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Charge transfer multiplet calculations of the Kβ x-ray emission spectra of divalent nickel compounds

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Abstract. The Kβ x-ray emission spectra of divalent nickel compounds are analysed with both the crystal field multiplet model and the charge transfer multiplet model. The spin-dependent Kβ x-ray emission spectrum is calculated and it is shown that the charge transfer effect is rather different in nature for spin-up ($^2A_2$) and spin-down ($^4A_2$) symmetry states. In case the of a spin-up symmetry state it is shown that *multiplet-induced mixing* strongly affects the spectral shape. It is argued that renormalized crystal field multiplet calculations remain a useful approach to describe the Kβ x-ray emission spectral shape.

1. Introduction

The Kβ x-ray emission, or fluorescence, spectra of 3d transition metal compounds have been the subject of research since at least 1925, when Seljakow and Krasnikow made their measurements [1, 2]. Although it soon became clear that the transition is related to the 3p → 1s decay process, the interpretation of the spectral shape of the Kβ x-ray emission was a topic of controversy for a long time, and as we will discuss in this paper, it remains so. An important paper for the interpretation of the shape was the 1959 study of Tsutsumi [3], in which the 3p3d exchange coupling was held responsible for the occurrence of the satellite structure on the low-energy side. The main peak was denoted as $K\beta_{1,3}$ and the satellite $K\beta'$. Throughout the 1960s and 1970s many controversies remained and as alternatives to the exchange mechanism, advocated in [4–6], other mechanisms were proposed. These alternative proposals were essentially based on the idea of a low-energy excitation accompanying the decay process. Proposed ideas include a shake-up mechanism [7] and energy loss due to plasmon absorption [8]. The plasmon model was used in 1979, and the results obtained were at least equivalent in reproducing the data when compared with the exchange model [9].

The exchange mechanism became considered as the best model mainly due to the improving resolution of photoemission experiments, for which Fadley and co-workers demonstrated the importance of the exchange mechanism [10, 11]. Later, more evidence was given, by the high-resolution 3p x-ray absorption results [12, 13] for example. A problem that remained was a quantitative interpretation of the Kβ spectral shape. Kawai and co-workers proposed that, in analogy to x-ray photoemission [14], charge transfer effects are important [15]. They explicitly included charge transfer effects in the analysis of the Kβ fluorescence spectra of nickel halides.

Recently, manganese Kβ experiments have been carried out using synchrotron radiation. The main goal in these experiments was not the analysis of the Kβ x-ray emission spectrum,

but the use of the Kβ decay channel as an internally referenced spin detector, which made possible spin-resolved x-ray absorption experiments [16]. For this purpose the Kβ x-ray emission spectral shape is important, for all its spin-dependence, and the manganese results obtained could be explained in detail with crystal field multiplet calculations without the necessity of charge transfer effects [17]. Furthermore, recent synchrotron radiation experiments on Kβ x-ray emission of nickel compounds [18] turned out not to be in agreement with the predictions of the charge transfer calculations from [15].

This apparent success of the crystal field model, and the apparent failure of the charge transfer model, is at odds with experience in core level photoemission. To study this further we carried out a series of both crystal field multiplet and charge transfer multiplet calculations for divalent nickel. In section 2, crystal field multiplet calculations are carried out and they are used as the constituents of the charge transfer model in section 3, where the emphasis is on the interplay of symmetry and configurational mixing. In section 4 a comparison is made with recent experiments.

