PHYSICAL REVIEW B VOLUME 19, NUMBER 12 15 JUNE 1979

Valence state at the surface of rare-earth metals

Börje Johansson
Sekt 214, Försvarets Forskningsanstalt, S-104 50 Stockholm 80, Sweden
(Received 8 December 1978)

The valence state of a rare-earth metal surface is investigated by using general properties of the surface tension of metals. Thereby it is concluded that samarium is likely to have a divalent or partly divalent surface on top of its trivalent bulk phase, which agrees with recent spectroscopic observations. Also californium metal is discussed from this point of view. Finally, the position of the $4f$ level in a bulk gold atom as compared to its position in a surface gold atom is briefly discussed.

From high-resolution x-ray photoemission spectra (XPS) of metallic samarium it was concluded that either the bulk or surface of samarium could very well be in an intermediate valence state.[1] However, since the trivalent metallic state of samarium is favored relative to the (hypothetical) divalent metallic state of samarium by about 6 kcal/mol and since the bulk properties of samarium fit nicely to the other trivalent rare-earth metals as well as to intra-rare-earth alloys,[2] the bulk interpretation seemed rather unlikely. Instead it was conjectured by the present author[3] that the conditions at the *surface* might be such that the divalent state is more favored there than it is in the bulk. This conjecture has now been confirmed in new XPS measurements on samarium by Wertheim and Crecelius.[4] In these experiments the XPS data were studied as a function of the takeoff angle. From the observed angular dependence it could be concluded that the divalent component of the spectrum originates from atoms in the surface layer. By employing a most-surface-sensitive photoelectron-spectroscopy technique Allen *et al.*[5] have arrived at the same conclusion in a somewhat more direct way. In this comment we will show that this finding is consistent with general cohesive properties of metal surfaces.

A characteristic feature of a surface is the incomplete atomic coordination which gives rise to a surface-tension force perpendicular to the surface. The surface tension γ_L has been experimentally determined for a substantial part of the elemental metals in their liquid phase (for a review, see Ref. 6). Further, in many cases, its temperature dependence has also been measured. These data extrapolated to lower temperatures, provide estimates of γ for elemental solids. The surface tension is numerically related to the Helmholtz surface free energy F^s as

$$\gamma = F^s/A , \tag{1}$$

where A is the surface area. In the theoretical treatment Skapski[7,8] found it more convenient to discuss the *molar surface tensions*, i.e., the values referred to a surface occupied (in a monoatomic layer) by 1 mol of atoms. The molar surface tension γ_M is thus defined by $\gamma_M = A_{\mathrm{mol}}\gamma$, where A_{mol} is the surface area of 1 mol of atoms. By using a nearest-neighbor broken-atomic-bond model, Skapski derived for a closed-packed metal, that at zero temperature the *molar* surface energy U_M^S can be related to the cohesive energy E_{coh} as

$$U_M^S \simeq 0.25 E_{\mathrm{coh}} . \tag{2}$$

To arrive at this relation Skapski made the simplifying assumption that the bond energies of surface and bulk atoms are equal. Evans[9] has criticized the main initial assumption, namely, that the total energy of the metal is due to pair wise bonds between the atoms. However, for our present purpose, it is more important that *empirically* the expression given above has been found to hold with a quite reasonable degree of accuracy, and it is in this sense we will employ relation (2). In doing this we will use the coefficient 0.20 rather than 0.25 in Eq. (2), since this has been found to better account for the known experimental data.[6,10] Thus we may give the following picture: It takes about $0.20E_{\mathrm{coh}}$ to bring a metal atom from the bulk solid to the surface (while enlarging the surface area), and then it costs another 0.80 E_{coh} to remove the atom from the surface to infinity.

For a trivalent rare-earth metal the cohesive energy is about 103 kcal/mol relative to the proper trivalent atomic state.[11,12] For a divalent metal such as (hypothetical) divalent samarium the cohesive energy relative to the divalent atomic configuration is 43 kcal/mol.[11,13,14] However, the measured cohesive energy for samarium is 49.3 kcal/mol. Since the atomic configuration of samarium is divalent, f^6s^2, this experimental value tells us first that metallic samarium is trivalent and second that the energy difference between the (hypothetical) divalent metallic samarium and the trivalent metallic state, $\Delta H_{\mathrm{II,III}}$, is $43-49=-6$ kcal/mol. Thus 6 kcal/mol is the energy margin by which samarium in the bulk phase maintains its trivalent character.

