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LETTER TO THE EDITOR

The inclusion of charge transfer to the conduction band in a cluster model analysis of core level line shapes

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Abstract. We have extended the single-impurity cluster model to include the effects of charge transfer to the conduction band for the interpretation of the core level photoemission spectra of highly correlated, small-gap semiconducting and metallic transition metal compounds. The model includes the charge fluctuations between the local transition metal site and the conduction band and has been successfully applied to reinterpret the spectra of some 3d transition metal chalcogenides, reproducing well the large asymmetry of the main peaks, as well as the other satellite structures.

The line shapes of the metal 2p core level x-ray photoelectron (XPS) spectra of transition metal (TM) compounds have provided much important information on their electronic structures [1–3]. These line shapes are usually interpreted within a single-impurity model where only local interactions between a single TM ion and the surrounding ligand atoms are considered. For many TM compounds, these local interactions dominate the electronic structure and the core level spectra can be successfully reproduced by considering only intracluster parameters such as the charge transfer energy Δ, the d–d Coulomb energy U and the ligand to metal transfer integral T. However, there are a number of structures in the core level spectra which cannot be explained within the single-impurity limit. These include the asymmetric line shapes of the main peaks of many strongly correlated small-gap semiconducting or metallic compounds such as NiS, NiSe and NiTe [4], the pyrite-type disulphides MS_2 (M = Fe, Co) [3] and the Fe 2p core level of the chalcopyrite-type compound $CuFeS_2$ [5]. These compounds display TM 2p core level peaks with considerable extra intensity on their high-binding-energy side reminiscent of the line shape of free-electron-like metals. In his letter, we show how the inclusion of charge transfer effects from the TM ion to the conduction band, to simulate the screening provided by strongly hybridized empty states, can explain these asymmetric features within a single-impurity model. To demonstrate the effects of conduction band screening on the line shapes of TM compounds, we reinterpret the Ni 2p spectrum of NiS and Fe 2p spectrum of FeS_2, neither of which can be satisfactorily explained using a simple cluster model with a single TM ion.

The model we use to describe the spectra is based on earlier single-cluster models [3, 6, 7], but includes the presence of an unfilled conduction band. In this cluster model, the band widths of the valence and conduction bands are collapsed to zero and considered as single levels for simplicity. Charge transfer between the d^n metal site and the ligand

sites produces the usual intracluster configurations d^n, $d^{n+1}L$, $d^{n+2}L^2$, ..., etc, while charge transfer between the local d site and the conduction band produces configurations such as $d^{n-1}C$, $d^{n-2}C^2$, ..., $d^n LC$, $d^n L^2C^2$, ..., $d^{n+1}L^2C$, $d^{n-1}LC^2$, ..., etc, where L denotes a hole in a ligand p orbital and C denotes an electron transferred to the conduction band. If the charge transfer energy is defined as $\Delta = E(d^{n+1}L) - E(d^n)$ as in previous models, we can also define a charge transfer energy to the conduction band as $\Delta^* = E(d^{n-1}C) - E(d^n)$ [8]. Thus the band gap, which is the energy required to transfer an electron from the valence band to the conduction band, is given by $\Delta + \Delta^* - U$, and the energy of each configuration can be described in terms of Δ, Δ^* and U. The diagonal part of the d–d exchange interaction is included by expressing the Coulomb exchange interaction of each configuration in terms of Kanamori parameters [9], and by calculating them using the Racah parameters A, B and C, where possible d orbital and spin state is considered explicitly.

For many transition metal compounds, the ligand p band is completely filled and the lowest-lying conduction band level will be the upper Hubbard band formed by empty d orbitals of neighbouring TM sites. The upper Hubbard band can be strongly hybridized with the ligand orbitals to have significant p character. In this case, the value of Δ^* will be exactly equal to U, the energy required to transfer an electron from the lower to the upper Hubbard band. Here, the model simulates in an approximate way part of the screening effect of additional d sites within the lattice. We can introduce an effective coupling parameter T^* to describe the interaction strength between the local d orbitals and the empty orbitals of the conduction band, analogous to the intracluster transfer integral T. Hence, T^* describes the ease with which an electron can hop from one d site to another, mediated by the intervening ligand orbitals, and so will also reflect the strength of the intracluster hybridization described by Δ and T. Charge transfer to the conduction band via the ligand orbitals will be more likely for compounds where the metal d and ligand p orbitals are strongly mixed, and we expect T^* to be significant for covalent compounds where Δ is small. T^* will diminish for more ionic compounds, such as the TM oxides, where Δ is larger and conduction band screening is expected to play a lesser role. T^* is left as an adjustable parameter in the fitting procedure. If the lowest-lying conduction band is the upper Hubbard band, the $d^{n+1}L$ and $d^n LC$ configurations in the unhybridized ground state should be degenerate at energy Δ as both states describe the transfer of an electron from a ligand orbital to a TM site [10].