2. The crystal field multiplet model

We start with an outline of the crystal field multiplet model as used for the description of Kβ x-ray emission spectra of 3d transition metal compounds. The ground state of the transition metal ion consists of only a partly filled 3d band. In the case of divalent nickel the 3d band consists of eight electrons, denoted as $3d^8$. In the initial state of Kβ x-ray emission a core hole exists in the 1s level. We will describe this initial state as $1s^1 3d^8$. Although this description seems to be at odds with the accepted ideas concerning screening of core holes [14], we prefer to use this configuration because of symmetry considerations. The main assumption made is that the creation of the 1s hole does not modify the symmetry of the 3d states, which is $^3A_2$ for divalent nickel [19]. Within this assumption the initial state of the Kβ process is either $^2A_2$ or $^4A_2$ depending on the relative spin directions of the 1s and 3d electrons or holes. An escaping spin-up electron leaves behind a spin-up hole ($1s^+$) which couples to the two 3d holes ($3d^- 3d^-$) to the doublet symmetry state. In the Kβ transition a 3p electron fills the 1s hole and the final state can be described as $3p^5 3d^8$. This final state contains two partly filled states, which do interact very strongly with each other. In particular, the atomic 3p3d exchange interaction is of the order of 15 eV. The crystal field multiplet includes the exchange interaction as an ingredient of the full two-electron Coulomb and exchange interactions [20]. Within the crystal field multiplet model the Kβ x-ray emission spectral shape is then given as

$$I_{K\beta} = |\langle 1s^1 3d^8 | \varepsilon p | 3p^5 3d^8 \rangle|^2 \delta_{(\Delta E - \hbar\omega)}. \tag{1}$$

The dipole operator (εp) sets the selection rules ($\Delta J = -1, 0, +1$); ΔE is the energy difference between the initial and final state, and $\hbar\omega$ the corresponding energy of the Kβ photon.

The crystal field multiplet calculations have been carried out by making use of the RCG9 [21] and RACAH [22] programs in the version modified by [23]. The results of the crystal field multiplet calculations are given in figure 1. The total Kβ x-ray emission spectral shape is given, and also the separate spectra for spin-up and spin-down electrons. Spin up denotes the spin direction of the 1s hole with respect to the spin direction of the 3d valence band, and it is named spin up with respect to the 3d spins. A spin-up 1s hole implies that the electron that has escaped in the core hole creation process is spin up referenced to the local

3d situation. The spin-resolved spectra are important for the use of Kβ detection of x-ray absorption, as they provide a basis for spin-resolved x-ray absorption measurements [16]. In terms of the crystal field multiplet calculations these spin-up and spin-down calculations identify with calculations for the $^2A_2$, respectively the $^4A_2$ ground states. (Note that spin up corresponds to the $^2A_2$ ground state). The bottom of figure 1 contains the calculation for divalent nickel and the spectra at the top show the results for monovalent nickel, for which the initial states are $1s^13d^9$ of respectively spin-up ^1E and spin-down ^3E symmetry. Both calculations have been carried out with a cubic crystal field of 1.0 eV.
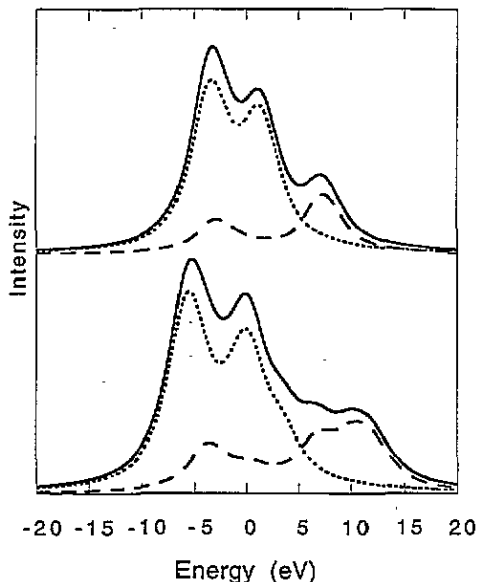

