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MULTIPLET EFFECTS IN NEAR EDGE XAS FOR GROUND STATE STUDIES

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ABSTRACT: Manifold aspects of high resolution near edge absorption spectroscopy in the soft X-ray range can reveal interesting information on the nature of the ground state in various materials. One method uses the near edge multiplet structure of the final states, in which the optical selection rules limit the terms that can be reached from a given ground state. Thus the observed multiplet can be used to diagnose the ground state. This will be illustrated for Ce impurities and for Ni compounds

1-INTRODUCTION

The near edge structures in X-ray absorption spectroscopy (XAS) have regained much interest with the progress of synchrotron radiation sources, high resolution monochromators,efficient detection systems and ultra high vacuum technique. Simultanuously powerful computers have become available to perform calculations on radiation transition matrix elements in atomic configurations with several open shells /1/. These calculations can be used to determine the local ground state configuration of the X-ray excited atom in a solid. This has recently been demonstrated for all the rare earth metals /2/ and for Mn impurities /3/. Here, however, we will give exemples of materials in which the ground state is a mixture of several configurations.

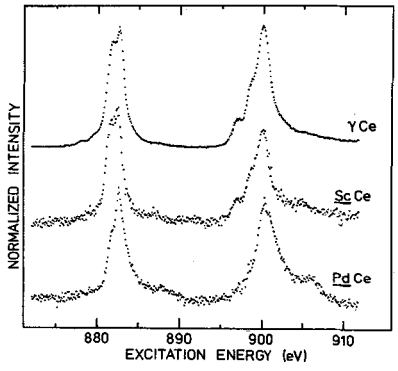
2-EXPERIMENTAL

X-ray absorption data were taken with the synchrotron radiation emitted by ACO (Orsay) using a double crystal monochromator equipped with beryl crystals (resolution 0.4 eV between 800 and 1000 eV). All spectra were recorded by electron yield detection. Ce compounds were mechanically scraped directly before measurements in a vacuum of better than 5×10^{-10} t. Ni compounds were sublimed in situ.

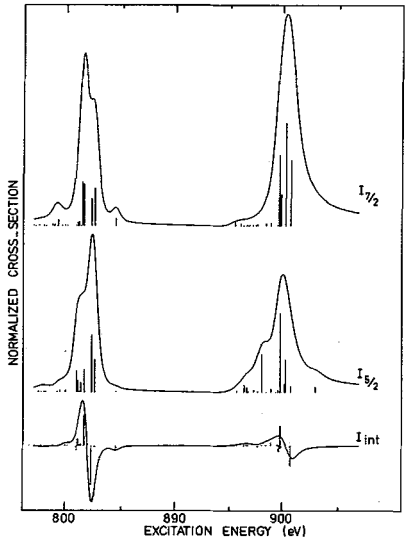
3-CERIUM ALLOYS

In the initial state the Ce $4f^1$ state is split by spin-orbit coupling (ξ=107 meV). The $M_{4,5}$ absorption spectrum in γCe in Fig.1 displays the accessible multiplet structure for the transition $3d^{10}4f^1(j=5/2) \rightarrow 3d^9 4f^2$. Whilst in many Ce compounds and alloys the $4f^1$ level is so weekly hybridized that only the lowest j=5/2 level is occupied, in some Ce systems the hybridization with the valence band is so large that it mixes also the higher j=7/2 level into the ground state. Whereas the $M_{4,5}$ absorption spectrum for ScCe 2.3% is the same as for γCe, it is quite different for PdCe 2.3%, indicating a large hybridization. In order to verify this, we have calculated the transition probability for the j=5/2 and 7/2 initial state configurations,together with the interference term (Fig.2). The initial and final state wave functions, energies and optical matrix elements were calculated with an atomic Hartree-Fock program using emperically scaled values for the Slater integrals.

