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Mixed valence of Sm on metal single-crystal surfaces

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Results of a photoemission study of Sm on a Cu(100) single-crystal surface are reported. From the binding energy of the Sm $4f$ levels it is concluded that the mixed valence of Sm on Cu(100) is of a heterogeneous nature. It is suggested that this conclusion also applies to Al(111) and Al(100).

Questions of the surface valency and surface valence transitions of lanthanide metals and intermetallic compounds have been addressed by a number of studies using photoemission. In an early study,[1] it was concluded that either the bulk or the surface of Sm could very well be in a homogeneous mixed-valence state. Later studies[2-6] have demonstrated that the mixed valence is of a heterogeneous nature, that is the bulk Sm is trivalent ($4f^5$) and the surface divalent ($4f^6$) as suggested by Johansson.[7] Surface valence transitions from a trivalent bulk to a divalent surface have been observed in a number of trivalent lanthanide intermetallic compounds such as $YbAu_2$ (Ref. 8), $SmAl_2$ (Refs. 9 and 10), $YbPd_3$ (Ref. 11), $EuPd_3$, and $EuPd_5$ (Ref. 12). It has been demonstrated that the surfaces of several homogeneous mixed divalent-trivalent compounds such as SmB_6 (Ref. 4), $YbAl_2$ (Ref. 13), and YbPd (Ref. 11) are divalent. Several studies[14-17] of thin layers of Yb evaporated onto single-crystal surfaces of Al and Ni showed that the Yb atoms at the surface were divalent, whereas the Yb atoms that had diffused into the bulk of the sample became trivalent[15-17] or had homogeneous mixed valency.[14] In all of these systems the mixed valence has a heterogeneous nature apart from in the bulk of the homogeneous mixed-valence compounds.

In a recent series of papers by Fäldt and Myers,[18-21] it has been claimed that thin layers of Sm on single-crystal surfaces of Cu and Al exhibit homogeneous mixed valence. In this Rapid Communication we report the results of a photoemission study of the $4f$ Sm levels of thin Sm layers on Cu(100) single crystals, which prove that the mixed valence of Sm on Cu(100) is heterogeneous.

Before describing our experimental results we briefly address the use of photoemission techniques for determining the valence state of Sm deposited on metal surfaces. Fäldt and Myers[18-21] made use of the fact that the binding energy of the Sm $3d$ core levels shifts by about 10 eV when going from the divalent to the trivalent state. The ratio between these two peaks was then used for assessing the valence. The claim that the mixed valence of the surface layer was homogeneous and not heterogeneous was based entirely on interpretation of the low-energy electron-diffraction (LEED) patterns that formed and on the assumption that the Sm stayed at the surface and did not alloy. In our opinion, the question whether homogeneous or heterogeneous mixed valence occur cannot be settled by such an analysis of the $3d$ Sm levels and the LEED patterns, unless angle-resolved measurements of the $3d$ emission are performed.[2] When using the method of Refs. 18-21, the homogeneity of the mixed valence has to be based on geometrical information obtained from other methods, and such unambiguous information is, in general, rather hard to obtain. A more direct way of investigating the possibility of homogeneous mixed valence is to perform a photoemission study of the $4f$ core levels of the lanthanide. The basic requirement for observing mixed valence is, of course, that emission features from both di- and trivalent Sm are seen. In order for the mixed valence of a layer of Sm to be homogeneous the energy separation per Sm atom $\Delta E_{\mathrm{II,III}}$ between the divalent and the trivalent state of the whole Sm layer has to be close to zero. It has been shown[22,23] that the energy difference is related to the measured binding energy (referred to the Fermi level) E_B of the divalent multiplet term closest to the Fermi level by

$$\Delta E_{\mathrm{II,II}} = E_B - E_{\mathrm{III}}^{\mathrm{imp}} , \tag{1}$$

where $E_{\mathrm{III}}^{\mathrm{imp}}$ is the solution energy of a trivalent Sm atom, that has not geometrically relaxed from its divalent size, in the unperturbed Sm layer.

Clearly, the impurity term $E_{\mathrm{III}}^{\mathrm{imp}}$ has to be estimated before using Eq. (1) for evaluating the possibility of homogeneous mixed valence. It has been shown[23] that in the bulk of a divalent lanthanide metal the impurity term $E_{\mathrm{III}}^{\mathrm{imp}}$ is smaller than ~0.5 eV. At the surface this value is expected to be reduced to $\alpha \times 0.5$ eV where $\alpha \sim 0.7$-0.8 (Refs. 10 and 23), i.e., to ~0.4 eV. In the case of a homogeneous mixed-valence Sm layer the impurity term will be even smaller; as the valence approaches 3 the impurity term will by definition tend to zero. In the case of lanthanide intermetallic compounds it has further been shown[10,23] that the equivalent impurity term is very close to zero. In dilute overlayers of Sm on metal single-crystal surfaces the above estimate of 0.4 eV is thus expected to be an overestimate of the impurity term. Stated alternatively, the most relaxed necessary (but certainly not sufficient) condition for homogeneous mixed valence of Sm on a metal single-crystal surface is that the binding energy of the Sm multiplet term closest to the Fermi level is smaller than 0.4 eV. If this condition is not satisfied the mixed valence is of heterogeneous type.

