

Calculation of surface core-level shifts in intermediate-valence compounds

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Taking into account energy changes both due to electronic- and Madelung-type atomic cohesion, the surface core-level shifts of $4f$ levels are calculated for Tm_xSe , $TmTe$, and $YbAl_2$. In particular, for Tm_xSe we determine the dependence of the surface core-level shift on the stoichiometry. It is shown that surface valency changes affect strongly the core-level shift. The numerical results are compared with recent photoemission data.

I. INTRODUCTION

Recently, many studies of surface core-level shifts have been performed. The surface shift is caused by a surface change in the electrostatic potential resulting from the different local chemical environment, the local electronic configuration, and the final-state screening at the core-excited site. From the study of such shifts various useful information can be obtained concerning the surface valency and structure of transition metals and their alloys.

We present here a generalized version of a semi-empirical model¹ introduced recently for the calculation of $4f$ surface core-level shifts in mixed-valence $Sm_{1-x}Y_xS$. In the case of a not fully screened $4f$ core hole the surface core-level shift Δ_c^s results from changes of the electronic cohesive energy and of Madelung potential energy. The surface shift Δ_c^s depends sensitively on the surface valency and the change of the core-hole screening at the surface.

The model presented here for calculating Δ_c^s applies to systems with both ionic type and metallic-like electronic cohesion. Thus we calculate Δ_c^s for semiconducting $TmTe$ with dominating ionic cohesion, for metallic $YbAl_2$ whose cohesion is due to electronic forces only, and for Tm_xSe where both electronic and Madelung-type contributions to Δ_c^s are of importance. The results are compared with

experimental ultraviolet photoemission spectroscopy (UPS) data.

In Sec. II details of the theory for calculating Δ_c^s in mixed-valence compounds are presented. In Sec. III numerical results are presented. A summary is given in Sec. IV.

II. THEORY

The surface core-level binding-energy shift of an atom with atomic number Z is given by²

$$\Delta_c^s(Z) = E_c^s(Z) - E_c^b(Z), \quad (2.1)$$

with $E_c^{s(b)} = E_f^{s(b)} - E_i^{s(b)}$. Here, $E_f^{s(b)}$ and $E_i^{s(b)}$ are the total energy of the system after and before a photoelectron is ejected, respectively (s and b refer to the surface and the bulk).

Δ_c^s can be written as^{1,2}

$$\Delta_c^s(Z) = \Delta_e(Z) + \Delta_M(Z), \quad (2.2)$$

where Δ_e and Δ_M denote the electronic and Madelung contributions, respectively.

The electronic contribution is given by

$$\Delta_e(Z) = \Delta E_{el}(Z^*) - \Delta E_{el}(Z), \quad (2.3)$$

where Z^* refers to atoms with one core hole present. Within the tight-binding approximation we have^{1,2}

$$\Delta_e(Z) = \frac{1}{2} \sum_i W_i \left\{ \left[\frac{z_s}{z_b} \right]^{1/2} \left[N_i^{s*} \left[\frac{N_i^{s*}}{N_i^0} - 1 \right] - N_i^s \left[\frac{N_i^s}{N_i^0} - 1 \right] \right] \right. \\ \left. - \left[N_i^{b*} \left[\frac{N_i^{b*}}{N_i^0} - 1 \right] - N_i^b \left[\frac{N_i^b}{N_i^0} - 1 \right] \right] \right\} + \Delta_{el-el}(Z). \quad (2.4)$$

Here, $z_s(b)$ denotes the coordination number of a surface (bulk) atom. N_i is the local occupancy of the band i ($i=s, p$, or d) with bandwidth W_i and maximum occupation number N_i^0 . An asterisk refers to atoms with a core hole. The contribution $\Delta_{\text{el-el}}$ results from interactions between the electrons and corrects the band-energy part of the electronic cohesive energy. The leading term is the difference of Coulomb terms in the atomic and band limit and is given by³

$$\frac{1}{2} \sum_i U_{ii} N_i \left[\frac{N_i}{N_i^0} - 1 \right],$$

where U_{ii} denotes the effective intraband Coulomb interaction. Owing to the valence change between surface and bulk there is an additional contribution^{2,4} to $\Delta_{\text{el-el}}$ given by $\sum_i U_{ci}(N_i^s - N_i^b)$, where U_{ci} is the Coulomb interaction between the core level and the band i . Thus we have

$$\begin{aligned} \Delta_{\text{el-el}}(\mathbf{Z}) = & -\frac{1}{2} \sum_i \left\{ U_{ii} \left[N_i^{s*} \left[\frac{N_i^{s*}}{N_i^0} - 1 \right] - N_i^s \left[\frac{N_i^s}{N_i^0} - 1 \right] \right] \right. \\ & \left. - \left[N_i^{b*} \left[\frac{N_i^{b*}}{N_i^0} - 1 \right] - N_i^b \left[\frac{N_i^b}{N_i^0} - 1 \right] \right] + 2U_{ci}(N_i^s - N_i^b) \right\}. \end{aligned} \quad (2.5)$$

