

CHARGE TRANSFER TRANSITION ACCOMPANYING X-RAY PHOTOIONIZATION IN TRANSITION-METAL COMPOUNDS

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ABSTRACT

Satellites, 5 to 10 eV below the main peaks, have been observed in the x-ray photoelectron spectra of the 2s, 2p, 3s, 3p and valence shells of the 3d transition-metal ions of nickel and copper oxides. They are believed to be the result of electron shake-up. Since shake-up satellites are present in ions with partially filled 3d shell but absent in ions with completely filled 3d shell, they may be attributed to monopole charge transfer transitions (ligand \rightarrow metal 3d) using the sudden approximation (monopole selection rules) and the ligand field theory.

INTRODUCTION

Satellite lines in x-ray photoelectron spectra can arise from simultaneous excitation of a second electron accompanying photoionization. Carlson et al.¹ and Siegbahn et al.² have successfully explained such multielectron excitation (electron shake-up) satellites in the rare gases using the sudden approximation. According to the sudden approximation^{1–4}, the probability that the photoemission of an electron with quantum numbers h from the N -electron system ψ_0 results in the particular $(N-1)$ electron system ψ_n^{ho} is given by

$$P_{n0}^h = |\langle \psi_n^{ho} | \psi_0^h \rangle|^2 \quad (1)$$

and the separation between the principal line and a satellite due to a simultaneous excitation ($0 \rightarrow n$) is given by

$$\Delta E_{n0}^{ho} = E_n^{ho} - E_0^{ho} \quad (2)$$

The subscript n and the superscript o denote the n -th excited state and the relaxed (final) state, respectively. In eqn. (1) we do not concern ourselves with the ejected photoelectron* but only with the consequence that is the result of a sudden change in the

* Since the overall process retains the selection rules for photoionization, viz., $\Delta L = \pm 1$, $\Delta S = 0$, the outgoing electron experiences the $\Delta l = \pm 1$ change.

net effective charge. In this paper an interpretation of shake-up satellites in 3d transition-metal compounds in terms of monopole charge transfer transitions (ligand \rightarrow metal 3d) is presented using the sudden approximation and the ligand field theory. Wertheim et al.⁵ and Jørgensen and Berthou⁶ have attributed satellites in the 3d x-ray photoelectron spectra of rare-earth ions to simultaneous charge transfer transitions (ligand \rightarrow metal 4f).

Shake-up satellites in 3d transition-metal compounds, 5 to 10 eV below the main peaks, have been proposed to arise from various transitions⁷⁻¹² of a second electron accompanying the primary photoionization. Two points appear in this work which will be critically evaluated: (1) the suggestion⁷⁻¹¹ that transitions related to the atomic notation $3d \rightarrow 4s$, $3d \rightarrow 4p$ and $3d \rightarrow 3d$ occur and (2) the suggestion that satellite lines due to shake-up occur in Cu^{I} compounds^{9, 10}. As to the first suggestion $3d \rightarrow 4s$, $3d \rightarrow 4p$ and $3d \rightarrow 3d$ transitions are not proper in the strictest sense of the sudden approximation since for an atomic model not only are $\Delta J = \Delta M_J = 0$ but for a single electron $\Delta j = \Delta l = \Delta m_l = \Delta m_s = 0$, although configuration interaction might make them allowed. It will be pointed out later in this paper that the energy for these transitions is probably inconsistent with the experiment. As to the suggestion that satellite lines occur in Cu^{I} compounds, data will be presented which contradict this suggestion and are in agreement with later studies¹¹⁻¹⁴.

The model given in this paper will be shown to be consistent with the experimental data, both with regard to when satellites occur and the energy of excitation.