Another possible scenario for the model includes the presence of unfilled orbitals at the ligand site, such as the empty p σ^* orbital of the chalcogen diatomic molecule in the pyrite-type TM dichalcogenide compounds, which will be heavily mixed with the empty metal 3d orbitals. In this case, Δ^* can also be set to U as the first unoccupied level consists of strongly hybridized TM 3d and chalcogen p orbitals [11]. Here, T^* will be proportional to the relative overlap between the metal d orbitals and the empty ligand p orbitals. Inverse photoemission studies show well mixed metal 3d and S 3p σ^* empty states for the TM disulphides [11] and electrons transferred to the conduction band will probably be transferred to empty orbitals on the ligand site. Thus, in this case, the $d^n LC$ configuration describes the transfer of an electron from the occupied to the unoccupied orbitals on the ligand site, via the local d electron site.

Within the model we have retained the same parameters Δ, U and T from previous models to describe the intracluster interactions. Interactions with the conduction band are described by the new parameters Δ^* and T^*. As Δ^* is an exactly defined quantity for TM compounds with a filled p band, the only extra parameter to be fitted in reinterpreting the spectra is T^*. Setting T^* to zero removes the screening channel to the conduction band and returns us to a simple cluster model.

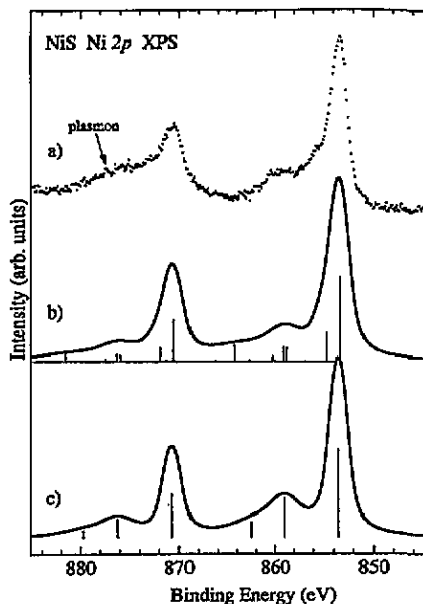The Ni 2p spectrum for NiS is shown in figure 1(a). The experimental spectrum displays

Figure 1. Experimental (a) and calculated (b, c) spectra for the Ni 2p core levels of NiS. A bulk plasmon satellite accompanying the main peak partially obscures the $2p_{1/2}$ satellite in the experimental spectrum. Spectra are calculated by a single-impurity cluster model including charge transfer effects to the conduction band (b) and a single-impurity cluster model with intracluster interactions only (c). Intracluster parameters for both calculated spectra are $\Delta = 2.5$ eV, $U = 5.5$ eV and $T_\sigma = 2.1$ eV. Conduction band parameters for (b) are $\Delta^* = U$ and $T_\sigma^* = 0.35$ eV.

a significant asymmetry on the high-binding-energy side of the main peak at ≈ 853.5 eV, with extra intensity appearing between it and the satellite structure at ≈ 859 eV. Before introducing interactions with the conduction band, we calculate the simple cluster model prediction for the Ni 2p spectrum (figure 1(c)), where the ground state is described as a linear combination of the intracluster states d^8, $d^9 L$ and $d^{10} L^2$. This spectrum will have a three-peak structure with best-fit parameter values of $\Delta = 2.5$ eV, $U = 5.5$ eV and $T_\sigma = 2.1$ eV, in accordance with earlier studies [3]. (Transfer integrals for the metal e_g and t_{2g} orbitals in an octahedral coordination are denoted by T_σ and T_π respectively where $T_\sigma / T_\pi \approx -2.2$ [3]. An energy-dependent Lorentzian lifetime broadening [3] is included, as well as a Gaussian broadening to simulate instrumental broadening.) As can be seen from the figure, although we can correctly model the satellite position and intensity, it is impossible to reproduce the large asymmetry of the main peak using only this three-peak structure. Retaining the intracluster parameters Δ, U and T_σ, we introduce the conduction-band-screened states $d^{8+l-m} L^l C^m$, where $m = 1, 2, 3$ and $l = 0, 1, 2, 3$. We now switch on the charge transfer channel to the conduction band by varying T^* to obtain the best fit to the experimental data, with the result for $T^* = 0.35$ eV shown in figure 1(b). The important new features of this calculation are the extra intensity on the higher-binding-energy side of the main peak, and the appearance of additional satellite structures at higher energies. We are able to reproduce the asymmetry of the main peak while keeping the correct satellite to main peak ratio, which cannot be achieved by previous single-cluster models.