The Madelung-energy contribution to Δ_c^s is given by

$$\Delta_M(\mathbf{Z}) = \Delta E_M(\mathbf{Z}^*) - \Delta E_M(\mathbf{Z}), \quad (2.6)$$

with $\Delta E_M(\mathbf{Z}) = E_M^s - E_M^b$. One finds for the bulk

$$E_M^b(\mathbf{Z}) = \alpha_b \frac{Q(\mathbf{Z})Q(A)}{r} \left[1 - \left[\frac{\rho}{r} \right]_b \right], \quad (2.7)$$

where

$$\left[\frac{r}{\rho} \right]_b = 2 + \frac{18Br^4}{\alpha_b Q(\mathbf{Z})Q(A)}.$$

Here, the adiabatic rigid lattice point-charge model is used. The repulsive interaction between nearest-neighbor (NN) atoms is described by a Born-Mayer potential, B denotes the bulk modulus, α_b is the bulk Madelung constant, and $Q(\mathbf{Z}), Q(A)$ are the absolute values of the charges of the cation and the NN anion at distance r , respectively, within the unit cell. At the surface one obtains^{1,2,5}

$$\begin{aligned} E_M^s(\mathbf{Z}) = & \frac{1}{2} \frac{Q(\mathbf{Z})Q(A)}{r} \\ & \times \left\{ \alpha_b \left[1 - \left[\frac{\rho}{r} \right]_b \right] \right. \\ & \left. + \alpha_s \left[\frac{z_s}{z_b} \right]^2 \left[1 - \left[\frac{\rho}{r} \right]_s \right] \right\}, \end{aligned} \quad (2.8)$$

where

$$\left[\frac{r}{\rho} \right]_s = 2 + \frac{18Br^4}{\alpha_s (z_s/z_b)^2 Q(\mathbf{Z})Q(A)}.$$

Here, α_s is the Madelung constant referring to the surface plane of atoms. Note, $E_M^{s(b)}(\mathbf{Z}^*)$ is obtained by replacing \mathbf{Z} by \mathbf{Z}^* in Eqs. (2.7) and (2.8) and taking into account that B and r depend on \mathbf{Z} . Depending on the number of itinerant electrons $N^{b(s)}$ the core-hole screening will be complete or incomplete.^{1,2} Thus

$$Q^{b(s)}(\mathbf{Z}^*) = Q^{b(s)}(\mathbf{Z}) + \delta Q^{b(s)},$$

with $\delta Q^{b(s)} < 1$, if $N^{b(s)} < 1$, and zero otherwise. In the following we use the expressions for Δ_e and Δ_M to calculate Δ_c^s for various systems.

III. NUMERICAL RESULTS

The surface core-level shift Δ_c^s is now calculated by using the expressions given in Sec. II. First, Δ_c^s of the homogeneous divalent semiconductor⁶ TmTe with NaCl structure is calculated for the (100) surface. According to experiment⁷ the Tm $4f$ level is about 0.3 eV below the bottom of the conduction band. Since the $6s$ and $5d$ bands are nearly empty, $\Delta_e \approx 0$ and the $4f$ hole is only screened by dielectric polarization. Then, $\Delta_c^s \approx \Delta_M$, and Δ_M is calculated with the help of Eqs. (2.6)–(2.8). We use $z_s = 5$, $z_b = 6$, $\alpha_b = 1.748$ [$=\alpha(\text{NaCl})$], $\alpha_s = 1.615$ ($=\alpha[\text{NaCl}-(100)]$),⁸ $r(\mathbf{Z}^*) = r(\mathbf{Z}) = 3.17 \text{ \AA}$, and $B(\mathbf{Z}^*) = B(\mathbf{Z}) = 3.8 \times 10^{11} \text{ dyn cm}^{-2}$, as measured by Ott *et al.*⁹ Since $4f$ -hole screening results only from fast dielectric polarization we set $\delta Q^b = 1/\epsilon_\infty$. The analogous value at the surface (Appendix) is

