

SURFACE CORE-LEVEL SHIFTS IN MIXED-VALENT SYSTEMS*

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A semiempirical model for surface core-level shifts Δ_C^S in mixed-valent compounds is presented. The interplay of electronic and Madelung-type contributions to Δ_C^S is discussed by including incomplete final state screening. It is shown that Δ_C^S depends sensitively on the surface change in the electronic configuration and screening capacity. In the core-level screening both the dynamic response via the itinerant charge and the dielectric polarizability of the medium are considered. To demonstrate the range of validity of this model, surface 4f-level shifts are calculated for TmSe, TmTe and YbAl₂ and for systems with varying binding character such as Sm_{1-x}Y_xS as a function of composition.

1. INTRODUCTION

For many solids surface core-level shifts have been observed. This shift is caused by a change in the electrostatic potential resulting from the local chemical environment, the local electronic configuration and the final state screening at the core-excited site. At transition metal surfaces the surface core-level shift has been directly related to the geometrical arrangement and other interesting thermodynamic properties^{1,2}. In this paper it is shown for the first time how this shift reveals also interesting information on the valence state of the solid and how it can be used to study mixed-valent systems. The surface core-level shift depends sensitively on the valence and the screening capacity.

In section 2 we develop a simple model for Δ_C^S . In section 3 this model is applied to mixed-valent systems such as Sm_{1-x}Y_xS³, TmSe, YbAl₂ and to TmTe. In section 4 a brief summary is presented.

2. THEORY

The surface core-level shift $\Delta_C^S(Z)$ of an atom with atomic number Z is given by⁴

$$\Delta_C^S(Z) = E_C^S(Z) - E_C^B(Z), \quad (2.1)$$

which is the difference of the core-level binding energies (with respect to the Fermi energy E_F) at the surface and in the bulk. The core-level binding energy can be expressed in terms of total energies E^{tot} of the system in the initial state and in the final state, after a photoelectron is emitted, as

$$E_C^B(Z) = E_f^{\text{tot}}(\text{core-excited atom } Z^* \text{ in the bulk (surface) of the unperturbed host}) - E_i^{\text{tot}}(Z \text{ atom in the bulk (surface) of the unperturbed host}). \quad (2.2)$$

For pure metal surfaces, where to a good approximation complete final state screening can be assumed, $\Delta_C^S(Z)$ is the difference of surface energies of Z and (Z+1) metal⁵. In the case of semiconductors and insulators $\Delta_C^S(Z)$ is expected to depend also on the final state screening. In solids with partial ionic character Δ_C^S can be

decomposed into an electronic part $\Delta_e(Z)$ and a Madelung part $\Delta_M(Z)$. Then,

$$\Delta_c^S(Z) = \Delta_e(Z) + \Delta_M(Z). \quad (2.3)$$

Δ_e and Δ_M can be decomposed as

$$\Delta_e(Z) = \Delta E_e(Z^*) - \Delta E_e(Z) \quad (2.4)$$

and

$$\Delta_M(Z) = \Delta E_M(Z^*) - \Delta E_M(Z), \quad (2.5)$$

where $\Delta E_{e(M)}$ is the difference between the electronic (Madelung) contribution to the cohesive energy at the surface and in the bulk, and where $Z^*(Z)$ denotes the core-excited (ground state) atom.

First consider the electronic part Δ_e of Δ_c^S in eq. (2.4). In the one-electron picture ΔE_e can be obtained by integration over the local density of states $g^i(E)$ and summation over all occupied bands i , as

$$\Delta E_e(Z) = \sum_i \left(\int_{-\infty}^{E_F} dE (E - E_S^i) g_S^i(E) - \int_{-\infty}^{E_F} dE (E - E_B^i) g_B^i(E) \right). \quad (2.6)$$

Here, E^i denotes the center of gravity of the band i . In the following, the indices S(B) refer to surface (bulk) properties. Note also that only partially filled bands will contribute to ΔE_e . Using rectangular band shapes⁶ for $g^i(E)$ and appropriate band parameters for the ground and excited state, $\Delta_e(Z)$ can easily be calculated from eq. (2.4) and eq. (2.6). A formula similar to eq. (2.6) can be obtained for the final Z^* -state if $g^i(E)$ is replaced by $g^{i,*}(E)$, etc.