The new features in the spectrum arise from a heavily mixed ground state where much weight has been distributed to the conduction-band-screened states, such as $d^8 LC$. If T^* is

made larger, the weight in the conduction-band-screened states increases, and the satellite intensity becomes weaker and spread out over a wide energy range. It should be noted that NiS is still described as a charge transfer insulator within the model and the intracluster interactions dominate the ground state. The strong core hole potential will mean that the lowest-energy eigenstates of the spectrum will still be due to the intracluster interactions, although they may be heavily mixed with those due to screening by the conduction band states. Thus, the character of the major features in the spectrum in the same as for the simple cluster model, while the conduction-band-screened states provide many new satellite structures leading to the asymmetric line shape.
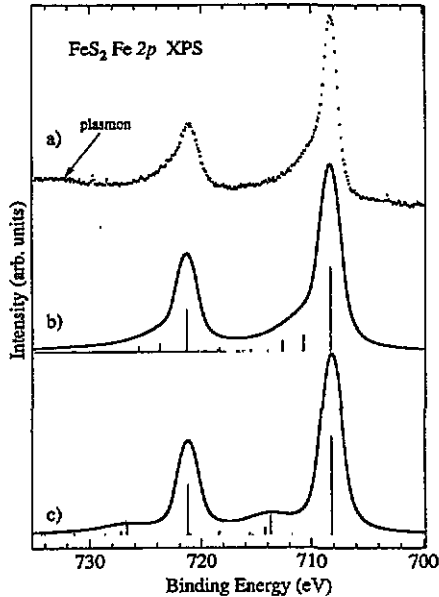

Figure 2. Experimental (a) and calculated (b, c) spectra for the Fe 2p core level of FeS$_2$, as for figure 1. Intracluster parameters for both calculated spectra are $\Delta = 3.0$ eV, $U = 3.5$ eV and $T_\sigma = 1.7$ eV. Conduction band parameters for (b) are $\Delta^* = U$ and $T_\sigma^* = 0.89$ eV.

The inclusion of conduction band screening has a more dramatic effect on the Fe 2p spectrum of FeS$_2$ shown in figure 2. FeS$_2$ is a semiconductor with a gap of 0.9 eV [12], with six electrons in a $S = 0$ low-spin configuration. In this system, the S 3p orbitals of the S_2^{2-} molecule are only partially filled with ten electrons. The experimental spectrum, shown in figure 2(a), displays a narrow main peak with an asymmetric tail on the high-binding-energy side, with apparently little satellite structure. The best-fit prediction using a simple cluster model is shown in figure 2(c), yielding parameters $\Delta = 3.0$ eV, $U = 3.5$ eV and $T_\sigma = 1.7$ eV in accordance with previous studies [3]. While these parameter values fit into the general trends found for many TM compounds [3], including other pyrite disulphide compounds, the calculated spectrum clearly cannot account for the large asymmetry of the experimental spectrum. Moreover, the satellite structure is somewhat overestimated despite the small value of U used.

Values for the metal to ligand transfer integrals within the S_6 space group between the occupied and unoccupied metal 3d and S 3p orbitals have been determined by a parametrized molecular orbital calculation using the relationships given by Harrison [13] and are listed

Table 1. Table 1. Ratios for the metal to ligand transfer integrals for the TM 3d and chalcogen p orbitals of pyrite-type compounds. The transfer integrals are normalized to the overlap of the metal E_g^2 orbitals and the occupied ligand orbitals (T_σ) which is set to 1.00. T_σ was treated as an adjustable parameter.