$\delta Q^s = 2/(1 + \epsilon_\infty)$. The high-frequency dielectric function ϵ_∞ is determined from

$$\epsilon_\infty^2 = (1 + \sqrt{R}) / (1 - \sqrt{R}).$$

Here, we assume for the reflectivity R a value of less than 1%.⁷ Thus we calculate for TmTe a shift, in eV,

$$\Delta_c^s \approx 0.45$$

to higher binding energy. This compares well with recent UPS data⁶ which yield $\Delta_c^s(\text{expt}) = 0.41$ eV.

Next, we calculate Δ_c^s for metallic YbAl₂. Then, $\Delta_M = 0$ and $\Delta_c^s = \Delta_e$, where Δ_e is calculated by assuming that the valency of Yb is 2.4 in the bulk and 2 at the surface.¹⁰ We assume also that the band structure of YbAl₂ is similar to YAl₂ for which augmented-plane-wave (APW) calculations are available.¹¹ Accordingly, we assume that the Al 3s band is full and that the 6s electrons of Yb and p electrons of Al hybridize and form a partially filled band with a width of the order of 13 eV. One of the Yb 4f electrons converts partly to a Yb 5d electron, and the d -band width of Yb metal is taken as 7 eV.¹² We also assume that a Yb atom with a core hole corresponds to a Lu impurity.² Furthermore, we use $N_{5d}^s = 0$, $N_{5d}^b = 0.4$, and $N_{sp}^b = N_{sp}^s = 3$ for the initial state. In the final state the electronic screening charge fills sp - and d -band states which are rigidly shifted down. Hence

$$N_i^{s(b)}(Z^*) = N_i^{s(b)}(Z) + \frac{1}{1 + \eta_i}, \quad (3.1)$$

with

$$\eta_{5d} = \frac{N_{sp}^0 W_{5d}}{N_{5d}^0 W_{sp}}, \quad \eta_{sp} = \frac{N_{5d}^0 W_{sp}}{N_{sp}^0 W_{5d}}.$$

Note, η_i weighs the distribution of the screening charge in the sp and d bands according to their bandwidths and occupation numbers. For the (100) surface we have $z_s = 9$, $z_b = 12$, and for the Coulomb interaction integrals we take $U_{ff} = 6$ eV,¹³ $U_{ss} = 3$ eV,¹⁴ and $U_{dd} = 2$ eV.¹⁵ The interband Coulomb integrals U_{ci} are approximated by the geometric average $(U_{cc} U_{ii})^{1/2}$. Using these values we obtain from Eqs. (2.3)–(2.5), for Δ_c^s , a shift, in eV,

$$\Delta_c^s = 1.35$$

to higher binding energy. This compares reasonably well with the experimental result¹⁰ $\Delta_c^s(\text{expt}) = 0.92$ eV. Note that mainly due to U_{4f5d} the 4f level shifts by about 1.3 eV to higher binding energy as a result of the Yb valence difference between bulk and surface with no 5d electrons. Mainly from the cohesion due to 5d electrons one obtains a small contribution (of about 0.15 eV) to Δ_c^s .

Finally, we calculate Δ_c^s for mixed-valence Tm_xSe compounds ($0.87 \leq x \leq 1.05$), where both Δ_e and Δ_M contributions are expected since the 6s and 5d bands are only partly filled. For $N_{5d}^{s(b)}(x)$, $\bar{v}_s(x)$, and $\bar{v}_b(x)$ we use the values shown in Fig. 1.^{6,16,17} The surface valency of Tm is taken to be $\bar{v}_s = 2$ for the considered composition range.⁶ For $0.87 \leq x \leq 1.05$ we have

$$N_{5d}^{b(s)}(x) = x [\bar{v}_{b(s)}(x) - 2] + 2(x - 1)\Theta(x - 1). \quad (3.2)$$

The first term results from the promotion of the Tm 4f electrons into the Tm 5d band. The Tm 5d band will be further filled by excessive Tm 6s electrons which can no longer be accommodated in the Se 4p band for $x > 1$. This is described by the second term where Θ is the unit step function. It is¹ $N_{5d}^{b(s)}(Z^*) = 0$, since $N_{5d}^{b(s)}(x) < 1$, and $W_{5d} = 2.5$ eV (referring to the t_{2g} part of the band¹⁸). To calculate the contribution to Δ_c^s resulting from interactions between the electrons we use $U_{ff} = 5.3$ eV,¹⁸ $U_{dd} = 3$ eV,¹⁵ and $U_{fd} = (U_{ff} U_{dd})^{1/2}$. Using these values for the various parameters and Eqs. (2.3)–(2.5) we obtain for $\Delta_e(x)$ the results shown in Fig. 2.

