

Local-field corrections to surface and interface core-level shifts in insulators

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(Received 19 June 1992)

We present a model for the extra-atomic contributions to core-level shifts in insulating thin films on polarizable substrates. The final-state shift is calculated from the screening-dependent local fields at a photoemitting atom and shown to be comparable to the initial-state Madelung potential shift in polar crystals. For Xe(111) films, our model completely accounts for experimental results. For NaCl(100) and CaF₂(111) surfaces, we present predictions of surface core-level shifts for simple bulk terminations. We discuss corrections which can be incorporated into our model.

At the surfaces and interfaces of solids, atomic core-level energies observed using x-ray photoelectron spectroscopy (XPS) often exhibit shifts relative to bulk values.¹ These shifts are commonly ascribed to changes in chemical states; however, two otherwise identical atoms can also have different core-level energies if they have a different arrangement of neighboring atoms. We have developed a simple model for these geometric contributions in insulators which can be used to infer information about the chemical state of atoms near surfaces and interfaces. In particular, we compute the local-field-dependent contribution which has previously been either neglected²⁻⁶ or approximated,⁷⁻⁹ and which leads to experimentally observable shifts.

In the usual interpretation of core-level shifts,¹ the contributions are classified as those arising at the atomic site (intra-atomic effects) and externally to the photoionized atom (extra-atomic effects). Furthermore, because XPS measures the total initial-state energy minus the total final-state energy of the system, the intra- and extra-atomic effects are in turn separated into initial- and final-state effects. For an isolated ion or atom, the potential, and hence the initial-state binding energy, felt by the core electron is determined by the wave functions of the remaining core and valence electrons. In the XPS final state, these electrons respond to the sudden appearance of an extra core hole by relaxing their configuration; the energy liberated is directly transferred to the outgoing photoelectron. Collectively, these dependencies on the electronic configuration of the ion are called the "chemical shift."

In a crystal, similar initial- and final-state contributions arise from extra-atomic electrons; these contributions are sensitive to the arrangement of the lattice. In this paper we show that for ionic solids, the change in final state between the surface and interior sites can be just as important as the initial-state shift. Although our analysis is strictly accurate only for insulating crystals, a general implication can be drawn: the assignment of core-level-shifted features in XPS spectra cannot be based only on a theoretical chemical shift, but the geometry and electron-

ic states of nearby atoms must also be taken into account.

For ionic crystals, the extra-atomic contribution to the XPS initial-state energy is given by the Madelung potential¹⁰

$$\Phi_M = \sum_{\mathbf{R}_i} q_i / R_i, \quad (1)$$

the electrostatic potential seen at the site of an ion due to the presence of neighboring ions of charge q_i at positions \mathbf{R}_i . To evaluate Eq. (1), we use the method of Parry,¹¹ in which the standard Ewald calculation for bulk solids is adapted to two-dimensional structures. For a typical bulk ion, the Madelung potential assumes a value of about 10 eV per unit charge transfer; the decreased coordination at surfaces causes a decrease in the magnitude of the potential of about 10%. In general this results in an apparent binding energy increase for cations and a decrease for anions.

The XPS final-state energy is also affected by the geometric distribution of atoms near the core hole. The effect of the relaxation of electrons on neighboring atoms has previously been computed for bulk solids; we demonstrate below significant changes at a surface or interface due to the proximity of stronger or weaker screening regions. While the details are valid only for insulators, the trends will be common to all materials.

Earlier studies^{8,12} of this extra-atomic relaxation considered the energy gain from a core hole of charge Q in a continuous dielectric of permittivity ϵ_∞ . In such a system, the relaxation energy is given by

$$R_{r>\rho}^{\text{bulk}} = - \left[1 - \frac{1}{\epsilon_\infty} \right] \frac{Q^2}{2\rho} \quad (2a)$$

for atoms in bulk solids and

$$R_{r>\rho}^{\text{surf}} = R_{r>\rho}^{\text{bulk}} \left[\left(\frac{1}{2} + \frac{z}{4\rho} \right) + \frac{Q'}{Q} \left(\frac{1}{2} - \frac{z}{4\rho} \right) \right] \quad (2b)$$

for atoms near a surface, where ρ is an effective radius for the core-hole excitation, within which no screening charge can enter. For the surface expression, Eq. (2b), the core hole is a distance $z \leq \rho$ from the surface, and an image charge $Q' = Q(\epsilon_\infty - 1)/(\epsilon_\infty + 1)$ is reflected across the surface. The minus sign before Eq. (2a) indicates that this relaxation always diminishes the apparent binding energy (positive by convention) of the core electrons.

