PHYSICAL REVIEW B VOLUME 22, NUMBER 8 15 OCTOBER 1980

Calculated transition-metal surface core-level binding-energy shifts

Anders Rosengren
Institute of Theoretical Physics, University of Stockholm, S-113 46 Stockholm, Sweden

Börje Johansson*
Institut für Theoretische Physik, ETH, Hönggerberg, CH-8093 Zürich, Switzerland

(Received 21 January 1980)

A theoretical treatment is given for the shifts in the core-level binding energies of surface atoms relative to bulk atoms. The theory which relates surface shifts to surface energies is applied to 5*d* elements. The calculated shifts show a strong dependence on the surface structure. The theory accounts in a simple way for the change of the sign of the shift through the series, and the quantitative agreement with recent experiments is good.

Due to the reduced coordination number, surface atoms experience a different potential than bulk atoms. Therefore, it was suggested earlier that core-electron binding energies should be different for surface and bulk atoms. However, it is only very recently that this expectation has been experimentally confirmed. At the present time, surface shifts have been observed in gold,[1] tungsten,[2] iridium, and tantalum[3] (all for the 4f core level). As pointed out in Ref. 3 these surface core-level shifts (SCS) give promise of becoming a most useful and simple "site-specific" tool in the study of transition-metal surfaces. Therefore, it is important that these shifts are understood theoretically. In this paper we present a theoretical treatment of the surface shifts for various surfaces of the 5d transition metals and compare with available experimental data. The surface shift for the Z element, $\Delta_c(Z)$, is in this treatment in a simple way related to the surface energy by $\Delta_c(Z) \simeq E_s(Z+1) - E_s(Z)$, where $E_s(Z)$ is the surface energy of the element of atomic number Z. The most important ingredients in the theory are the assumption of a fully screened final state and the $(Z+1)$ approximation for the screening valence charge distribution around the core ionized site. Thus this site is treated as a $(Z+1)$ impurity dissolved in the Z metal host. The energy involved for dissolving this metal impurity is almost negligible due to the small heat of solution between neighboring elements. This picture of the metallic screening of a core hole has recently been shown to very accurately account for the core-level binding-energy shift between the free and condensed atom for all metals in the periodic table.[4]

The dominating bonding in transition metals originates from the valence d electrons, which here will be described by means of the tight-binding approximation.[5,6] The total energy of the solid may then be obtained from the sum of the one-particle band energies, and the cohesive energy due to d-electron bonding may be written as

$$E_{\text{bond}}[N(Z)] = \int^{E_F(Z)} (E - C_Z) n_Z(E) dE , \qquad (1)$$

where Z is the atomic number, $N(Z)$ the number of d electrons, and $n_Z(E)$ is the density of states of the d electrons. The quantities $E_F(Z)$ and C_Z are the Fermi energy and the center of the d band, respectively.

The core-electron binding energy is referred to the Fermi level and will be denoted by $E_{c,F}$. This can then be identified with the energy required to excite the core electron to the Fermi level.[7] Therefore, for a metal of atomic number Z we can write for the bulk core-level excitation $E^B_{c,F}$,

$$E^B_{c,F} = E^f[(N-1) \text{ sites } Z \text{ atoms, one site } Z^* \text{ atom}] - E^i(\text{perfect metal}) , \qquad (2)$$

where Z^* is the core-excited bulk atom, E^f and E^i are the total final and initial energies, and N is the total number of atoms. From the picture of the fully screened core hole, E^f may be written as[8]

$$E^f = (N-1) \int^{E_F(Z)} (E - C_Z) n_Z(E) dE + E_{c\to d} + \int^{E_F(Z^*)} (E - C_{Z^*}) n_{Z^*}(E) dE + E^{\text{imp}}_{Z^*}(Z) . \qquad (3)$$