Next we turn to the Madelung shift Δ_M . From the definition of the quantities in eq. (2.5) it follows that

$$\Delta E_M(Z^*) = \int d^3r \int d^3r' \frac{(\varrho_S^*(r) - \varrho_B^*(r)) \varrho(r')}{|r - r'|}, \quad (2.7)$$

which represents the interaction of the charge distribution $\varrho_{S,B}^*(r)$ at the core-excited site with the charge distribution of the host. Note that ϱ^* depends sensitively on the screening mechanism. The corresponding formula for $\Delta E_M(Z)$ is given by just omitting the asterisks in eq.

(2.7). In a simple approximation both $\Delta E_M(Z)$ and $\Delta E_M(Z^*)$ can be obtained from the lattice energy in the adiabatic rigid lattice point-charge model⁷. In evaluating ΔE_M , the appropriate Madelung constants⁷ reflecting the crystal symmetries in the bulk and at the surface must be chosen, and one has to take into account the nuclear core-repulsion by using, e.g., a Born-Mayer-like potential.

$\Delta_c^S(Z)$ can in principle be calculated, once the relevant parameters for the ground state of a system are known. The only remaining point to be discussed is the charge distribution $\varrho^*(r)$ or the total charge Q^* at the core-excited site in eq. (2.7). Clearly, the charge distribution after the core-ionization must be considered in evaluating both $\Delta E_e(Z^*)$ from eq. (2.6) and $\Delta E_M(Z^*)$ from eq. (2.7).

In the following we briefly discuss the screening capacity of the host in terms of extra-atomic dynamic screening and of dielectric static screening. The latter gets especially important in the case of semiconductors.

Consider now a rare-earth atom Z in the host, where a 4f-photoelectron is being emitted. Screening of the core-hole can be achieved by itinerant conduction band electrons locally available at the core-excited site. Complete screening is obtained if the initial state occupation number N is larger than one. A positive excess charge, however, is expected to remain at the core-excited site in the case where N is smaller than one. A localized state will form in this case due to the new attractive scattering potential. It will accommodate the screening charge, thereby draining the conduction band and hence reducing the electronic binding energy at the Z^* -site. In such a case of incomplete local screening we expect the surrounding electron cloud to relax toward the core-excited site and to produce some charge transfer for additional screening of the excess charge. As there is no simple way to describe this process quantitatively, we introduce an adjustable parameter S to account for this effect. In addition to this dy-

dynamic screening we expect the bound electronic charge of the host to get polarized by the positive excess charge. We can account for this static screening by considering the host as an effective medium whose electronic polarizability is described by a high-frequency dielectric constant ϵ_{00} . Hence, the final state charge Q^* of the rare-earth ion can be obtained as

$$Q^*_{B(S)} = Q_{B(S)} + f_{B(S)} (\epsilon_{00}^{B(S)}) \cdot S_{B(S)} \cdot (1 - N_{B(S)}) \quad (2.8)$$

where Q is the ground state ionic charge and N is the conduction band occupation number. The function $f(\epsilon_{00})$ and the parameter S describe static and dynamic screening effects, respectively. f is a well-behaved function which - alike S - differs for bulk and surface. Note that eq. (2.8) also reproduces correctly the limiting cases of a metal ($f_{B(S)} = S_{B(S)} = 0$) and that of an insulator ($f_{B(S)} = S_{B(S)} = 1$).

As the Madelung energy of a crystal can be much larger than the electronic binding energy, the final state charge and the screening parameters turn out to be of crucial importance for the surface core-level shift. Due to the sensitivity of Δ_C^S to the screening mechanism, it should be possible to obtain information about the electronic configuration (valence) and the screening of charged impurities in intermediate-valent systems from photoemission measurements.