CLUSTER MODEL

Theoretical emphasis in the study of transition-metal compounds has concentrated on clusters containing a metal ion (M) surrounded by its neighboring anions or ligands (L) as being representative of the crystal¹⁵⁻¹⁷. The optical transitions in many crystals are ordinarily rather localized excitations, in which spin orbitals concentrated on one atom or a cluster are the initial or final states of the transition. Thus as a first approximation, spin orbitals of a cluster can be used to describe optical transitions such as charge transfer transitions. Let us consider an octahedral cluster (ML_6 , $(t_{2g})^x(e_g)^y$) of a transition-metal ion using the sudden approximation. According to eqn. (1), monopole charge transfer transitions such as $\pi t_{2g}^b \rightarrow 3d^a e_g^{ao}$, $\sigma e_g^b \rightarrow 3d^a e_g^{ao}$, $\sigma a_{1g}^b \rightarrow 4s^a a_{1g}^{ao}$, etc. (in the order of increasing energy) are allowed. That is, there is no change in the molecular orbital symmetry as the result of the transition. The superscripts a and b denote antibonding and bonding orbitals, respectively. (Satellite position is determined by the transition energy in the relaxed system according to eqn. (2). For example, a satellite due to the $\sigma e_g^b \rightarrow 3d^a e_g^{ao}$ transition is separated from the principal line by the $\sigma^a e_g^{bo} \rightarrow 3d^a e_g^{ao}$ transition energy¹⁸.) Since 4s-like virtual orbitals contribute to the formation of conduction band in many crystals, the use of the cluster model in this paper is confined to the description of charge transfer transitions from π - and σ -like ligand orbitals to empty 3d-like orbitals.

Shake-up satellite structure in ions with a $(t_{2g})^x(e_g)^y$ configuration will be quite different from that in ions with a $(t_{2g})^6(e_g)^4$ configuration, since neither $\pi t_{2g}^b \rightarrow 3d^o t_{2g}^{ao}$ nor $\sigma e_g^b \rightarrow 3d^o e_g^{ao}$ satellites are present in the latter. This point can be used to verify the monopole charge transfer transition mechanism. Transition-metal ions with a $(t_{2g})^x(e_g)^y$ configuration such as Cu^{II} , Ni^{II} , Ni^{III} , Co^{II} , Co^{III} , Fe^{II} , Fe^{III} , Mn^{II} , etc. show the 2p shake-up satellite structure lying 5 to 10 eV below the principal line^{7-12, 19, 20} and Zn^{II} ions with a $(t_{2g})^6(e_g)^4$ configuration do not show such satellite structure⁷, which is in accordance with the monopole charge transfer transition mechanism. However, the presence of intense 5 ~ 10-eV shake-up satellite structure in the 2p electron spectra of Cu^{I} ions with a $(t_{2g})^6(e_g)^4$ configuration has been reported^{9, 10, 21}. In connection with this point the following Cu^{I} and Cu^{II} compounds and NiO were investigated: Cu_2O , CuCl , CuBr , CuI , CuCN , CuO , CuF_2 , $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, CuCl_2 , CuBr_2 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cu}_2(\text{CH}_3\text{COO})_4$, $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$, and $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.

EXPERIMENTAL RESULTS

Spectra were obtained on a Hewlett-Packard ESCA spectrometer using monochromatic $\text{Al K}\alpha$ x-rays. The instrumental resolution yields a linewidth of 0.8 eV on the Au 4f lines under the experimental conditions in this work. Commercially obtained compounds were used except Cu_2O , NiO and CuO , which were prepared by heating^{12, 22} Cu and Ni plates and commercially obtained CuO in air at 200, 800 and 600°C, respectively.

The experimental results related to multielectron excitations are as follows: (a) there is present satellite structure lying 5 ~ 10 eV below the principal lines in the Cu^{II} 2s, 2p, 3s, 3p and valence-band photoelectron spectra, and these satellites depend on the ligands; (b) there is an absence of such distinctive satellites in the Cu^{I} photoelectron spectra; (c) a greater full width at half maximum (FWHM) for the Cu^{II} line occurs than the corresponding Cu^{I} line (for example, 2.5 ± 0.5 eV vs. 1.2 ± 0.2 eV for the $\text{Cu 2p}_{3/2}$ peaks); (d) there is present a satellite line 6 to 7 eV below the principal lines of the Ni 2s, 2p, 3s, 3p and valence-band photoelectron spectra of NiO . The spectrum arising from photoionization in the Cu 2p shell was taken for each Cu compound, but spectra for the other subshells were taken only for CuO , CuCl_2 , CuF_2 , Cu_2O and CuI_2 . These results agree with those reported previously. Wertheim and Hüfner⁸ have reported a similarity in shake-up satellite structure in the cation 2p and valence-band spectra of CuO and NiO . In a recent study of a number of copper compounds in the Cu 2p, 3s and 3p regions which was carried out contemporaneously with the present work, Frost et al.¹¹ have reported similar results. Regarding the spectral data of Cu^{II} compounds, see ref. 11.