Here $E_{c\to d}$ is the excitation energy of the core electron c into the d level (which in the presence of the core hole has a center of gravity C_{Z^*}). The quantities $E_F(Z^*)$ and $n_{Z^*}(E)$ are the Fermi energy and density of states for a hypothetical metal composed of Z^* atoms and having $N(Z^*)$ d electrons. Finally, $E^{\text{imp}}_{Z^*}(Z)$ is the heat of solution of a metallic Z^* impurity in the Z metal. The valence-electron distribution for the Z^* metal can be accurately represented by that of the $(Z+1)$ metal.[4] Thus in the last two terms in Eq. (3) Z^* can be replaced by $(Z+1)$. Since the heat of solution between neighboring transition metals is known to be small[9, 10] the last term can to a first-order approximation be neglected in comparison with the other terms. Thus we obtain

$$\begin{aligned} E^B_{c,F} &\simeq \int^{E_F(Z+1)} (E - C_{Z+1}) n_{Z+1}(E)\, dE \\ &\quad - \int^{E_F(Z)} (E - C_Z) n_Z(E)\, dE + E_{c\to d} \\ &= -E^B_{\mathrm{coh}}(Z+1) + E^B_{\mathrm{coh}}(Z) + E_{c\to d}\,, \end{aligned} \tag{4}$$

where E^B_{coh} is the bulk cohesive energy (assumed dominated by the d electrons).[11] The same arguments can be repeated for a surface atom and thereby we obtain for the surface core-level excitation energy $E^S_{c,F}$,

$$E^S_{c,F} \simeq -E^S_{\mathrm{coh}}(Z+1) + E^S_{\mathrm{coh}}(Z) + E_{c\to d}\,, \tag{5}$$

where E^S_{coh} is the surface cohesive energy, i.e., the energy gained when a free atom is adsorbed at the surface (while the surface area is increased by one atomic surface area unit). Thus the surface core-level shift Δ_c may be written as

$$\begin{aligned} \Delta_c(Z) &= E^S_{c,F} - E^B_{c,F} \\ &= E^B_{\mathrm{coh}}(Z+1) - E^S_{\mathrm{coh}}(Z+1) \\ &\quad - [E^B_{\mathrm{coh}}(Z) - E^S_{\mathrm{coh}}(Z)] \\ &= E_S(Z+1) - E_S(Z)\,, \end{aligned} \tag{6}$$

where E_S is the surface energy. Since the surface energy is known to vary parabolically through a transition series we immediately realize that Eq. (6) predicts an increased surface-atom core-level binding energy for the earlier transition elements, while the shift will be of the opposite sign for the heavier elements. This difference was first pointed out in Ref. 12. The reason for this behavior can be traced back to the fact that for the earlier transition elements the screening takes place in the bonding part of the d band, while for the heavier elements antibonding states are utilized.[4] This shift in sign has also been discussed in somewhat different terms in Ref. 13.

The variation of energy per surface atom when cleaving the crystal is given by[14]

$$\begin{aligned} E_S(Z) &= \int^{E_F(Z)} E \sum_i \Delta n_i(E, u_0)\, dE - Z_M u_0 \\ &\quad - \tfrac{1}{2}(Z_S - Z_M) u_0\,, \end{aligned} \tag{7}$$

where u_0 is the surface perturbing potential due to the charge rearrangement at the surface, $\Delta n_i(E,u_0)$ is the variation of the local density of states on the ith plane, and Z_M and Z_S are, respectively, the number of d electrons per atom in the bulk and on the surface. This expression has been used by Desjonquères and Cyrot-Lackmann to calculate the variation of the anisotropy of the surface tension of transition metals with the bandfilling $N(Z)$.[15, 16] As can be seen from Eq. (6) these results can be directly used for the present study of surface core-level shifts. Desjonquères and Cyrot-Lackmann present their results in the form $\gamma a^2/W$, where γ is the surface tension, a is the lattice parameter, and W the bandwidth. From a knowledge of the bandwidth the surface energy E_S for a given bandfilling is then easily deduced. We will here employ the bandfillings and bandwidths recently calculated by Glötzel and Andersen.[17] These are the results of self-consistent, hybridized, semirelativistic local-density linear muffin-tin orbitals (LMTO) calculations. If the so-derived values of E_S for the $5d$ transition metals are used in Eq. (6), the surface core-level shifts presented in Fig. 1 are obtained. We note the strong dependence of the surface core-level shift on the plane of cleavage, especially for the bcc structure. Thus the core-level binding energy for a surface atom is very sensitive to the geometrical arrangement of neighboring atoms. The agreement, seen in Fig. 1, with currently available experiments is satisfying. For tantalum the experiments were made on a polycrystalline sample, but its surface should, however, be dominated by