Figure 1. Crystal field multiplet calculation for Ni^{2+} [$1s^13d^8$] (bottom) and Ni^+ [$1s^13d^9$] (top). Plotted are the $^4A_2$ and ^3E spin-down (dotted curve), the $^2A_2$ and ^1E spin-up (broken curve) and the total spectra (full curve).
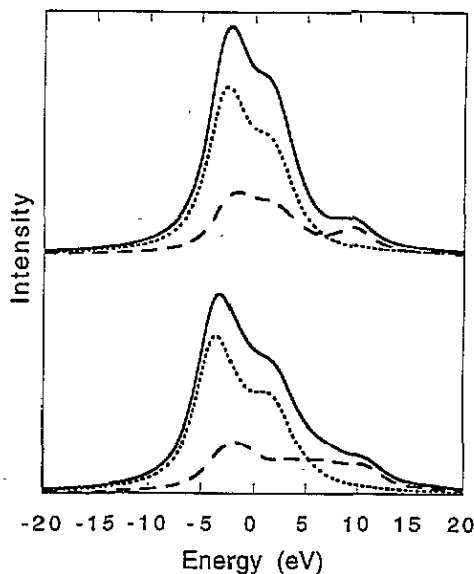
Figure 2. Charge transfer multiplet calculations for NiF_2 (bottom) and $NiBr_2$ (top). Plotted are the spin-down (dotted curve), the spin-up (broken curve) and the total spectra (full curve).

Figure 1 identifies with figure 2 of [15]. As can be checked in the present figures, the spin-up ($^2A_2$) nature is not confined to the satellite at higher energy, but also has some intensity at the lowest energy peak, both for $3d^8$ and $3d^9$. This is due to final-state effects: the large 3p3d Slater integrals make possible transitions from $1s^+3d^-3d^-$ not only to $3p^+3d^-3d^-$, but also to $3p^-3d^-3d^+$. Because of the octahedral crystal field, both 3d holes will be of e_g symmetry. Similar reasoning can be applied to $3d^9$. In the next section we will use the crystal field multiplet calculations as the building blocks of the charge transfer multiplet model.

3. The charge transfer multiplet model

In this section the charge transfer multiplet model is described. The divalent nickel compounds have been much studied within the framework of the charge transfer model. Their 2p x-ray photoemission spectra have been analysed by Zaanen and co-workers [14].

Okada and co-workers re-analysed the 2p x-ray photoemission data including also the multiplet effects [24]. In this manner they were able to describe 2p x-ray photoemission and 2p x-ray absorption within the same model and with a unified set of parameters. Okada and co-workers showed that, with the inclusion of multiplet effects, the parameters in the charge transfer multiplet model must be slightly modified [24].

The important improvement with respect to the crystal field multiplet model is that, in the charge transfer multiplet model, the ground state is described as a linear combination of the configurations $3d^8$, $3d^9\underline{L}$ and $3d^{10}\underline{LL}'$; $\underline{L}$ denotes a hole in the valence band, in particular the halide p orbitals. To make the $\underline{L}$ configurations tractable for the inclusion of multiplet effects the functions are described in the symmetry of the metal sites. In practice, they are included in the form of nd functions, where nd stands for a d function with an irrelevant high main quantum number. The nd functions are described without correlation. We start with the assumption that the core hole is created with a high-energy x-ray, and the 1s electron is ejected. This state, the initial state of the $K\beta$ process, is constructed from the configurations $1s^13d^8$, $1s^13d^9\underline{L}$ and $1s^13d^{10}\underline{LL}'$. This means in practice $1s^13d^8nd^{10}$, $1s^13d^9nd^9$ and $1s^13d^{10}nd^8$. It will be assumed that the core hole potentials of both a 1s core hole and a 3p core hole are equal to that of a 2p core hole. It has been argued in [25] that, for 3p x-ray photoemission, slightly better agreement can be obtained with U_{3p3d} equal to 5.5 eV. However, to limit the degrees of freedom in the present analysis, we have used a constant core potential.

The model parameters are given in table 1. The values given have been derived from 2p photoemission experiments [24]. The charge transfer energy (Δ) is the energy difference between $3d^8$ and $3d^9\underline{L}$; V_{e_g} is their single-particle hybridization. The energy positions are given for the average of the configuration. Multiplet effects lower the ground state of E_{s1d8} with 2.6 eV and of E_{s1d9} with 0.6 eV (for the used crystal field splitting of 1.0 eV); n_{s1d8} denotes the occupation of this state in the initial state of $K\beta$ x-ray emission. The final states are formed by the configurations $3p^53d^8nd^{10}$, $3p^53d^9nd^9$ and $3p^53d^{10}nd^8$.