The inner-shell photoelectron spectra of CuO , Cu_2O and NiO are shown in Figures 1-3. The binding energies are referenced to C 1s peak of graphite at 284.4 eV. Regarding their valence-band spectra, see ref. 8. The intensities of extra oxygen peak

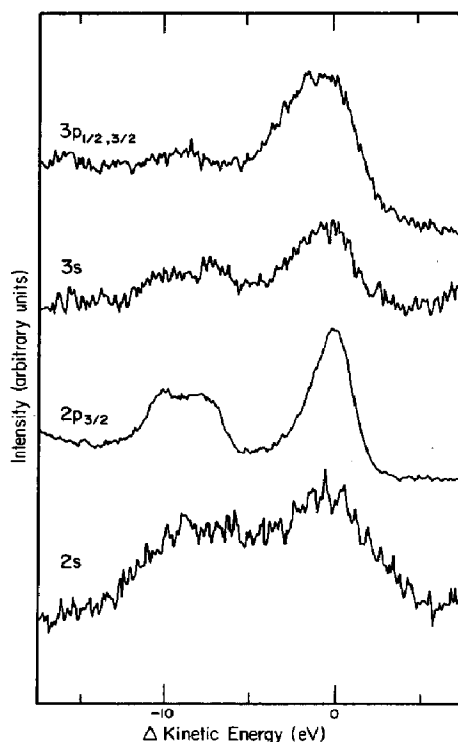


Figure 1. X-ray photoelectron spectra of the Cu 2s, 2p_{3/2}, 3s and 3p_{1/2,3/2} shells of CuO. The binding energies of their principal lines are 1099.4, 934.5, 124.9, 79.6 and 78.0 eV, respectively.

in these samples which has higher binding energy than the oxide oxygen are 15, 15 and 0% of total O 1s intensity, respectively, whereas those in commercially obtained CuO, Cu₂O and NiO are 20, 50 and 40%, respectively. Any effects of the amount of the high binding energy oxygen on satellite structure were not observed. For example, satellites were absent in Cu₂O regardless of the amount of the high binding energy oxygen. However, shake-up satellites have been reported to be observed in Cu₂O (and Cu^I halides) and to be attributable to the presence of the high binding energy oxygen because both the satellite intensity and the amount of the high binding energy oxygen decreased upon raising the temperature in the vacuum^{9, 10, 21}. Satellites in NiO were also attributed to the presence of the high oxygen binding energy¹⁰. It has been reported elsewhere^{12, 23} that the high binding energy oxygen in NiO arises from Ni₂O₃ (the gross surface defect structure of NiO) and is not responsible for shake-up process.

Cu₂O used in refs. 9, 10 and 21 may have been contaminated with CuO. CuO was found to be reduced to Cu₂O by heating at 200°C and 10⁻⁴ torr, which was confirmed by disappearance of satellites and change of the Cu 2p and O 1s binding energies. This agrees with the temperature-pressure-composition relationship of Cu–Cu₂O–CuO system²². The spectra of Cu₂O reported in refs. 9, 10 and 21 could be reproduced from either mixtures of Cu₂O and CuO or CuO samples partially

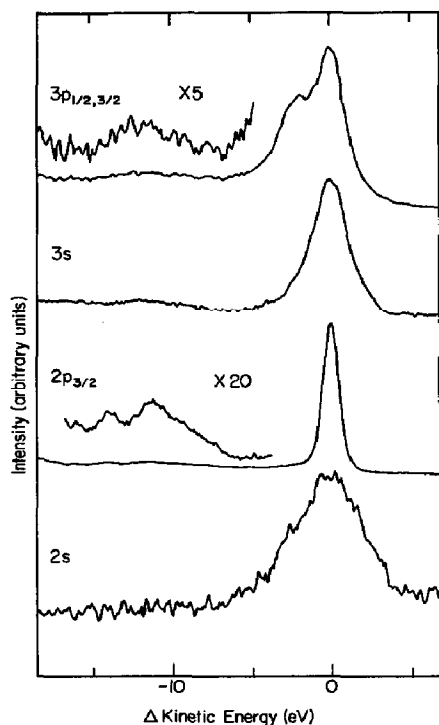


Figure 2. X-ray photoelectron spectra of the Cu 2s, 2p_{3/2}, 3s and 3p_{1/2,3/2} shells of Cu₂O. The binding energies of their principal lines are 1096.9, 933.1, 123.0, 77.5 and 75.9 eV, respectively.