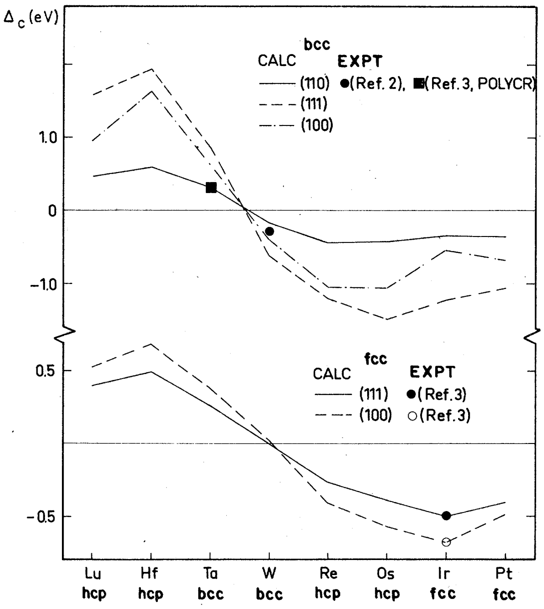

FIG. 1. Calculated and experimental shifts, Δ_c, in the core-level binding energies of surface atoms relative to bulk atoms for the $5d$ transition metals. Note the different scales used for the bcc and fcc structures. For the hcp phase, the calculation performed for the fcc (111) surface should be a good approximation for the hcp (0001) surface.

the most dense plane.

The good agreement found between theory and experiment requires some explanation of the accuracy of the approximations used and the calculations performed. Let us start by noting that Eq. (6) could be derived without reference to the tight-binding approximation,[4] but since we employ tight-binding calculations for the surface energies we have preferred to give the presentation within this scheme. In fact Eq. (6) is, except for leaving out the impurity terms and except for using the $(Z+1)$ approximation, exact for a thermal-excitation process. The actual photoionization process is, however, vertical, but since the atomic volume of the Z and $(Z+1)$ metals does not differ very much, the difference between the thermal and vertical excitations will be small. Since the core-level shifts have been identified for the $4f$ level it is appropriate to compare with the $4f$ excitations in the rare-earth metals, where the thermal treatment has been shown to very accurately account for the experimental binding energies.[18] The use of the $(Z+1)$ approximation is discussed in Ref. 4, where it is concluded that it does not introduce any appreciable error. Let us now justify our omission of the impurity terms in the actual calculation of the curves in Fig. 1. The term $E_{Z+1}^{\text{imp}}(Z)$ could in principle be obtained from thermochemical measurements, but to get at its surface counterpart $E_{Z+1}^{\text{imp,surf}}(Z)$, which has been left out of Eq. (5), is more difficult. However, since[19] $E_S = E_{\text{coh}}^B - E_{\text{coh}}^S \simeq 0.2 E_{\text{coh}}^B$ (for a dense surface), the same ratio should be rather appropriate to what is omitted from Eq. (6), i.e., $E_{Z+1}^{\text{imp}}(Z) - E_{Z+1}^{\text{imp,surf}}(Z) \simeq 0.2 E_{Z+1}^{\text{imp}}(Z)$, which in general is smaller than 0.05 eV.[9,10] From Fig. 1 we notice that this impurity contribution is small compared to the other contributions to the shift. It is gratifying that computations with Eq. (6) involve the difference between two surface energies. As is obvious from Ref. 15 the calculated surface tensions are somewhat questionable on an absolute scale since they would be zero for an empty or completely filled d band. However, since the tight-binding description leaves out the s electrons, and these could be assumed to give an approximately constant contribution to the surface energy,[20] the *differences* in surface energies should be more accurate. Still the main uncertainty in the present treatment is due to the calculated surface energies and most likely this uncertainty is larger than the magnitude of the impurity contribution left out of Eq. (6).