From the observed empirical relation for the molar surface energy $U_M^S = 0.20E_{\mathrm{coh}}$, we can state that by taking a bulk atom in trivalent samarium and bringing it to the surface (and thereby enlarging the surface as well as keeping the atom in the trivalent state) we lose the energy $0.20\times103 \simeq 21$ kcal/mol. Similarly, the same process in hypothetical divalent samarium or in europium will cost about $0.20\times43 \simeq 9$ kcal/mol. Thus in a relative sense we "gain" energy in the divalent case as compared to the trivalent one, the gain being about $21-9=12$ kcal/mol. If we compare this gain with the energy margin by which samarium is a trivalent metal, we note that the gain is certainly large enough to convert the surface atoms of samarium into the divalent state. However, it is true that a divalent surface on a trivalent bulk material is not directly comparable to the situations from which we derived the molar surface energy. From the experimental fact that europium has a most limited solubility in the trivalent rare earths, it seems likely that there will be some energy loss involved when bringing a divalent atom from a divalent metallic host into a trivalent host. This would mean that the energy gain of 12 kcal/mol, as derived above, is likely to be somewhat reduced for the actual situation of having a divalent layer on top of a trivalent bulk material. From their experimental results, Wertheim and Crecelius[4] concluded that the valence state at the surface was of an intermediate type, the formal valency being about 2.6. This would indicate that the energy actually gained in having a divalent surface is close to 6 kcal/mol. From our numbers above this is not unrealistic. Still, as pointed out by Wertheim and Crecelius[4] the experimental result may also be interpreted as if the surface is totally divalent but that due to the surface roughness the orientation of the surface may vary somewhat from one small region to another thereby invalidating the analysis which gave rise to the intermediate valence-state interpretation. However, the experiments by Allen *et al.*[6] also point towards a mixed valence at the surface. Although it is somewhat less likely that their results could also be due to surface roughness, it still cannot be totally ruled out. On this point we cannot give any firm statement with our approach. From recent bremsstrahlung isochromat spectroscopy measurements the position of the unoccupied $4f$ level (corresponding to the divalent state) in samarium was found to be 0.65 eV (15 kcal/mol) above the Fermi energy.[15] If we interpret this experiment as actually creating a divalent samarium atom in a trivalent host, we find that the solution energy of a divalent samarium impurity in trivalent samarium is $15-6=9$ kcal/mol (see Ref. 16; note its positive value). By applying Miedema's semiempirical scheme[17] to this situation a similar value is obtained. At the surface the corresponding solution energy would be somewhat reduced, and by applying the same kind of arguments as those used in Eq. (2) we can estimate the "surface solution energy" to be about $0.8\times9 \simeq 7$ kcal/mol. Thus the above "energy gain" at the surface of about 12 kcal/mol is actually reduced to about $12-7=5$ kcal/mol when we account for the "impurity effect." However, this gain is just about equal to the energy required to transform trivalent samarium into a divalent metallic state. Admittedly, the derivation of the impurity effect is somewhat crude, but at least it serves to illustrate that the conditions at the surface of metallic samarium actually are such that a mixed valence state is not at all unlikely.

How about the surface state of the other rare-earth metals? For all of them we know very accurately the energy difference between the divalent and trivalent bulk state.[2,14,18] In Fig. 1 we plot these numbers against the "energy gain" 12 kcal/mol (for clarity we disregard the impurity effect here). As can be immediately noted, the surface layer will remain trivalent for all the trivalent rare-earth metals except samarium. Not even in thulium could there be a divalent surface. This is confirmed by the experimental results on thulium obtained by Allen *et al.*[6] If instead of considering a surface we consider atoms at a perfect edge of a single crystal, it seems reasonable that the molar edge energy should be something like $U_M^{\mathrm{edge}} = (1-2\times0.20)E_{\mathrm{coh}}$. The reason for the factor of 2 is that at the edge two planes meet instead of just one as in the case of a surface. The "energy gain" would in this situation be about $2\times12=24$ kcal/mol (again disregarding the impurity problem). From Fig. 1 we notice that in this case thulium might show a valence change although probably it will not. Finally for a "corner atom" the same "energy gain" would be about $3\times12=36$ kcal/mol. From Fig. 1 we now find that several of the rare-earth metals might show divalent behavior at the corners of a single crystal. Naturally, these critical energy numbers (24 and 36 kcal/mol, respectively) should not be taken too literally, but rather they represent a trend. In an earlier work[19] we discussed the valency of the rare-earth metals in the liquid phase not too far away from the critical point. A similar discussion for the surface state at high temperatures could be given, but since detailed experimental