3.1. Symmetry effects in the charge transfer multiplet model

The charge transfer multiplet calculations have been carried out by making use of the BANDER program, in the version written/modified by Thole and Ogasawara. Calculations have been performed for NiF_2, NiO, $NiCl_2$ and $NiBr_2$. As discussed in the section on the crystal field multiplet calculations there are two distinct symmetries for the ground state of $1s^13d^8$: spin-up $^2A_2$ and spin-down $^4A_2$. Both are single irreducible representations belonging to a different total symmetry. This implies that one can carry out two separate calculations.

In figure 2 we show the results for NiF_2 (bottom) and $NiBr_2$ (top). Results are given for spin-down $^4A_2$ (dotted curve) and spin-up $^2A_2$ (broken curve) symmetries and the total $K\beta$ spectrum (full curve). A difference in behaviour is observed: the $^4A_2$ result shows a combination of both spin-down spectra of d^8 and d^9. However the spin-up ($^2A_2$) result does not show a simple addition of the spin-up d^8 and d^9 spectra, but it also shows an admixture of the spin-down $d^9[^3E]$ spectral shape, evidenced by the weight transfer to the main peak. The total $K\beta$ x-ray emission spectral shape can be found by adding the $^2A_2$ and $^4A_2$ spectra.

The reasons for this behaviour can be formulated as follows. The holes of the $3d^8[^4A_2]$ initial state are $1s^-3d^-3d^-$. A $K\beta$ transition is made to $3p^-3d^-3d^-$. The charge transfer effect implies the replacement of a 3d hole by a ligand hole ($\underline{L}^-$). To limit the complexity we omit the $3d^{10}$ configuration for the moment. The complete calculation for the $^4A_2$ symmetry is

$$I_{K\beta}(^4A_2) = |\langle 1s^-3d^-3d^- + 1s^-3d^-\underline{L}^-|\varepsilon p|3p^-3d^-3d^- + 3p^-3d^-\underline{L}^-\rangle|^2\delta_{(\Delta E-\hbar\omega)}. \qquad (2)$$

For $^2A_2$ symmetry the only difference is the positive spin of the 1s core hole. This implies an important difference for the final states. As already noticed in the crystal field multiplet model $1s^+3d^-3d^-$ can decay to both $3p^+3d^-3d^-$ and $3p^-3d^-3d^+$; $3p^+3d^-3d^-$ is identified with the $K\beta$ satellite and $3p^-3d^-3d^+$ is the $^2A_2$ intensity of the main peak. The inclusion of charge transfer implies that $3p^+3d^-3d^-$ mixes with $3p^+3d^-\underline{L}^-$. Similarly $3p^-3d^-3d^+$ mixes with both $3p^-3d^-\underline{L}^+$ and $3p^-3d^+\underline{L}^-$. The overall situation of the $^2A_2$ symmetry is sketched in figure 3. The left-hand side of the final state identifies with the crystal field model. Charge transfer couples the right-hand side of the figure and the overall spectrum depends on the relative energy positions and coupling strength of the different configurations.
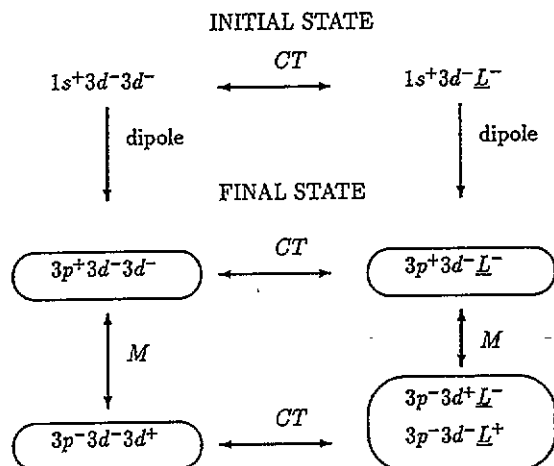

Figure 3. The combination of multiplet effects (M) and charge transfer effects (CT) on the final-state configurations of the spin-up $^2A_2$ ground state.