The Madelung contribution Δ_M is calculated using for $B(x)$ and $r(x)$ experimental data^{16,19} and the values shown in Figs. 1(c) and 1(d) obtained by interpolation between experimental results. For ϵ_∞ we use the same value as in the case of the TmTe. Then we have^{1,2}

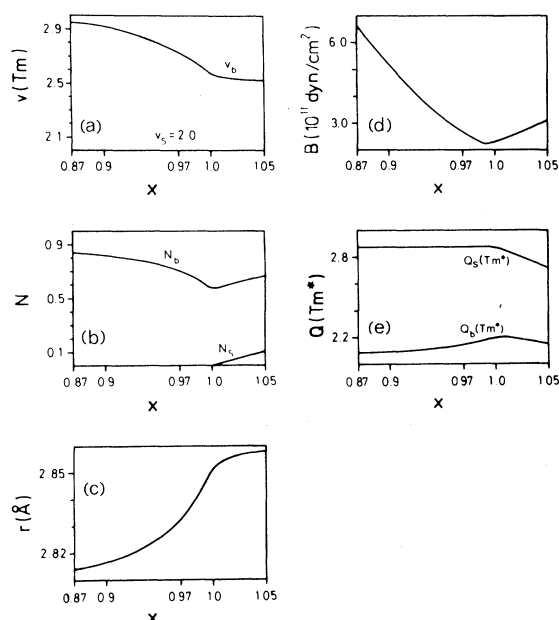


FIG. 1. (a) Mean valency, (b) occupation number of (5d,6s) band, (c) NN distance $r(x)$, (d) bulk modulus $B(x)$, and (e) charges $Q(Z^*)$ for Tm_xSe.

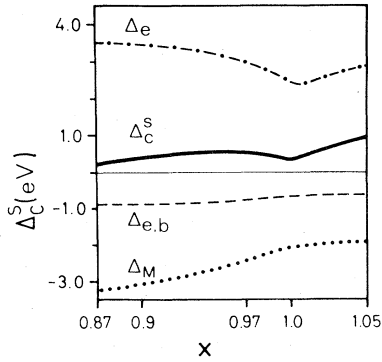


FIG. 2. Numerical results for $\Delta_c^s(x)$ in Tm_xSe . Δ_e and Δ_M denote the electronic and Madelung contribution, respectively, and $\Delta_{e,b} = \Delta_e - \Delta_{\text{el-el}}$.

$$Q^s(\text{Tm}^*) = Q(\text{Tm}) + \frac{2}{1 + \epsilon_\infty} S_s (1 - N_{5d}^s) \quad (3.3)$$

and

$$Q^b(\text{Tm}^*) = Q(\text{Tm}) + \frac{1}{\epsilon_\infty} S_b (1 - N_{5d}^b). \quad (3.4)$$

For $S_s = 1$ and $S_b(x=1) = 0.61$ we obtain from the expressions for Δ_e and Δ_M given in Sec. II the shift $\Delta_c^s(x=1) = 0.32$ eV to higher binding energy. $S_b(x)$ is linearly interpolated between $S_b(x=0) = 1$ for the semiconducting Se and between $S_b(x=1)$, which yields $S_b(x) = 1 - 0.39x$. Δ_M is then calculated in accordance with the fact¹⁸ that the conduction-electron concentration increases as x increases. The results are shown in Fig. 2. From Δ_e and Δ_M we obtain finally $\Delta_c^s(x)$ shown also in Fig. 2.

IV. DISCUSSION

The results for Δ_c^s obtained for TmTe , Tm_xSe , and YbAl_2 show that the surface core-level shifts reflect sensitively the valency of the atoms and screening of the core hole. For incomplete screening both ionic and electronic forces contribute to Δ_c^s . In the case of YbAl_2 we obtain at the surface a shift of the $4f$ -energy level to larger binding energy mainly as a result of the change of the Coulomb interaction between band and $4f$ electrons due to the decrease in the number of d electrons at the surface. This causes, as physically expected, a stronger binding of the $4f$ state, since fewer d electrons screen the attractive nuclear potential. The band contribution to Δ_e is expected to be small since it is approximately given by² $\gamma(Z^*) - \gamma(Z)$, where $\gamma(Z) > 0$ denotes the surface energy. γ is mainly given by the change in d -electron cohesive energy at the surface, and for $N_d^b(Z) = 0.4$ it is expected to be of the order of a few

tenths of an eV. This explains on general physical grounds for YbAl_2 a shift to larger binding energy of the $4f$ level at the surface.