As written, Eqs. (2) exhibit unacceptable sensitivity to the parameter ρ . For typical insulators $\epsilon_\infty \approx 2$ and $R \approx 2$ eV so that ρ is on the order of the bond length between anion and cation. On this scale, the atomicity of the solid becomes important, and the continuum approximation in Eqs. (2) is invalid. A proper calculation must consider the local fields near the core hole which, in general, do not have the magnitude and direction of the macroscopic fields used in the continuum approximation. A further unwanted sensitivity in Eq. (2b) is on the effective position of the surface, which cannot for real insulators be exactly at the surface atomic sites. Furthermore, the validity of the image charge approximation is questionable when z is comparable to the lattice constant.

Far from the hole, however, the continuum approximation should be valid. This suggests a method first considered by Mott and Littleton,¹³ and recently reviewed for bulk crystals.¹⁴ We allow ρ to become much larger than the lattice constant, so that Eqs. (2) are valid for the relaxation energy of this "far" region. In the remaining "near" region, the method treats the i th ion as a point dipole with a polarizability α_i . The i th near dipole moment \mathbf{p}_i is calculated self-consistently as

$$\mathbf{p}_i = \alpha_i \mathbf{E}_{\text{loc},i} = \alpha_i \mathbf{E}_{\text{fixed},i} + \sum_{j \neq i} \vec{\mathbf{M}}_{ij} \cdot \mathbf{p}_j, \quad (3)$$

where $\mathbf{E}_{\text{loc},i}$ is the local field on the i th dipole, $\mathbf{E}_{\text{fixed},i}$ is the fixed field $\mathbf{E}_0 = Q\mathbf{r}/r^3$ from the core hole plus the field from the far dipoles (discussed below), and the summation represents the field from other near dipoles. The matrix $\vec{\mathbf{M}}_{ij}$ encodes the locations and polarizabilities of the near dipoles. From the dipole moments, the near relaxation energy

$$R_{r < \rho} = -\frac{1}{2} \sum_i \mathbf{E}_0 \cdot \mathbf{p}_i \quad (4)$$

may be easily computed. The total energy (far plus near) becomes the sum of Eqs. (2) ($r > \rho$) and (4) ($r < \rho$).

The far dipoles thus enter the computation in two ways. First, the fields of these dipoles influence the orientation of the near dipoles; this effect is negligible for large ρ . Second, the relaxation of the far dipoles themselves is estimated using Eqs. (2). We repeat the calculation for a sequence of ρ values until the total energy (far plus near) converges. For further details refer to the paper by Wang,¹⁵ and to a future publication.¹⁶

For the surface calculation [Eq. (2b)], the effective position z_s of the atom closest to the surface is allowed to be a free parameter such that the computed energy is independent of ρ . Typically $z_s \approx 1.0 \pm 0.5$ Å; for sufficiently large ρ the corresponding uncertainty in R is only about $\pm 0.1\%$.

The relaxation energy within bulk insulators has been computed with the above method for solid Xe, NaCl, and CaF₂ (see Table I). For bulk Xe, the experimental data (discussed further below) from Chiang, Kaindl, and Mandel⁹ (CKM) of $R = -1.44 \pm 0.1$ eV is in excellent agreement with our calculated value of -1.37 ± 0.01 eV. The calculation is in far better agreement than previous estimates^{8,9} of $R = -1.83$ and -1.66 eV based on the continuum dielectric approximation in Eq. (2a). These estimates included arbitrary choices of $\rho \approx 2$ Å, while our calculation is free of this ambiguity. For bulk NaCl, we are in good agreement with calculations by Mahan²⁰ and by Wang.¹⁵

In Fig. 1 we show calculated results for Xe (111), NaCl (100) and CaF₂ (111) surface regions, where we plot extra-atomic relaxation energies relative to the bulk relaxations in Table I. The binding energy shows an apparent increase at the surface for all atoms due to the proximity of the nonpolarizable vacuum. In these calculations, we assumed bulklike positions, valences, and polarizabilities for the surface atoms; these assumptions are not always valid for ionic crystal surfaces. The latter two assumptions are coupled: a slight departure from rare-gas electronic configuration will greatly change the cation polarizability. This modifies the above results, in addition to introducing a new chemical shift and altering the Madelung energy. Our model can accommodate the removal of these restrictions; however, our purpose here is to illustrate the magnitude of the lowest-order contributions to the energy shifts.