From the symmetry point of view there is an important difference between the $^4A_2$ and $^2A_2$ calculations. While $^4A_2$ mixes only with states which are reached from triplet d^9-like states, $^2A_2$ mixes with both triplet and singlet d^9-like states. The consequence for $^4A_2$ is that it has only intensity at the main peak. The overall $^2A_2$ final state is formed from (i) doublet d^8 states at the main peak plus at the satellite, (ii) singlet d^9 states again at the main peak plus at the satellite and (iii) triplet d^9 states with intensity only at the main peak. The consequence is that effectively the inclusion of charge transfer will transfer weight to the main peak. This weight transfer effect is denoted as *multiplet-induced mixing*. The important consequence is that the effective spin-polarization of the main peak decreases, as can be seen if one compares figures 1 and 2.

We note that these results are different to those obtained by the charge transfer multiplet calculations of [15]. Their results have been obtained by addition of the different transitions from $1s^13d^8$, $1s^13d^9$ and $1s^13d^{10}$ initial states with factors related to their relative occupations. In the calculations presented here both the initial- and final-state configurations are mixed, which causes the multiplet-induced mixing in the final states as discussed above. Additionally, the coupled description of the ground state and final state causes interference effects if the $K\beta$ intensity is calculated (see equation (1)). We return to this point in the discussion.

4. Comparison with experiments

Figure 4 shows the comparison with the $K\beta$ x-ray emission spectra of NiF_2 and $NiBr_2$.

All spectra are normalized from 0 to 1 and the experimental spectrum of NiF_2 has been aligned to its theoretical spectrum. The $K\beta$ x-ray emission experiments were carried out at the X21 beamline of the National Synchrotron Light Source (NSLS). The excitation energy was 8400 eV and the spectrum was measured by detecting the fluorescence radiation at 90° scattering angle. The overall resolution was 0.95 eV. The samples were anhydrous fine powders dispersed as a thin layer on Mylar tape. More details on the experiments will be described elsewhere [18]. The theoretical curves in figure 4 are charge transfer multiplet calculations as discussed in section 3. For the calculations atomic values have been used for the 3p and 3d spin–orbit couplings, and also for the 3p3d and 3d3d Slater integrals (for details see [20]). The parameters of the charge transfer model have been taken from [24] and are reproduced in table 1.

Table 1. The charge transfer parameters. $U_{1s3d} = U_{3p3d} = 7.5$ eV; $U_{3d3d} = 7.3$ eV; $E_{s^1d^8}$ is set to zero.

Compound	NiF_2	Ni_0	$NiCl_2$	$NiBr_2$
Δ	4.3	2.0	1.3	0.3
V_{eg}	2.0	2.0	1.7	1.4
$E_{s^1d^9}$	−3.2	−5.5	−6.2	−7.2
$E_{s^1d^{10}}$	0.9	−3.7	−5.1	−7.1
$n_{s^1d^8}$	29%	13%	9%	4%
$n_{s^1d^9}$	63%	67%	67%	62%
$n_{s^1d^{10}}$	8%	20%	23%	34%