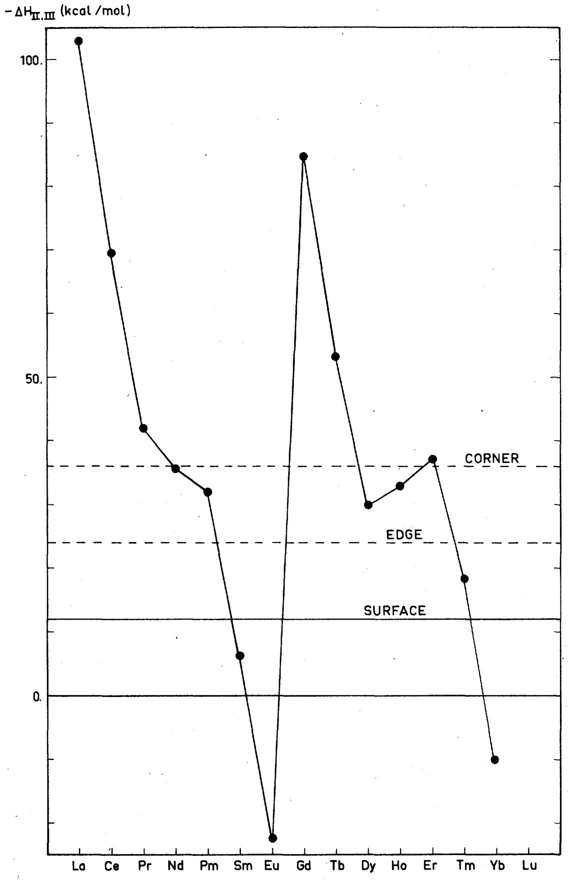

FIG. 1. Energy difference $\Delta H_{\mathrm{II,III}}$, between divalent and trivalent rare-earth metals. For those elements where $-\Delta H_{\mathrm{II,III}}$ falls below the critical line labeled "surface," the surface state will be divalent. The critical values for divalent edges and corners are also indicated.

surface studies under such conditions presently seems too difficult we just mention this here as a future possibility to experimentally realize divalent rare-earth surfaces.

For the heavier actinide metals it has in recent years become increasingly clear that they behave like the rare-earth elements. Therefore it is just as meaningful to discuss them in terms of valency as it is for the lanthanides. Recent experimental crystallographic work by Noé and Peterson[20] indicated that californium might be a mixed-valence metal. That this is not unreasonable could also be derived from the relevant atomic spectroscopic levels for californium[21] (i.e., the $5f^9 6d7s^2$ level relative to the ground state $5f^{10}7s^2$). However, a recent experimental determination of the heat of sublimation of californium made by Ward *et al.*[22] gave $\Delta H^0_{298} = -46.9$ kcal/mol. This value certainly indicates that californium is a good trivalent metal and casts serious doubts on the validity of the observations of a bulk intermediate valence state by Noé and Peterson. This is especially so since the experiment by Ward *et al.* was performed on a 2-mg sample, while Noé and Peterson used much smaller samples (weighing less than 10 μg). However, undoubtedly the divalent metallic state of californium will be quite close in energy to the trivalent state. Therefore, as is clear from the discussion given above for samarium, it is quite likely that the surface layer of californium is divalent. This means that even for thin films it cannot be excluded that californium will be divalent. In the x-ray powder diffraction study by Noé and Peterson a lot of surface area might have been scanned. Thus, their observations of a purely divalent, a purely trivalent as well as of a mixed-valence state might to a large extent orginate from surface properties of californium. The apparent contradiction between the experiment by Ward *et al.* on the one hand and the experiments by Noé and Peterson on the other, could then find its explanation in that Ward *et al.* were investigating a truly bulk sample, while Noé and Peterson were working on a microscale. Since experiments on californium necessarily must be performed on small samples, this indicates that caution must be taken so that real bulk properties are being studied.

