spectral shape of MnO and $MnCl_2$ at temperatures below T_N. Solid lines denote mostly cation-d contributions and the dashed lines anion-p contributions. [In the case of TMO's, the p (d) contribution in the d (p) band region is about 20%, but is not indicated separately to avoid complicating the figures.] For MnO and NiO, d DOS's with energy shifts associated with creation of d hole are also shown by dotted lines. As the energy shifts, we took 2 eV for both of NiO and MnO in AF II ($T < T_N$) and 1 eV for MnO (paramagnetic, $T > T_N$). See Sec. III for details. Energy zero taken as in Fig. 1.

be compared with Fig. 1. For NiO the relevant DOS is AF II ($T<T_N$) and for MnO it is the CPA DOS ($T>T_N$). For $NiCl_2$ and $MnCl_2$ the DOS's of the FM state are shown. They should provide the upper limit of the width of both the t_{2g} and e_g bands at $T>T_N$. In order to interpret the UPS spectra, we have to take account of the localization effect caused by the *d*-*d* Coulomb correlation and the polaronic effect as stated earlier. A very narrow e_g band, except in paramagnetic MnO, implies that the *d* hole created in the e_g band may be well localized. This may also be true for the t_{2g} band in NiO and MnO in the AF II configuration. The *d* hole in the t_{2g} band in $NiCl_2$ and $MnCl_2$ may not be so well localized because of the significant overlap with Cl *p* states, although a calculation by a more accurate method than the ASW method is necessary to have strong confidence on this prediction.[16] Turning to the paramagnetic MnO on the other hand, we see that the e_g band has more than a 2 eV width and overlaps with the t_{2g} band, thus enhancing t_{2g}-e_g hybridization. Therefore, the t_{2g}-e_g hybrid band with a width of more than 3 eV is the object that we must deal with. Now, the *d* hole in question will be fairly mobile, although it may not exactly be in a Bloch state. The rounded upper-edge shape of UPS spectrum of MnO is interpreted as a manifestation of the enhanced *d*-*d* hopping in the paramagnetic state.

In conclusion, the DOS's in Fig. 3 account excellently for the edge shapes in Fig. 1, the sharp edge in NiO, $NiCl_2$, and $MnCl_2$ and the much rounder edge in MnO. The lowest panel of Fig. 3 displays the DOS's of MnO and $MnCl_2$ in the antiferromagnetic ground state corresponding to measurements at $T<T_N$. The temperature-independent sharp *d*-band edge in $MnCl_2$ (also in $NiCl_2$ and $NiBr_2$) and the clearly temperature-dependent edge in MnO are predicted.

III. ENERGY SEPARATION BETWEEN ANION *p* AND CATION *d* STATES

As stated in the preceding section, one of the apparent discrepancies between DOS's of band calculations and UPS spectra exists in the anion *p* to cation *d* energy separation. The experimental value of this quantity for NiO is smaller than that of the band DOS by about 2 eV, which is just the value obtained by Kübler and Williams[5] as the energy shift of the *d* state associated with creation of a *d* hole (the value being half of their effective-*U* value). The theoretical value was obtained by assuming that the hole is localized on a single Ni ion surrounded by anions. On the other hand, the corresponding value for paramagnetic MnO is assigned to be only 1 eV by comparison between Fig. 2 of Ref. 7 and Fig. 3 of this paper. Since we do not notice any meaningful difference between NiO and MnO in the *p*-*d* hybridization, we expect an almost identical *d*-band shift for the two materials, if both are in the AF II configuration. Therefore, the reduction in the *d*-band shift in the paramagnetic state of MnO may be another indication of the enhanced *d*-*d* hopping: the *d* hole is no longer well localized, thereby reducing the effective-*U* value. This way, we predict not only a sharper upper-*d*-band edge but also a reduction in the anion *p* to cation *d* energy separation by about 1 eV, when measurement is done at $T<T_N$ for MnO. A similar temperature effect may also be observed in the photoemission spectrum of NiO, and it would be particularly interesting to probe the temperature dependence of the unoccupied e_g band by BIS: at $T>T_N$, the d^9 peak will become broader and will be shifted closer to the Fermi level by about 1 eV. Unfortunately, however, such an experiment will certainly be very difficult, because of oxygen evaporation from the sample surface at $T>T_N$.

As for TMH's, our ground-state DOS's have good values for the *p*-*d* energy separations. We may be able to take this fact as an indication of a reduced *U* value due to a stronger *p*-*d* hybridization in TMH's, because of rather diffuse anion *p* orbitals. However, as the ASW method is not accurate enough for these materials, it may be rather dangerous to derive definitive conclusions at the present stage.[16] Anyhow, we are able to predict temperature-independent *p*-*d* separation in TMH's.

IV. CONCLUDING REMARKS

We have shown that electronic structure calculations account well for the qualitatively different shape of the upper edge of the UPS measurements in MnO compared with NiO and TMH's. This stresses the importance of the effect of magnetic order and thus *d*-*d* hopping on the electronic structure of TMO. We have also suggested a significant change in the effective-*U* value of TMO, which reflects the degree of localization of *d* holes or additional *d* electrons. The change in the effective *U* will then be reflected in the energy separations between occupied *d* states and unoccupied ones, and also between the occupied anion *p* and cation *d* states. UPS and BIS measurements carried out both below and above T_N for MnO (or equivalently for α-MnS with $T_N=150$ K) and NiO are strongly urged in order to have a more direct assessment of the importance of *d*-*d* hopping in TMO.

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