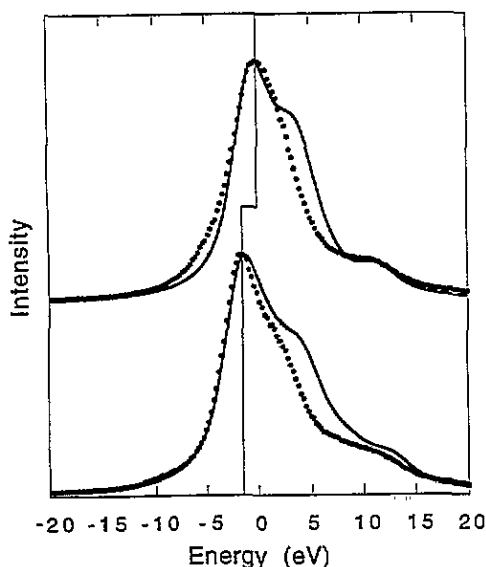**Figure 4.** Comparison of the charge transfer multiplet calculations with experimental $K\beta$ x-ray emission spectra (see text) for NiF_2 (bottom) and $NiBr_2$ (top).
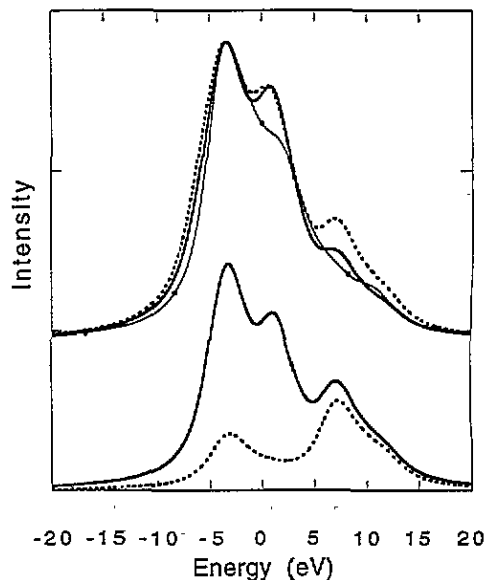
Figure 5. Top: charge transfer multiplet calculations for NiF_2 (thin full curve) compared with a summation of d^8 and d^9 (broken curve) and the modified result including multiplet-induced mixing (full curve). Bottom: corresponding results for the spin-up $^2A_2$ state only.

The experiments for NiF_2 and $NiBr_2$ show a similar shape, with a main peak and a satellite at about 12 eV lower energy. This satellite is reproduced in the calculations at approximately the correct energy and with the correct intensity. Both in experiment and theory the peak position of $NiBr_2$ is shifted by 1.5 eV compared to NiF_2. This is due to the larger covalency (smaller Δ value in table 1) of $NiBr_2$, which reduces the asymmetry of the main peak and effectively shifts the peak position to higher energy. The experimental and theoretical spectral shapes of NiO and $NiCl_2$ (see [18]) are intermediate between the two spectra shown, which is in line with the trend in their ground-state configurations. A discrepancy between experiment and theory is that the main peak is split into two clearly distinguishable peaks in the calculations, while in experiment only an asymmetry is visible (see below).

We would like to point out that the charge transfer multiplet calculations presented improve considerably the description of the spectral shapes. Crystal field calculations always show a too large satellite intensity (see figure 1). The intensity of the satellite is reduced in the charge transfer model due to multiplet-induced mixing as discussed above. This brings the satellite intensity into agreement with experiment. The coupled description of the ground state and the final state within the charge transfer model results in relatively small variations in their spectral shape in agreement with experiment but in contrast to the predictions from the charge transfer calculations of [15]. This shows that it is necessary to perform the complete charge transfer calculations coupling the initial-state and final-state configurations. Due to the interplay of multiplets, charge transfer couplings and interference effects in the transition strengths the situation is too complex to approximate the spectral shape from the initial-state mixings as was done in [15] (see discussion). The remaining discrepancy that the asymmetry of the main peak is too large has its origin in the too large atomic Slater integrals used. This is a well known feature of multiplet calculations [26]. The inclusion of charge transfer effects effectively reduces the multiplet splittings, which can be seen by comparing figure 1 with figure 2. The comparison with experiment shows that this reduction is not enough, which implies that there are other configurations which effectively decrease the Slater integrals. As far as the spectral shape is concerned the easiest way to include this effect is to optimize the Slater integrals to experiment [26].