reduced at 200°C and 10^{-4} torr. The high binding energy oxygen in Cu₂O reported by Novakov and Prins¹⁰ and Schön²¹ which disappeared by heating in vacuum may be attributable mainly to the gross surface defect structure of Cu₂O^{13, 23}. (The O 1s binding energies of Cu₂O, CuO and their high binding energy oxygens are 530.8, 530.1, 532.0 and 531.6 eV, respectively.) Note that excess oxygen in the ordinary Cu₂O samples, whose intensity is in the range of 40 and 60 % of total O 1s intensity, disappears by heating in vacuum. Further studies of copper-oxygen surfaces using an argon ion gun and a residual gas analyzer attached to the ESCA spectrometer are in progress to characterize various oxygen species. In several recent studies, it also has been reported that the Cu 2p spectrum of Cu₂O does not show shake-up satellites¹¹⁻¹⁴. Although it is not obvious why strong satellites were observed in the Cu 2p electron spectra of Cu^I halides by Novakov^{9, 10}, his samples may also have been contaminated with Cu^{II} ions.

DISCUSSION

Since Cu^I and Zn^{II} ions with a $(t_{2g})^6(e_g)^4$ configuration do not show any satellite lines due to multielectron excitation, satellite lines in 3d transition-metal ions must be interpreted in terms of L → M charge transfer transitions using the sudden

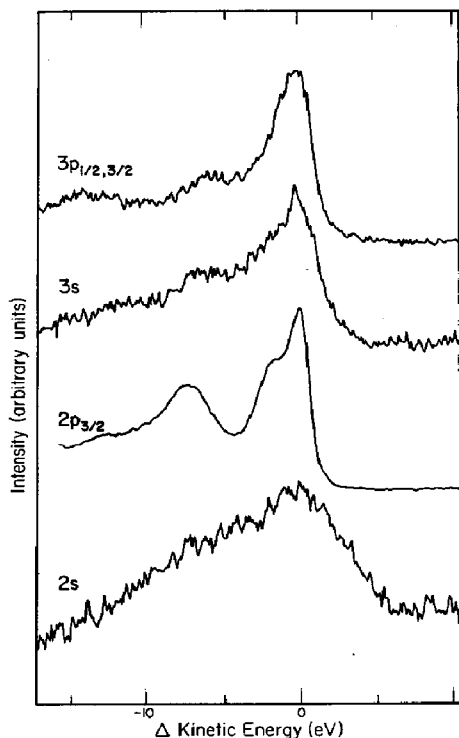


Figure 3. X-ray photoelectron spectra of the Ni 2s, 2p_{3/2}, 3s and 3p_{1/2,3/2} shells of NiO. The binding energies of their principal lines are 1010.6, 854.4, 112.2, and 67.4 (3p) eV, respectively.

approximation and the ligand field theory if they do not arise from multiplet splitting^{24–28}, configuration interaction^{20, 29} and characteristic energy losses. Data given in this paper rule out the interpretation of observed satellites in terms of the latter two sources of multicomponent structure, because satellite structure from configuration interaction will usually occur only when photoionization takes place in the valence shell and the intensity of energy loss peak will vary roughly as $\sqrt{E_e}$. Note that from previous theoretical and experimental studies^{24–28} multiplet splitting in the 2s and 3s shells of Ni^{II} and Cu^{II} ions will be much smaller than 5 eV.

The ground state¹⁵ of an octahedrally coordinated Cu^{II} ion is ${}^2E_g(t_{2g})^6(e_g)^3$. Therefore, 5 ~ 10-eV satellite structure in the Cu inner-shell and valence-band photoelectron spectra of Cu^{II} compounds is attributable to the $\sigma e_g^b \rightarrow 3d^0 e_g^{a0}$ transitions, if they are in an octahedral field. Since Cu^{II} compounds have the structure of a distorted octahedron¹⁵, more ligand \rightarrow Cu 3d transitions may be allowed in Cu^{II} ions depending on the effective symmetry. Therefore, the complex satellite structure, which consists of at least two peaks as clearly seen in the 2p and 3s photoelectron spectra of Cu^{II} ions (see Figure 1 and ref. 11), may be due to the distorted octahedral structure of Cu^{II} compounds. Note that the NaCl-structure compounds, e.g., NiO, CoO, show simple satellite structure as compared with CuO. The broader width and unsymmetrical shape of principal lines found in the inner-shell photoelectron spectra