In summary we would like to stress that the pronounced dependence which has been found for the surface core-level shifts on the geometry is certainly promising for the future application of the SCS to detailed surface studies. Also, as pointed out in Ref. 4, the present picture of the surface core-level shift corresponds directly to the heat of segregation of a $(Z+1)$ substitutional impurity in the Z metal.[21] Thus a negative shift shows that a $(Z+1)$ impurity will segregate to the surface.[22] The classical example is the enrichment of Cu at the surface of NiCu alloys.[23] This agrees with the negative SCS expected for pure nickel. Since the SCS strongly depends on the surface plane the surface segregation should show a corresponding anisotropic behavior, an effect which should be most pronounced for bcc metals (compare Fig. 1). Thus measurements of surface core-level shifts can provide important and accurate parameters for the theory of surface segregation. We also want to stress that the formula in Eq. (6) relates surface core-level shifts to surface energies. Different techniques of measuring and extrapolating the surface energy very often give scattered or contradictory results. It might be that measurements of surface core-level shifts could be used to give increased insight to this technologically important quantity.

We would like to thank Professor F. Cyrot-Lackmann and Dr. M. C. Desjonquères for reprints and discussions, Professor O. K. Andersen and Dr. D. Glötzel for discussion and allowing us to use results of their calculations prior to publication, and Professor D. E. Eastman for making Ref. 3 available to us. This research has been supported in part by the Swedish National Science Research Council.

---

*On leave of absence from the Department of Physics, FOA He2, S-104 50 Stockholm, Sweden.

[1] P. H. Citrin, G. K. Wertheim, and Y. Baer, Phys. Rev. Lett. 41, 1425 (1978).

[2] T. M. Duc, C. Guillot, Y. Lassailly, J. Lecante, Y. Jugnet, and J. C. Vedrine, Phys. Rev. Lett. 43, 789 (1979).

[3] J. F. van der Veen, F. J. Himpsel, and D. E. Eastman, Phys. Rev. Lett. 44, 189 (1980).

[4] B. Johansson and N. Mårtensson, Phys. Rev. B 21, 4427 (1980).

[5] J. Friedel, in *The Physics of Metals*, edited by J. Ziman (Cambridge University Press, London, 1969), Chap. 8.

[6] D. G. Pettifor, J. Phys. F 7, 613 (1977).

[7] This is more fully discussed in Ref. 4.

[8] Compare D. G. Pettifor, Phys. Rev. Lett. 42, 846 (1979).

[9] O. Kubaschewski, E. L. Evans and C. B. Alcock, *Metallurgical Thermochemistry* (Pergamon, London, 1967), 4th ed.

[10] A. R. Miedema, J. Less-Common Met. **46**, 67 (1976).

[11] The results in Eqs. (4) and (5) are more general than the present derivation within the tight-binding approximation might indicate (Ref. 4).

[12] B. Johansson, Phys. Rev. B **19**, 6615 (1979).

[13] P. J. Feibelman, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. B **20**, 1433 (1979).

[14] G. Allan, J. Phys. (Paris) **31**, C1 67 (1970).

[15] M. C. Desjonquères and F. Cyrot-Lackmann, Surf. Sci. **50**, 257 (1975).

[16] M. C. Desjonquères and F. Cyrot-Lackmann, J. Phys. F **5**, 1368 (1975).

[17] D. Glötzel and O. K. Andersen (unpublished).

[18] B. Johansson, Phys. Rev. B **20**, 1315 (1979).

[19] B. C. Allen, in *Liquid Metals Chemistry and Physics*, edited by S. Z. Beer (Dekker, New York, 1972), p. 161.

[20] J. Friedel and C. M. Sayers, J. Phys. (Paris) **38**, 697 (1977).

[21] Within the present picture the only difference is that the heat of segregation would correspond to the surface shift of the *thermal* core-electron excitation while experimentally the shift of the *vertical* excitation is observed.

[22] F. L. Williams and D. Nason, Surf. Sci. **45**, 377 (1974).

[23] Y. S. Ng, T. T. Tsong, and S. B. McLane, Jr., Phys. Rev. Lett. **42**, 588 (1979).