The change in relaxation ΔR from the bulk to the surface, while confined in large part to the surface layers, penetrates somewhat into the crystals. The observed dependence of ΔR on the atom position is

$$\Delta R(z) = -Q^2(\epsilon_\infty - 1)/[4\epsilon_\infty(\epsilon_\infty + 1)(z - z_0)], \quad (5)$$

which, when $z_0 = 0$, is the same as predicted for a point charge in a continuous dielectric. The correction z_0 represents an effective distance of the sample surface above the highest atom and is related to the correction z_s discussed earlier. We have plotted Eq. (5) for comparison with the computed results in Fig. 1 where z_0 was picked by a least-squares fit to the computed points for Xe, NaCl, and CaF₂ ($z_0 = 2.0, 1.5,$ and 1.0 Å, respectively). For these materials, z_0 is roughly equal to half the bond length between the anion and cation, a rule that is useful

TABLE I. Parameters used and results for bulk extra-atomic relaxation calculations. d_0 is the nearest-neighbor distance, $\alpha(\pm)$ are the polarizabilities of the cation and anion, $R(\pm)$ are the computed relaxations (ignore the \pm signs for neutral Xe).

Insulator	d_0 (Å)	$\alpha(+)$ (Å ³)	$\alpha(-)$ (Å ³)	$R(+)$ (eV)	$R(-)$ (eV)
Xe	4.33	4.043 ^a		1.37	
NaCl	2.82	0.255 ^b	2.974 ^b	2.48	1.60
CaF ₂	2.36	0.979 ^c	0.759 ^c	2.24	2.19

^aSee Ref. 17.

^bSee Ref. 18.

^cSee Ref. 19.

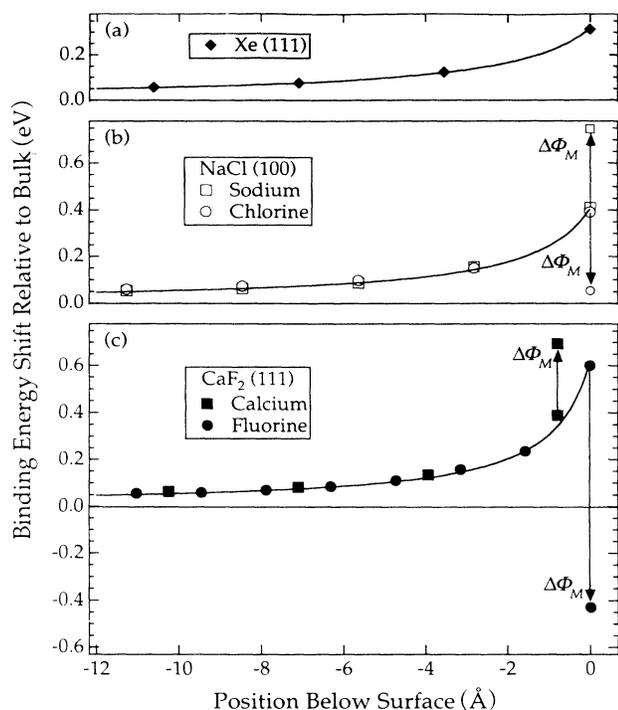


FIG. 1. Computed surface relaxation and Madelung shifts for (a) Xe (111), (b) NaCl (100), and (c) CaF₂ (111) surfaces. The curves are a simplified theory as described in the text. The arrows labeled $\Delta\Phi_M$ represent the contributions from the surface Madelung shifts, which are negligible for atoms other than those shown.

in estimating $\Delta R(z)$. The agreement between Eq. (5) and the full calculation shows that the image charge approximation has validity for surface charges.