For those rare-earth metals which remain trivalent up to the last surface layer, the $4f$ electron of the surface atoms will be somewhat more bound than for the bulk atoms, the increase could very well be as large as 8–9 kcal/mol (0.3–0.4 eV). This shift should be observable in XPS measurements, at least if the relaxation processes are as effective at the surface as they are in the bulk. The position of the unoccupied f levels will decrease somewhat for surface atoms as compared to bulk atoms.

Recently, it has been demonstrated that samarium monoxide can be prepared as a bulk material.[23] From the measured lattice constant it was concluded that SmO is in an intermediate-valence state. Thus it could be that the experimental samarium XPS-results are due to an oxidized surface, mainly of the SmO type. The present study cannot of course exclude this possibility, but on the other hand the given analysis shows that a divalent component at the surface layer of pure samarium metal is quite likely. An even more likely contamination than oxygen at the surface is hydrogen. In fact even under quite good vacuum conditions a formation of a dihydride has been observed at the surface of rare-earth metals.[24] However, since there are reasons to believe that a trivalent (metallic) rare-earth dihydride is more stable in its trivalent state relative to the divalent state than is the pure metal itself,[25] it seems unlikely that the observation of divalent samarium at the surface could be due to a dihydride. On the contrary, it might be that the presence of some hydrogen at the surface *prevents* an observation of a totally divalent surface layer in samarium. Interesting future experiments would be direct experimental determinations of the surface tension of liquid samarium as well as for europium and gadolinium. The latter two metals would be of value in order to establish the behavior of a normal divalent and a normal trivalent rare-earth metal, respectively.

As pointed out by Wertheim *et al.*[26] the surface valence of rare-earth systems may be anticipated to be lower (or rather have a tendency to be lower) than that of the bulk. This is consistent with the picture given in this work. A trivalent rare-earth atom always forms stronger bonds than a divalent atom. Therefore the loss of bonding in forming a surface will always be larger for the trivalent case than for the divalent one and thus the lower valence will become somewhat favored at the surface. This means that experimental results, obtained from a surface-sensitive technique such as XPS, must be carefully analyzed before a specific structure of the spectrum can be said to originate from the bulk or the surface, respectively.

As a side remark, we want to comment on some very recent XPS results on gold obtained by Citrin *et al.*[27] It was found that a $4f$ electron is more bound in a bulk atom than in a surface atom, the measured difference being 0.40 eV. Before we discuss this experimental result, we consider the excitation of a $4f$ electron to the Fermi energy in bulk metallic gold. This process can be decomposed into two steps: first we excite the Au $\cdots 4f^{14}\cdots 6s$ atom into Au* $\cdots f^{13}\cdots 6s^2$, and then we dissolve this Au* atom in the Au host. The Au* atom will have chemical properties which are almost identical to those of a mercury atom. Thus the final state is close to that of having a mercury atom dissolved in gold (assuming a reasonable lifetime of the f^{13} state). The same picture is then applied for the excitation of a $4f$ electron from a surface gold atom to the Fermi energy. To derive the change in the position of the $4f$ level when comparing a bulk and a surface gold atom, we can then apply the same arguments as above for samarium, namely, that it will be 0.2 times the cohesive energy difference between gold and mercury. (The "impurity effect" should be relatively small here.) However, since the surface tensions are known experimentally for gold and mercury, it is preferable that we use these data instead of the approximative relation, Eq. (2). Doing this we find that a $4f$ electron is more bound in a bulk gold atom than in a surface gold atom by about 0.6 eV. If we now apply the "complete screening picture"[28] for the XPS experiments, namely, by assuming that the final state after the $4f$ photoionization is a charge-neutral site, then the reasoning above for the position of the $4f$ level should be applicable to the experimental situation. The rather small disagreement with the measured shift could originate from slightly different relaxation properties in the bulk as compared to the surface or some small "impurity effect." Citrin *et al.*[27] also investigated the shift of the $2p$ and $3d$ levels when located at bulk and surface atoms in Cu and Ag, respectively, and found smaller shifts than for the $4f$ level in Au. Applying the same scheme as above for these two cases we obtain shifts which are about 40% (Cu $2p$) and 25% (Ag $3d$) of that of the $4f$ level in Au. These results seem to map the experimental results reasonably well.