5. Discussion

One can generalize the present results for divalent nickel to all high-spin compounds of the late 3d transition metals. That is, for all high-spin $3d^n$ systems (with $n > 4$) the $3d^n$ spin-down spectra will mix only with the spin-down spectra of $3d^{n+1}\underline{L}$, in contrast to their spin-up spectra which will mix with both. These multiplet-induced mixing effects are absent for low-spin compounds and also for early transition metal compounds. For these systems there is (as a general rule) always a symmetry which will mix due to charge transfer, both for spin up and spin down. To calculate the spectrum of a $3d^n$ system one can start by calculating the $3d^n$ crystal field multiplet spectrum and then include the effects of charge transfer with $3d^{n+1}\underline{L}$, etc. However, in practice there are some complications. The calculations become very large for systems in the middle of the transition metal series; in fact, too large for the computer we used. Also, it is not known exactly which charge transfer parameters should be used for $K\beta$ x-ray emission, i.e. whether the effective parameters are identical to the parameters determined by 2p x-ray photoemission, for example. The experimental spectra do not show much structure, so they are not very favourable to use for the precise determination of these parameters.

Because of this it is still useful to use directly the crystal field multiplet results and to compare to experiment. One can include part of the charge transfer effects by reducing the atomic Slater integrals. We have shown that the important effect of charge transfer is the multiplet-induced mixing. This effect will always give more spin-down character in the main peak than predicted by the crystal field multiplet model. This spin dependence is important for the use of the $K\beta$ decay channel for local spin-selective x-ray absorption. A procedure to estimate the spectral shape and its spin dependence would be to perform crystal field multiplet calculations for $3d^n$ and $3d^{n+1}$ for spin up and spin down. Then the total spin-down spectrum can be estimated by adding $3d^n$ and $3d^{n+1}$ according to their ground-state occupation. To account for multiplet-induced mixing effects the spin-up spectrum can be estimated by adding $3d^n$ spin up with to spin-up and spin-down $3d^{n+1}$. This procedure simulates the multiplet-induced mixing effect, but neglects effects due to interference of $3d^n$ and $3d^{n+1}$.

Figure 5 shows two estimates of the charge transfer result for NiF_2. The broken curve represents the summation of the spectra for $3d^8$ and $3d^9$ according to their ground-state occupation. For the thick full curve the multiplet-induced mixing is included. The spin-down spectra are added to form the overall spin-down spectrum and the spin-up spectrum is formed by adding the spin-up $3d^8$ spectrum to the total $3d^9$ spectrum, which roughly approximates the charge transfer effects apart from interference. Both estimates are rather poor, but the multiplet-induced mixing result correctly reproduces the decrease of the satellite. An important difference is the amount of spin-up character of the main peak, which is shown at the bottom. Due to the mixing with the total spectrum the amount of spin-up character of the main line increases significantly. The important consequence is that because of this increased spin-up character of the main peak its degree of spin-purity decreases with increasing 'covalence', i.e. the amount of $1s^1 3d^9 \underline{L}$ character in the initial state. In contrast the satellite remains 100% spin-polarized (see figures 1 and 2). We conclude that if charge transfer results are not available the multiplet-induced mixing simulation is useful, as it is expected to give an accurate account of the spin-polarization of the main peak and a reasonable simulation of the spectral shape.

It has been found that divalent manganese compounds are well described with crystal field multiplet calculations [17] without the need of the inclusion of charge transfer effects. High-spin Mn^{2+} has a $3d^5[^6A_1]$ ground state. The $K\beta$ x-ray emission spectrum can be described as a transition from $1s^1 3d^5$ to $3p^5 3d^5$. The initial state has the symmetries $^7A_1$, related to an escaped spin-down electron, and $^5A_1$, related to spin up. In analogy with nickel, transitions from $1s^+$ states to $3p^-$-like final states are possible. For Mn^{2+} the structures related to these final states are distinguishable as separate structures, as can be seen in figure 6. The main peak is related to $^7A_1$, its shoulder to $^5A_1$ transitions to $3p^-$-like states and the satellite to $^5A_1$ transitions to $3p^+$-like states. The *multiplet-induced mixing* will again have the tendency of lowering the satellite, but because of the relatively large energy difference between satellite and main peak the effect will be much smaller than for nickel. This large energy separation between main peak and satellite make the spectrum appear close to the crystal field multiplet result.