Comparison of the calculated spectra with the experimental data shows that γCe and ScCe 2.3% have a j=5/2 ground state, whereas in PdCe2.3% the ground state must have a 4f(7/2) weight between 20 and 40 %. The increased intensity of the ∿5 eV satellite in the observed spectrum (Fig.1) is due to the $4f^0$ contribution in the ground state as a consequence of the large hybridization /4/. The values obtained for the $4f^0$, $4f^1(5/2)$ and $4f^1(7/2)$ weight are in agreement with those expected from the hybridization using the Gunnarsson-Schönhammer model /5,6/.



↑ Fig.1: The absorption spectra of γCe, ScCe 2.3% and PdCe 2.3%.



→ Fig.2: The calculated Ce $M_{4,5}$ absorption spectra for initial states j=7/2 and 5/2 together with the interference term I_{int}.

4-NICKEL COMPOUNDS

The beautiful variation in the spectral shape of the Ni $L_{2,3}$ absorption edges for the Ni dihalides and Ni oxide is shown in Fig. 3. The L_3 white line is roughly separated into two peaks (a and b). The separation decreases stongly in more covalent compounds. In the L_2 region a similar behaviour is observed (e and f). Satellite stucture (c) with a different shape for each compound is clearly observed at 3 to 7 eV above the L_3 edge. Also at higher energy the 4s continuum edge is visible (d).

A multiplet calculation for the dipole transitions Ni $3d^8 \rightarrow 2p^5 3d^9$ is shown in Fig.4, taking into account the octahedral crystal field and using Hartree-Fock values for the Coulomb and exchange integrals. As seen, this calculation agrees quite well for NiF_2, which is the most ionic compound. The differences in the spectra of the other compounds indicate that their ground state is not $3d^8$, but a mixture of several configurations /7/.

We therefore performed model calculations which take into account the configuration interaction in the initial as well as in the final state. In the initial state we have the configurations $3d^8$, $3d^9\underline{k}$ and $3d^{10}\underline{k}\ \underline{k}'$ ($\underline{k}$ denotes a hole in the ligand band), schematically displayed in Fig.5. The energy separation of these states is equal to the charge transfer energy Δ, which value strongly varies along the nephelauxetic series. For the $3d^{10}\underline{k}\ \underline{k}'$ also the effective d-d Coulomb interaction U has to be included. The states with a ligand hole are broadened into bands. In the final state the separation of the centoids of the multiplet split $2p^5 3d^9$ states and the $2p^5 3d^{10}\underline{k}$ band is different from the $3d^9\underline{k}$ to $3d^{10}\underline{k}\ \underline{k}'$ initial state separation, due to the corehole potential Q. For each irreducible representation in the symmetry group of the crystal field we can independently calculate the configuration interaction. This has been done with a cluster model as well as with the Gunnarsson-Schönhammer impurity model /5/. An example of the results is given for

NiI_2 in Fig.6. The satellite structure, which is due to the covalent mixing, is nicely reproduced in both models. The same type of calculation for the satellite structure can be used in XPS /8/ and UPS /9/ even though the spectral shapes in these methods are strongly different compared to XAS, due to the very different final states. The appearence of the satellite structure, with an energy separation from the main line equal, in first approximation, to $\Delta + U - Q$ is a clear proof for important correlation effects in the Ni band /7,9/.

As seen in Fig.6, the clustermodel greatly overestimates the peak splitting in the white line, whereas the impurity model gives good agreement for all measured Ni compounds. The reason for this is that in the impurity model the atomic exchange integral G^1 (2p,3d), which dominates the multiplet splitting,is reduced by the hybridization with the valence band. In the cluster model this effect is underestimated.

The multiplet splitting in the main line can be used to obtain the relative populations and the energy separations of the initial state configurations. Further details can be found in Ref. /7/ and /9/. Note that here we only have studied compounds with octahedral symmetry in order to facilitate a direct comparison.