The Madelung potential corrections $\Delta\Phi_M$ have also been shown for the surface layers in Fig. 1 (indicated by arrows) using the valences Na⁺, Cl⁻, Ca²⁺, and F⁻ (for other layers, $\Delta\Phi_M \lesssim 0.015$ eV). The directions of the Madelung shifts $\Delta\Phi_M$ are true for anions and cations in any ionic solid. We find relaxation will always act to enhance (diminish) surface core-level shifts for cations (anions) as predicted by the shift in Madelung potential alone. Near interfaces with a more polarizable medium, such as semiconductors or metals, this conclusion is reversed. In either case, the relaxation shifts ΔR significantly modify the predicted core-level shifts based on Madelung shifts $\Delta\Phi_M$ alone.

Model systems for these relaxation shifts are rare-gas solids, in which chemical and Madelung contributions are minimal.^{9,21} Experimental data supporting our surface computation may be found in the measurements of CKM,⁹ who report a surface-bulk energy shift $\Delta R = 0.26 \pm 0.04$ eV for Xe 4*d* core levels. Using the measured electron escape depth of 3.65 Å, a weighted average of the subsurface data of Fig. 1(a) yields $\Delta R = 0.22$ eV, which is in good agreement with experiment. CKM, who model their data with Eq. (5), find a slightly better agreement ($\Delta R = 0.25$ eV) with experiment. However, they have arbitrarily chosen the free parameter $z_0 = 1.8$ Å; only experimentally verifiable param-

eters have gone into our calculation.

For very thin films, the substrate induces both initial- and final-state changes. Consequently, we have modified our model to include a polarizable metallic or semiconducting substrate. Because it is inappropriate to apply a simple model of point-polarizable dipoles to these substrates, we model the substrates as continuous dielectrics with permittivity ϵ_s (for metals, we let $\epsilon_s \rightarrow \infty$). We consider the final state of the near region to consist of a core hole Q , an image charge $Q_s = -Q[(\epsilon_s - 1)/(\epsilon_s + 1)]$ located in the substrate, a set of near dipoles p_i in the film, and a corresponding set of image dipoles in the substrate. These image dipoles have a magnitude $|Q_s/Q|$ relative to their real counterparts, and a direction which is inverted parallel to the interface. The local field seen by the near dipoles in Eq. (3) is now modified to include the fields of all of the image dipoles as well as that of the image charge Q_s . In this thin-film geometry, the far dipoles contribute only about 0.2% of the total relaxation.

To compare to experimental data, we again turn to rare-gas multilayers grown on metallic substrates. In this system, there has been controversy over whether the substrate work-function shift is localized to the interface or is distributed over the overlaying layers. This question is equivalent to whether the initial-state or final-state factors dominate; the competing arguments are discussed by Jacobi.²¹ Our results discussed below fully support the final-state model, within experimental accuracy.

In Fig. 2 we show computed results for 1-, 2-, 3-, and 4-monolayer films of Xe on Pd(111), and we compare to the experimental data of CKM.⁹ We assumed a bulklike structure for the film, and fit to a Xe-to-image plane distance of 2.3 Å. For Xe on Al(111) (not shown), we find a best fit to data with a larger distance of 2.8 Å, which suggests that the surface electronic structure of Al(111) differs from that of Pd(111). From Fig. 2, we conclude that the final-state model accounts for the observed shifts beyond 1 monolayer. A discrepancy illustrated in Fig. 2 is that the experimentally observed shift is negligible between a monolayer and a monolayer covered by a second layer, while our theory predicts an enhanced binding energy of ≈ 0.2 eV for the uncovered monolayer. For data from Xe on Pd(100) and Al(111) (not shown),⁹ the agreement with experiment is somewhat better. While this

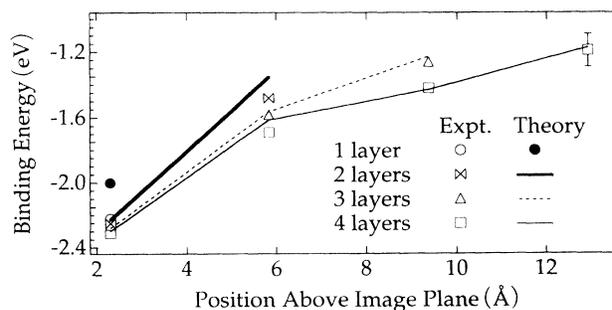


FIG. 2. Experimental (open symbols) and theoretical (● and lines) Xe 4*d* core-level shifts for Xe on Pd(111) relative to gas phase Xe. The error bar indicates the experimental uncertainty in locating the vacuum level.

discrepancy may be due to uncertainties in determining the vacuum level (± 0.1 eV), the single-monolayer value may also be accounted for if the Xe-Pd distance is contracted by 0.3 Å. This could happen if the Xe settles into hollow sites at submonolayer coverage, but is forced out when the layer becomes incommensurate.