of Cu^{II} ions as compared with analogous studies on Cu^{I} ions are attributed to multiplet splitting (see Figures 1 and 2). The splittings are approximately 1.3, 1.8 and 2.0 eV in the $2p_{3/2}$, 3s and $3p_{3/2}$ levels of CuO, respectively. The distinctive 1.6-eV shoulder in the Cu 3p photoelectron spectrum of Cu_2O is due to spin-orbit coupling and in CuO its intensity is enhanced by multiplet splitting. The very weak satellites in the Cu 2p and valence-band photoelectron spectra of Cu_2O were assigned to energy-loss peaks⁸, which are also seen in the Cu 3s and 3p photoelectron spectra (Fig. 2) and the O 1s photoelectron spectrum. They are not clearly seen in the Cu 2s photoelectron spectrum probably because of low signal-noise ratio.

The ground state¹⁵ of an octahedrally coordinated Ni^{II} ion is ${}^3\text{A}_{2g}(\text{t}_{2g})^6(\text{e}_g)^2$ and NiO has the NaCl structure. Therefore, 6 ~ 7-eV satellites in the Ni inner-shell and valence-band photoelectron spectra of NiO are assigned to the $\sigma\text{e}_g^b \rightarrow 3\text{d}^0\text{e}_g^{\text{ao}}$ transitions. The broad width of the 7-eV 2p satellite structure is attributed to multiplet splitting as that of the principal structure. The Ni $2p_{3/2}$ 1.8-eV and 3s 2.2-eV satellites in NiO were assigned to multiplet splitting¹². The broad 3p band slanted to higher binding energy seems due to multiplet splitting as well as spin-orbit coupling. Both the principal line and satellite in the 2s electron spectrum are also considerably broadened by Coster-Kronig processes, which are also seen in CuO and Cu_2O .

It is interesting to note that shake-up satellite structure is less intense in the 3s and 3p photoelectron spectra than in the 2s, 2p and valence-band photoelectron spectra (see Figures 1 and 3). The transition energy and the probability will be different depending on where the primary vacancy occurs. From the theory of electron shake-up one would expect satellite structure for core electrons, viz. 1s, 2s, 2p, to be similar both in intensity and excitation energy. Comparison of data in Figures 1 and 3 shows that the satellite structure found with photoionization in the 2s and $2p_{3/2}$ subshell are indeed nearly the same. For the 3s and 3p shells the intensities are lower because they are close to the 3d subshell, although electron correlation tends to increase the intensities. For the valence level the intensities are as strong as for the 2p shell because of the effects of strong electron correlation. Hartree-Fock MO SCF calculations¹⁶ on the transition-metal clusters are in progress regarding these items.

Similarly, 5 ~ 10-eV shake-up satellite structure in the 2p photoelectron spectra of other transition-metal ions^{7, 12, 19, 20} such as Ni^{III} , Co^{II} , Co^{III} , Fe^{II} , Fe^{III} , Mn^{II} , etc. may be attributable to either the $\pi\text{t}_{2g}^b \rightarrow 3\text{d}^0\text{t}_{2g}^{\text{ao}}$ transitions or the $\sigma\text{e}_g^b \rightarrow 3\text{d}^0\text{e}_g^{\text{ao}}$ transitions or both of them depending on the configuration of ground state and the nature of ligands, if these ions are in an octahedral field. In the 2s, 3s and 3p photoelectron spectra of these ions, 5 ~ 10-eV satellite structure can be due to either multielectron excitation or multiplet splitting²⁴⁻²⁸ or both of them. Through careful analysis, the different contributions may be determined. Carrying out photoionization studies in the 1s and 2p shells of Fe^{III} ion for FeCl_3 and FeBr_3 , Carlson²⁰ has attributed most of the multicomponent structure observed with the 2p subshell to electron shake-up because substantial contributions from satellite structure are seen in the Fe 1s spectra of these compounds. Note that multiplet splitting in the 1s shell

as calculated from Hartree-Fock wave functions should have a negligible energy spread (< 0.1 eV)²⁰. It is strongly suspected that shake-up satellite structure would be seen in the 2s region of Fe^{III} ion for FeCl₃ and FeBr₃.