6. Concluding remarks

The experimental $K\beta$ x-ray emission spectra of the nickel halides can be reproduced with charge transfer multiplet calculations for the $1s^1 3d^8$, $1s^1 3d^9 \underline{L}$ and $1s^1 3d^{10} \underline{LL}'$ initial state configurations by using the charge transfer parameters as optimized for 2p x-ray
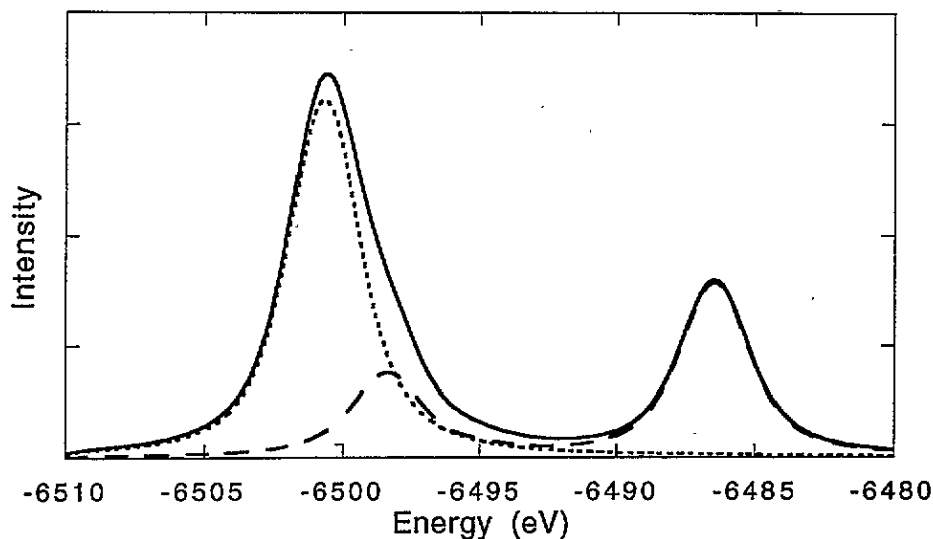
Figure 6. Crystal field multiplet calculation for Mn^{2+}. For $1s^1 3d^5$ the spin-down $^7A_1$ symmetry (dotted curve), the spin-up $^5A_1$ symmetry (broken curve) and the total spectrum (thick full curve) are given.

photoemission. Both the experimental trend and the correct intensity of the $K\beta'$ satellite are reproduced. A remaining discrepancy is the too large calculated splitting between the main peak and its shoulder.

The charge transfer multiplet calculations carried out in this work differ from those published in [15]. It has been shown in detail that mainly the *multiplet-induced mixing* is responsible for the fact that the spin-up $^2A_2$-symmetry spectral shape changes completely upon hybridization and strongly mixes with both the spin-up and the spin-down $3p^5 3d^9\underline{L}$ character. This is possible due to the large 3p3d Slater integrals. If the ground state is dominated by $1s^1 3d^9\underline{L}$ this gives the spin-up spectral shape the same form as the total $3d^9\underline{L}$ spectrum, while the spin-down spectral shape retains its spin-down character. This is the origin of the low intensity of the satellite, as found experimentally.

For the determination of the spin-dependence of the $K\beta$ x-ray emission spectral shape of divalent nickel a consequence of the charge transfer multiplet model, in particular of the *multiplet-induced mixing*, is that the main peak will contain more spin-up character than predicted by the crystal field multiplet model. The satellite will remain 100% spin up. This trend is believed to be general for the late 3d transition metal systems. One can estimate the charge transfer effect by the procedure as described above.

Acknowledgments

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