	Ligand p	
	Occupied (σ, π, π^*)	Unoccupied (σ^*)
Metal 3d		
E_g^2 (e_g)	1.00 (T_σ)	0.51 (T_σ^*)
$A_g + E_g^1$ (t_{2g})	0.87 (T_π)	0.15 (T_π^*)

as ratios in table 1. Here, the occupied A_g and E_g^1 (equivalent to the t_{2g} orbitals in the O_h space group) metal orbitals are considered to be degenerate as are the five occupied ligand S 3p orbitals. For the transfer integrals to the occupied ligand S 3p σ, π and π^* orbitals in table 1, $T = T_\sigma$ for the metal E_g^2 orbitals (equivalent to the e_g orbitals in the O_h space group) and $T = T_\pi$ for the metal A_g and E_g^1 orbitals. The unoccupied S 3p σ^* orbitals will have a non-zero overlap with the metal A_g and E_g^1 orbitals, meaning $T_\pi^* > 0$, and we expect the ratio T_σ / T_σ^* to be ≈ 1.9. T_σ is retained as an adjustable parameter with the other transfer integrals determined by the ratios of table 1. Introducing the screening channel to the conduction band has a remarkable effect on the line shape of the Fe 2p spectrum, as can be seen in the best-fit result of $T_\sigma = 1.7$ eV and $T_\sigma^* = 0.89$ eV in figure 2(b). Here we can obtain good agreement with experiment without changing the intracluster parameters obtained by previous cluster models. We have used a basis set including the intracluster states $d^6, d^7 L, d^8 L^2, d^9 L^3$, and the conduction-band-screened states $d^{6+l-m} L^l C^m$, where $m = 1, 2, 3$ and $l = 0, \ldots, 5$. The calculated spectrum reproduces well the asymmetry of the experimental data, and the absence of distinct satellite peaks. As T^* is relatively large for FeS$_2$, the conduction-band-screened states will have a lot of weight in the ground state. Thus, despite the strong core hole potential at the d site, the lowest-energy eigenstate of the spectrum is predominantly due to the conduction-band-screened states, while the intracluster states contribute to the weaker satellite structures. This calculation represents a great improvement over the simple cluster model, where the effects of the empty S 3p orbitals are not accounted for.

We can compare the present model to the original model of Kotani and Toyozawa [14] for XPS core level spectra. The asymmetric line shapes found in this early model were due to the excitation of electron–hole pairs caused by the changes of the d level position in the core hole final state. The present model is analogous to that situation except that the valence and conduction bands, while they are treated as single levels, have different characters and hence different hybridization strengths with the d level. Further, the degeneracy of the d level is explicitly considered in the present model, producing many additional satellite structures. The mechanism here is different to that responsible for the Doniach–Šunjić [15] core level line shape for metallic compounds. In the latter case, the electron–hole pair excitations are caused by the core hole potential directly acting upon the conduction electrons.

We believe the present model may provide a good starting point to explain the metal core level line shapes of many strongly correlated, small-gap semiconducting or metallic TM compounds, or other compounds where metal–metal screening is important for the electronic structures, such as U or Th compounds. The analysis of the core level spectra of U intermetallic compounds has been difficult to achieve using previous single-impurity

approaches, such as Anderson impurity model calculations [16, 17], where only the lowest-order terms in the $1/N$ expansion are retained and electron–hole pair excitations are neglected.

In conclusion, we have extended the single-impurity cluster model to include the effects of charge transfer to the conduction band and shown that these effects can have a considerable influence on the line shapes of the 2p core level spectra. The charge fluctuations between the TM site and the conduction band can be described by a few, well defined parameters. Conducting-band-screened states can mix heavily with the intracluster states in the ground state, causing the appearance of new satellite structures in the spectra. These new structures reproduce well the asymmetry found in the experimental data of NiS and FeS_2.

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[10] When the hybridization is switched on, no direct overlap is considered between the ligand orbital and the neighbouring metal site within this single-cluster model, causing the degeneracy between the $d^{n+1}L$ and $d^n LC$ configurations to be removed. Thus we must add an extra energy δ to the configurations $d^n LC, d^n L^2 C^2, \ldots$ in the hybridized ground state to account for the hybridization between the ligand orbitals and the orbitals of the neighbouring d sites. δ will simply reflect the hybridization splitting between the $|d^n\rangle$ and $|d^{n+1}L\rangle$ states and can be approximately calculated by diagonalization of the Hamiltonian for a given set of parameters. We obtain $\delta = 2.6$ eV for NiS.
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