An evaluation of the energies expected for the proposed monopole charge transfer transitions seem consistent with the experimental data. Consider the following points:

(a) The first Laporte-allowed $L \rightarrow M$ charge transfer transition energies are 4~8 eV in a number of octahedral complexes of 3d transition-metal ions^{30, 31}.

(b) Powell and Spicer³² have given two alternative interpretations for the structure in the optical reflectance spectra of NiO between 4 and 9 eV. One interpretation involves O 2p and Ni 3d states in localized excitations, and the other involves Ni 3d states and Ni 4s band. Satellite data in this work agree remarkably well with the first interpretation given by Powell and Spicer. The $\sigma e_g^{bo} \rightarrow 3d^o e_g^{ao}$ transition energies estimated from the satellite data are 6 ~ 7 eV and therefore the $\sigma e_g^b \rightarrow 3d e_g^a$ transition energies will be 7 ~ 9 eV¹⁸. Also, satellite data of NiO agree³³ well with its theoretical electronic structure reported by Wilson³⁴. However, it is to be noted that the interpretation of the NiO optical data is hardly settled^{32, 34-37}. The assignments of shake-up satellites in the Ni 2p_{3/2} spectrum of NiO to $d^8 \rightarrow d^7s$ and O 2p \rightarrow Ni 4s transitions¹¹ are based on the interpretation of the NiO optical data given by Adler and Feinleib³⁵.

(c) In the octahedral cluster $\text{Co}(\text{NH}_3)_6^{3+}$, $^1A_{1g}(t_{2g})^6$, the calculated $\sigma e_g^b \rightarrow 3d e_g^a$ transition energy is 11.8 eV³⁸ and the principal line-satellite separation energy in the Co 2p electron spectrum of $\text{Co}(\text{NH}_3)_6^{3+}$ is 10.0 eV.

(d) The optical data³⁹ of free ions can be used to help in assigning satellites if the following considerations are made: (i) Since an inner-shell hole increases the effective nuclear charge of the outer-shell electrons by approximately one, the position of satellites ΔE_{n0}^o in the inner-shell electron spectra of an ion $M(Z)^{z+}$ will correspond better to the optical excitation energy of its isoelectronic ion $M(Z+1)^{(z+1)+}$. (ii) ΔE_{n0}^o in the valence electron spectrum of an ion $M(Z)^{z+}$ will correspond better to the optical excitation energy of an ion $M(Z)^{(z+1)+}$. (iii) The larger overlap interaction of the higher-lying metal orbital with ligand orbitals will increase the separation of the energy levels. According to these considerations and the optical data of free ions³⁹, a vacancy in free 3d transition-metal ions increases the 3d \rightarrow 4s transition energy by a factor of 1.5 ~ 2. Since the 3d^o \rightarrow 4s^o transition energy is greater than 10 eV, it is unlikely that the 4 ~ 10-eV shake-up satellite observed in the 3d transition-metal ions can be assigned to 3d \rightarrow 4s, or 4p transitions. Furthermore, ligands will increase the 3d^o \rightarrow 4s^o transition energy even more. In transition-metal oxides and halides from which most of the satellite data have been obtained, the 4s orbital lies higher than σ and π orbitals, and therefore the $\sigma e_g^{bo} \rightarrow 4s^o a_{1g}^{ao}$ transition energy will be greater than 10 eV. Rosencwaig et al.⁷ used the free ion transition energies without consideration of the effect of a vacancy or the effect of ligands.

In summary, 5 ~ 10-eV satellite lines in x-ray photoelectron spectra of 3d

transition-metal ions can be attributed to monopole charge transfer transitions (ligand \rightarrow metal 3d) accompanying the primary photoionization if they do not arise from multiplet splitting.