3. APPLICATIONS

First we use our model to calculate Sm 4f-level shifts³ at the (100) surface of $\text{Sm}_{1-x}\text{Y}_x\text{S}$ as a function of x . The bulk valence of Sm, $V_B(x)$, has been obtained by Tao and Holtzberg⁸ for the whole composition range from lattice parameter measurements. We assume a common d-band for Y and Sm and obtain for the 5d-band occupation number in the bulk

$$N_B(x) = (1-x)(V_B(x)-2) + x. \quad (3.1)$$

At the surface, there is strong evidence⁹ for

divalent Sm, so that only Y will contribute to the conduction band filling, giving

$$N_S(x) = x \quad (3.2)$$

As $V_B(x)$ is always less than 3, the d-band occupation never reaches one. Hence, we expect incomplete final state screening and zero contribution to Δ_e from the final state. The 5d-bandwidth of $\text{Sm}_{1-x}\text{Y}_x\text{S}$ has been obtained from linear interpolation between those of SmS and YS as done previously¹⁰. The contribution of the 4f-electrons to the cohesive energy turns out to be negligible due to the small 4f-bandwidth.

In the calculation of the Madelung shift Δ_M the core-repulsion term can be related to the bulk modulus $B(x)$ ¹¹. With increasing Y concentration in $\text{Sm}_{1-x}\text{Y}_x\text{S}$, the system undergoes a semiconductor-metal transition at $x = 0.15$ at room temperature. At this point $B(x)$ drops to zero and also causes Δ_M to vanish. The structure in the Madelung shift is predominantly due to discontinuities in the $V_B(x)$ and $B(x)$ curves, especially near the transition point.

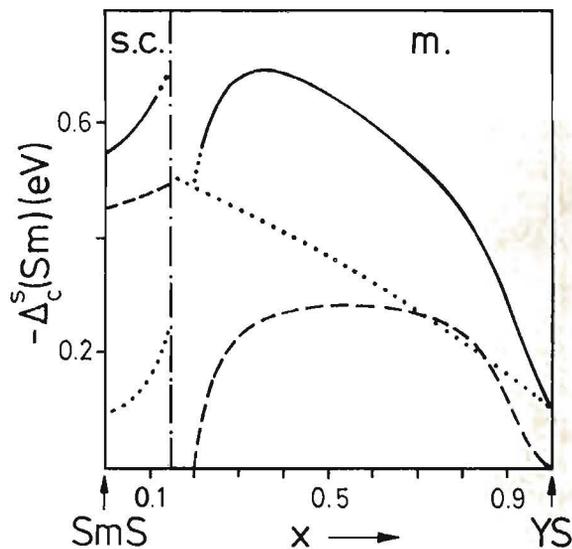


Fig. 1

Surface 4f-level shift Δ_C^S of Sm in $\text{Sm}_{1-x}\text{Y}_x\text{S}$, together with the constituent electronic and Madelung shift Δ_e and Δ_M (dotted and dashed)

Δ_M is expected to be large in the semiconduc-

ting phase for small x and to vanish in the limit of metallic YS. In Fig.1 the calculated 4f-level shifts $\Delta_C^S(x)$ of Sm for one set of screening parameters $S_{B(S)}$ is presented together with data for $\Delta_e(x)$ and $\Delta_M(x)$.

It is interesting to see that by applying the simple model presented in this paper and using experimental data for the surface (bulk) valence $V_{S(B)}$, the density of states, the bulk modulus and optical reflectivity one obtains for some other related systems the following results:

	TmSe	TmTe	YbAl ₂
V_B	2.55	2.0	2.4 ¹²
V_S	2.0	2.0	2.2 ¹²
Δ_e (eV)	0.6	0	~0.6..0.7
screening	incomplete		full
Δ_M (eV)	~-0.3..-0.2	~0.2..0.6	0
Δ_C^S (theor)(eV)	~0.3...0.4	~0.2..0.6	~0.6..0.7
Δ_C^S (exp) (eV)	0.32	0.41	0.92 ¹²

4. SUMMARY AND CONCLUSIONS

We have presented a simple model for the calculation of surface 4f-level shifts Δ_C^S in both semiconducting and metallic mixed-valent compounds. In the general case, Δ_C^S consists of an electronic and of a Madelung part. Especially the latter is very sensitive to changes in the valence and the screening capacity between bulk and surface. We have shown that Δ_C^S contains direct information about screening of excited atoms or charged impurities and the electronic configuration.

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