Finally, we would like to comment that the $4f$ surface shift in gold is opposite in sign to that of the $4f$ shift for the rare-earth metals. (That the $4f$ level is more bound at the surface than in the bulk for the rare earths is demonstrated by the divalent component at the surface of samarium.) When a $4f$ electron is excited to the Fermi energy for the rare earths, the valence is increased by one and therefore we *gain* metallic bonding [compare for example the cohesive energies of divalent ($2A$), trivalent ($3A$), and tetravalent ($4A$) metals]. However, for gold, when exciting a $4f$ electron to the Fermi energy, a "mercury" atom is created, and thereby, although the valence state is increased, we *lose* metallic bonding (compare the cohesive energies of the $1B$ and $2B$ metals). Then at the surface of the rare earths, due to incomplete atomic coordination, the gain in metallic bonding will be less than in the bulk, and therefore the $4f$ electron becomes more bound at the surface than in the bulk. In contrast to this, for gold, the loss of metallic bonding is less at the surface than in the bulk, and therefore the $4f$ electron will be less bound at the surface.

ACKNOWLEDGMENTS

Discussions with Dr. R. Evans, Dr. J. R. Peterson, and Dr. J. W. Ward are gratefully acknowledged.

[1] G. K. Wertheim and M. Campagna, Chem. Phys. Lett. 47, 182 (1977).

[2] B. Johansson and A. Rosengren, Phys. Rev. B 11, 2836 (1975).

[3] B. Johansson, Inst. Phys. Conf. Ser. No. 37, Chap. 3, p. 39 (1978).

[4] G. K. Wertheim and G. Crecelius, Phys. Rev. Lett. 40, 813 (1978).

[5] J. W. Allen, L. I. Johansson, R. S. Bauer, I. Lindau, and S. B. M. Hagström, Phys. Rev. Lett. 41, 1499 (1978).

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

[7] A. S. Skapski, J. Chem. Phys. 16, 389 (1948).

[8] A. S. Skapski, Acta Metall. 4, 576 (1956).

[9] R. Evans, J. Phys. C 7, 2808 (1974).

[10] A. A. Lucas, in *Collective Properties of Physical Systems* edited by B. Lundqvist, S. Lundqvist, and V. Runnström-Reio (Academic, New York, 1973), p. 169.

[11] L. Brewer, LBL Report No. 3720, 1975 (unpublished).

[12] B. Johansson (unpublished).

[13] L. J. Nugent, J. L. Burnett, and L. R. Morss, J. Chem. Thermodyn. 5, 665 (1973).

[14] B. Johansson and A. Rosengren, Phys. Rev. B 11, 1367 (1975).

[15] J. K. Lang, Y. Baer, and P. A. Cox, Phys. Rev. Lett. 42, 74 (1979).

[16] The term, 6 kcal/mol, is the energy required to form the divalent metallic state. The energy beyond this value then corresponds to the solution energy of divalent samarium in the trivalent host.

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

[18] B. Johansson (unpublished).

[19] B. Johansson, J. Phys. F 5, 1241 (1975).

[20] M. Noé and J. R. Peterson, in *Transplutonium Elements*, edited by W. Müller and R. Lindner (North-Holland, Amsterdam, 1976), p. 69.

[21] B. Johansson, in *Proceedings of the Second International Conference on the Electronic Structure of the Actinides* edited by J. Mulak, W. Suski, and R. Troć (Polish Academy of Science, Wroclaw, 1977), p. 49.

[22] J. W. Ward, P. D. Kleinschmidt, and R. G. Haire, J. Phys. (Paris) C4, 233 (1979).

[23] J. M. Leger (to be published).

[24] A. E. Curzon and O. Singh, J. Phys. F 8, 1619 (1978).

[25] B. Johansson (unpublished).

[26] G. K. Wertheim, J. H. Wernick, and G. Crecelius, Phys. Rev. B 18, 875 (1978).

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

[28] J. F. Herbst, R. E. Watson, and J. W. Wilkins, Phys. Rev. B 13, 1439 (1976).