To summarize, we have computed the surface and interface changes in extra-atomic relaxation due to the final-state-induced polarization in insulating films. We have shown that the image-charge approximation has validity in insulators even for surface charges. By testing our model in the case of a van der Waals insulator, we have shown the accuracy and usefulness of our calculation of binding-energy shifts due to this mechanism.

For ionic solids, we have shown that this relaxation change can be comparable to the surface Madelung potential previously identified as causing the major surface core-level shifts in such systems, and hence must be considered in interpreting core-level shifts. Moreover, if surface or interface ions have a different ionicity than those in the bulk, then the polarizability can be modified, hence further contributing to the relaxation change at surfaces and interfaces. This correction was not considered here,

but may be accommodated easily within our model. Other corrections not considered here are the initial-state lattice relaxation at surfaces and interfaces, and the possibility of strained layer films. These corrections will be considered at length in a future publication.¹⁶ Finally, these accurate calculations of interatomic contributions can be used in combination with experimental data to deduce the intra-atomic chemical shifts in surface and interface XPS.

Note added in proof. We have recently resolved surface, bulklike, and interface Ca and F atoms in thin films of CaF₂ grown on Si(111) substrates using a combination of XPS and x-ray photoelectron diffraction. This experiment and comparison with theory will be reported on in a future publication.¹⁶

We wish to thank J. D. Denlinger and G. Wong for useful discussions. E.R. was supported by the U.S. Department of Education. Work was supported by the National Science Foundation (Contract No. DMR-8657623) and by the Department of Energy (Contract No. DE-AC03-76SF00098).

¹W. F. Egelhoff, Surf. Sci. Rep. **6**, 253 (1987).

²R. E. Watson, J. W. Davenport, M. L. Perlman, and T. K. Sham, Phys. Rev. B **24**, 1791 (1981).

³W. Mönch, Solid State Commun. **58**, 215 (1986).

⁴V. Hinkel, L. Sorba, and K. Horn, Surf. Sci. **194**, 597 (1988).

⁵P. A. Schultz and R. P. Messmer, Surf. Sci. **209**, 229 (1989).

⁶R. Courths, J. Noffke, H. Wern, and R. Heise, Phys. Rev. B **42**, 9127 (1990).

⁷R. Browning, M. A. Sobolewski, and C. R. Helms, Phys. Rev. B **38**, 13 407 (1988).

⁸F. J. Himpsel, N. Schwentner, and E. E. Koch, Phys. Status Solidi B **71**, 615 (1975).

⁹T. C. Chiang, G. Kaindl, and T. Mandel, Phys. Rev. B **33**, 695 (1986).

¹⁰P. H. Citrin and T. D. Thomas, J. Chem. Phys. **57**, 4446 (1972).

¹¹D. E. Parry, Surf. Sci. **49**, 433 (1975); **54**, 195 (1976).

¹²C. S. Fadley, S. B. M. Hagstrom, M. P. Klein, and D. A. Shir-

ley, J. Chem. Phys. **48**, 3779 (1968).

¹³N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

¹⁴S. E. Schnatterly and C. Tarrío, Rev. Mod. Phys. **64**, 619 (1992).

¹⁵J. C. Wang, Phys. Rev. B **22**, 2725 (1980).

¹⁶Eli Rotenberg, J. D. Denlinger, and M. A. Olmstead (unpublished).

¹⁷Consistent with $\epsilon_{\infty} = 2.25$, using the Clausius-Mossotti relation.

¹⁸J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

¹⁹C. R. A. Catlow, M. Dixon, and W. C. Mackrodt, in *Computer Simulation of Solids*, edited by C. R. A. Catlow and W. C. Mackrodt (Springer, Berlin, 1982), p. 133.

²⁰G. D. Mahan, Phys. Rev. B **21**, 4791 (1980).

²¹K. Jacobi, Phys. Rev. B **38**, 6291 (1988).