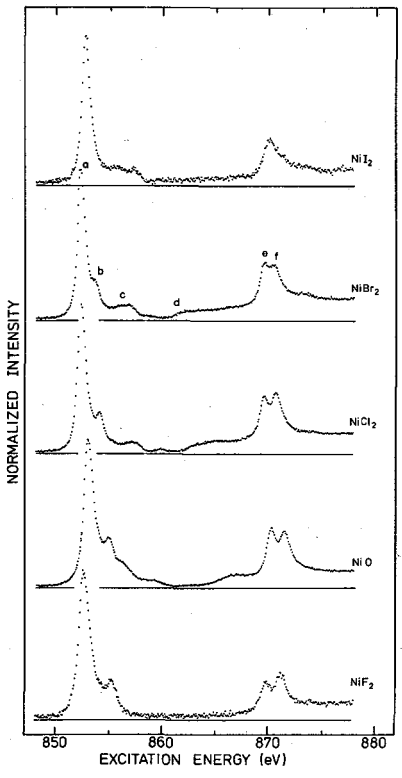


Fig.4

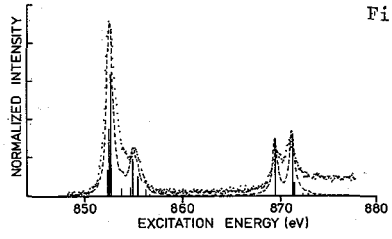


Fig.5

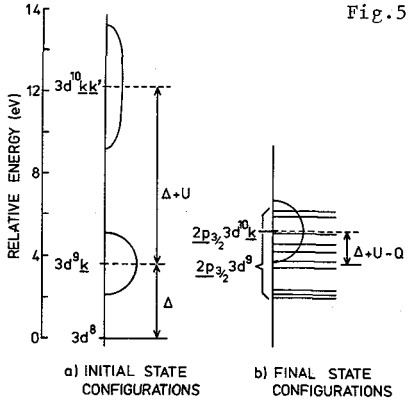


Fig.3: $L_{2,3}$ absorption spectra of Ni compounds.

Fig.4: Calculated multiplet structure for a dipole transition Ni $3d^8 \rightarrow 2p^5 3d^9$ (G_1 = 5.79, F_2 = 7.72, G_3 = 3.29 and 10Dq = 1.5 eV); the dashed line is a convolution by a 0.6 FWHM Lorentzian. For comparison, the experimental $L_{2,3}$ spectrum of NiF_2 is shown (dots).

Fig.5: Schematic representation of the energy for the different configurations: a) initial state; b) final states in the L_3 absorption for the case of $NiCl_2$. Configurations with a ligand hole ($\underline{k}$) have a bandwidth W. The $2p_{3/2}3d^9$ configuration is multiplet-split. Not drawn is the mixing between the configurations.

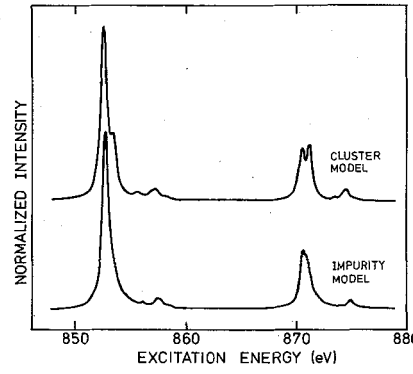


Fig. 6: Clustermodel and impurity model compared for the case of NiI_2 (Δ = 1 eV).

5-CONCLUDING REMARKS

The use of X-ray absorption near edge structure to diagnose chemical environments as well as the site and symmetry characteristics of unoccupied electronic states, has a long history /11,12/. However it is only in the last few years that experimental and computational technology has sufficiently advanced to permit utilization of the multiplet structure that arises near the edges in narrow band materials. In this paper we have shown that although we have used excitation energies in the order of 1 KeV, and multiplet splittings on a scale of many volts, we have been able to probe ground state splittings of $\sim$ 100 meV and give details of the ground state configurations. In other work /13/ we have been able to detect splittings which only become observable below ca 60 Kelvin (i.e. kT = 5 meV).

By comparison with other techniques, such as those based on low energy optical or magnetic transitions XAS in the soft X-ray regime has rather special properties. These include moderate surface sensitivity and applicability to thin films, well defined site and symmetry selectivity, and well defined final states. These, and other features convince us that the aspects of XAS treated here have until now been underexploited.

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