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REFERENCES

- 1 T. A. Carlson, M. O. Krause and W. E. Moddeman, *J. Phys. (Paris)*, 32 (1971) C4-76, and references cited therein.
- 2 K. Siegbahn et al., *ESCA Applied to Free Molecules*, North-Holland Publ. Co., Amsterdam, 1969.
- 3 R. Manne and T. Åberg, *Chem. Phys. Lett.*, 7 (1970) 282.
- 4 H. W. Meldner and J. D. Perez, *Phys. Rev. A*, 4 (1971) 1388.
- 5 G. K. Wertheim, R. L. Cohen, A. Rosencwaig and H. J. Guggenheim, in D. A. Shirley (editor), *Electron Spectroscopy*, North-Holland, Publ. Co., Amsterdam, 1972, p. 813.
- 6 C. K. Jørgensen and H. Berthou, *Chem. Phys. Lett.*, 13, 186 (1972).
- 7 A. Rosencwaig, G. K. Wertheim, and H. J. Guggenheim, *Phys. Rev. Lett.*, 27 (1971) 479.
- 8 G. K. Wertheim and S. Hüfner, *Phys. Rev. Lett.*, 28 (1972) 1028.
- 9 T. Novakov, *Phys. Rev. B*, 3 (1971) 2393.
- 10 T. Novakov and R. Prins, in D. A. Shirley (editor), *Electron Spectroscopy*, North-Holland Publ. Co., Amsterdam, 1972, p. 821.
- 11 D. C. Frost, A. Ishitani and C. A. McDowell, *Mol. Phys.*, 24 (1972) 861.
- 12 K. S. Kim and R. E. Davis, *J. Electron Spectrosc.*, 1 (1972/73) 251.
- 13 T. Robert, M. Bartel and G. Offergeld, *Surface Sci.*, 33 (1972) 123.
- 14 A. Rosencwaig and G. K. Wertheim, *J. Electron Spectrosc.*, 1 (1973) 493.
- 15 C. J. Ballhausen, *Ligand Field Theory*, McGraw-Hill, New York, 1962.
- 16 J. W. Richardson, T. F. Soules, D. M. Vaught and R. R. Powell, *Phys. Rev. B*, 4 (1971) 1721.
- 17 J. C. Slater and K. H. Johnson, *Phys. Rev. B*, 5 (1971) 844.
- 18 J. W. Richardson, personal communication. A vacancy in an inner or valence shell of 3d transition-metal ions will decrease the $L \rightarrow M$ charge transfer transition energies by $1 \sim 2$ eV. This estimation is based on Hartree-Fock MO SCF calculations (ref. 16).
- 19 D. C. Frost, C. A. McDowell and I. S. Woolsey, *Chem. Phys. Lett.*, 17 (1972) 320.
- 20 T. A. Carlson, personal communication and presented at the VIII ICPEAC Conference, Beograd, Yugoslavia, 1973.
- 21 G. Schön, *Surface Sci.*, 35 (1973) 96.
- 22 A. Ronnquist and H. Fischmeister, *J. Inst. Metals*, 89 (1960-61) 65.
- 23 K. S. Kim and N. Winograd, *Surface Sci.*, submitted.
- 24 C. S. Fadley and D. A. Shirley, *Phys. Rev. A*, 2 (1970) 1109.
- 25 J. C. Carver, G. K. Schweitzer and T. A. Carlson, *J. Chem. Phys.*, 57 (1972) 973.
- 26 S. Hüfner and G. K. Wertheim, *Phys. Rev. B*, 7 (1973) 2333.

- 27 S. P. Kowalczyk, L. Ley, R. A. Pollak, F. R. McFeely and D. A. Shirley, *Phys. Rev. B*, 7 (1973) 4009.
- 28 P. S. Bagus, A. J. Freeman and F. Sasaki, *Phys. Rev. Lett.*, 30 (1973) 850.
- 29 G. K. Wertheim and A. Rosencwaig, *Phys. Rev. Lett.*, 26 (1971) 1179.
- 30 C. K. Jørgensen, *Progr. Inorg. Chem.*, 12 (1970) 101.
- 31 H. Basch, A. Viste and H. B. Gray, *J. Chem. Phys.*, 44 (1966) 10.
- 32 R. J. Powell and W. E. Spicer, *Phys. Rev. B*, 2 (1970) 2182.
- 33 K. S. Kim, *Chem. Phys. Lett.*, submitted.
- 34 T. M. Wilson, *Int. J. Quantum Chem. Symp.*, 3 (1970) 757.
- 35 D. Adler and J. Feinleib, *Phys. Rev. B* 2, (1970) 3112.
- 36 J. B. Goodenough, *Progr. Solid State Chem.*, 5 (1971) 271.
- 37 L. F. Mattheiss, *Phys. Rev. B* 5 (1972) 290 306.
- 38 K. S. Kim and J. W. Richardson, unpublished results. See B. L. Kalman and J. W. Richardson, *J. Chem. Phys.*, 53 (1971) 4443.
- 39 C. E. Moore, Atomic Energy Levels as Derived from Optical Spectra, NBS Circular No. 467, Vol. II, 1951.