In semiconducting TmTe only a vanishingly small number of thermally excited conduction electrons contribute to Δ_e and thus

$$\Delta_c^s \approx \Delta_M = \Delta E_M(Z^*) - \Delta E_M(Z).$$

One expects $\Delta_M > 0$ since obviously $\Delta E_M = E_M^s - E_M^b > 0$ if $Q^b(Z^*) \approx Q^s(Z^*)$ and $|Q(Z^*)| > |Q(Z)|$, and thus $|\Delta E_M(Z^*)| > |\Delta E_M(Z)|$. Consequently, $\Delta_c^s > 0$ is expected on general grounds for TmTe .

For mixed-valence Tm_xSe with $5d$ electrons and incomplete screening of the core hole one expects $\Delta_c^s = \Delta_e + \Delta_M$. In contrast to TmTe one has for Tm_xSe , $\Delta E_M(Z^*) < 0$, since $Q^b(Z^*) \lesssim 2.2$ and $Q^s(Z^*) = 2.87$ for $x \leq 1$. Therefore, $\Delta_M \approx \Delta E_M(Z^*) < 0$. Owing to U_{fd} one expects a shift of the $4f$ level to larger binding energy, since $N_d^b \leq 1$ and $N_d^s \simeq 0$. The surface shift of ϵ_{4f} due to d -electron cohesive energy is $\gamma(Z^*) - \gamma(Z) \approx -\gamma(Z)$, and thus small since $N_d < 1$. Since the ionic and electronic forces shift ϵ_{4f} oppositely, the net surface shift is relatively small. Finally, we want to note that we presumably overestimate the dielectric screening of the Coulomb interactions between Z^* and its nearest neighbors. However, the resulting error is expected to cancel partly in the energy differences between surface and bulk and furthermore will not change qualitatively our conclusions.

In summary, a model has been presented which is used to calculate the surface core-level shift in compounds with surface valency different from the bulk valency and with incomplete screening of the core hole.

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APPENDIX: DIELECTRIC SCREENING AT THE SURFACE

Using classical arguments we estimate the screening of a charge Q at the surface of a dielectric medium. Clearly, a charge centered in a spherical cavity inside the bulk is effectively reduced by a factor of $1/\epsilon_\infty$. According to Gauss's law the screening polarization charge

$$Q_{p,\text{tot}} = -\frac{\epsilon_\infty - 1}{\epsilon_\infty} Q \quad (\text{A1})$$

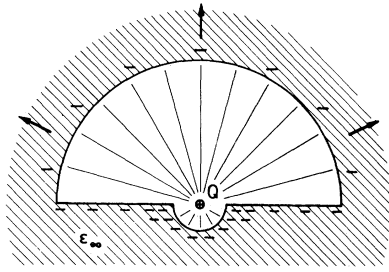


FIG. 3. Dielectric screening of a positive charge Q at the surface of a jelliumlike medium with dielectric constant ϵ_∞ .

at the inner surface of the cavity is conserved upon a continuous deformation of the spherical cavity. We imagine the upper half-sphere radially expanded to infinity (Fig. 3) in order to represent a charge at a dielectric surface. The polarization charge density is largest near Q and results in a screened effective

charge δQ^s which is pointlike when compared with the dimensions of the upper half-sphere. δQ^s induces on the upper half-sphere a polarization charge

$$Q_{p,u} = -\frac{1}{2} \frac{\epsilon_\infty - 1}{\epsilon_\infty} \delta Q^s. \quad (\text{A2})$$

The polarization charge $Q_{p,l}$ at the surface and lower half-sphere is given by

$$Q_{p,l} = Q_{p,\text{tot}} - Q_{p,u}. \quad (\text{A3})$$

On the other hand,

$$Q_{p,l} = \delta Q^s - Q. \quad (\text{A4})$$

It follows from (A3) and (A4) that

$$\delta Q^s = \frac{2}{\epsilon_\infty + 1} Q. \quad (\text{A5})$$

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