The experiments were performed at the Flipper II beamline[24] at the DESY storage ring DORIS in Hamburg. The Cu(100) crystal was cleaned by a combination of sputtering and annealing. High-purity Sm was evaporated onto the Cu(100) crystal close to room temperature, the amount was determined by using a quartz crystal oscillator. Cleanness of the deposited Sm layers was checked by x-ray photoelectron spectroscopy (XPS) and by photoemission with a photon energy of either 141 or 30 eV. The deposited layers were found to be free from contamination; special attention was paid to oxygen which, if present, should have shown up clearly in the 30 eV photoemission spectra. The emitted photoelectrons were collected and energy analyzed by a double-pass cylindrical mirror analyzer (CMA) operated in the constant pass energy mode. The angle between the surface normal and the CMA axis was 10 deg. Photoemission spectra of the Sm overlayers were measured at two photon energies, 60 and 141 eV. At 141 eV both the di- and the trivalent Sm shown resonantly enhanced photoemission[4] leading to an increased sensitivity for Sm at this photon energy. At 141 eV a somewhat higher bulk sensitivity is obtained than in the 60-eV photon energy measurements. The 60-eV photon energy was chosen as a compromise between resolution and cross section of the Sm 4*f* levels.

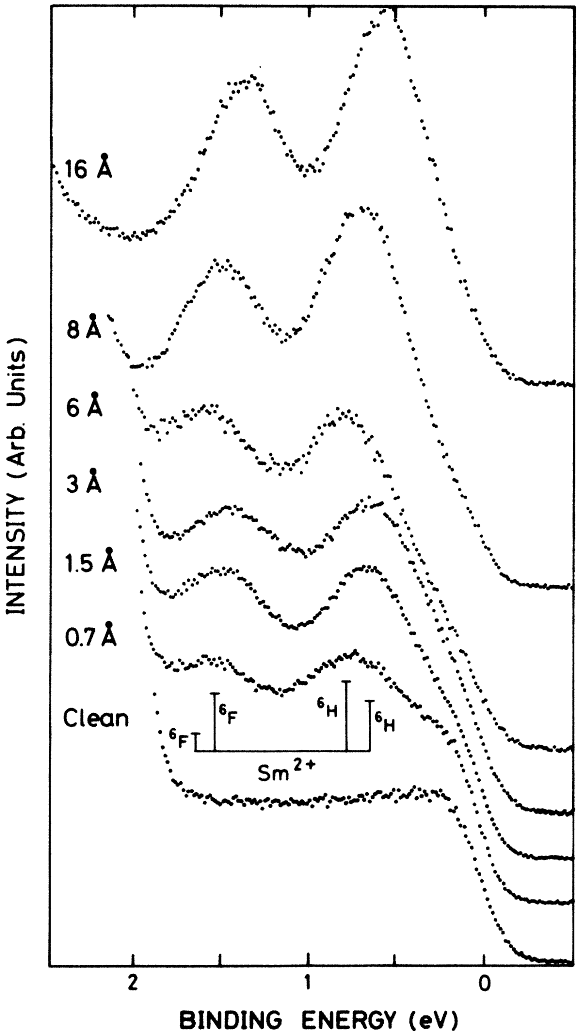

FIG. 1. Photoemission spectra of the region close to the Fermi level for clean and Sm-covered Cu(100) surfaces. $h\nu = 60$ eV. The extra features at low binding energy are due to emission from divalent Sm. The divalent Sm multiplet pattern (Ref. 28) is shown at an energy corresponding to the 0.7 Å coverage.

Figures 1 through 3 show representative photoemission spectra of the clean and of Sm-covered Cu(100) surfaces. On the high binding-energy side of the Cu 3*d* band the final-state multiplet pattern of trivalent Sm is seen in Figs. 2 and 3. In the region between the Cu 3*d* band and the Fermi level the emission features of the divalent Sm appear. A weak divalent Sm feature at about 4 eV binding energy is totally obscured by the strong Cu 3*d* emission.

It can be seen from Fig. 1 that the peak originating from the divalent multiplet terms closest to the Fermi level has a binding energy of about 0.55 eV for all coverages shown. Towards low coverage this binding energy is seen

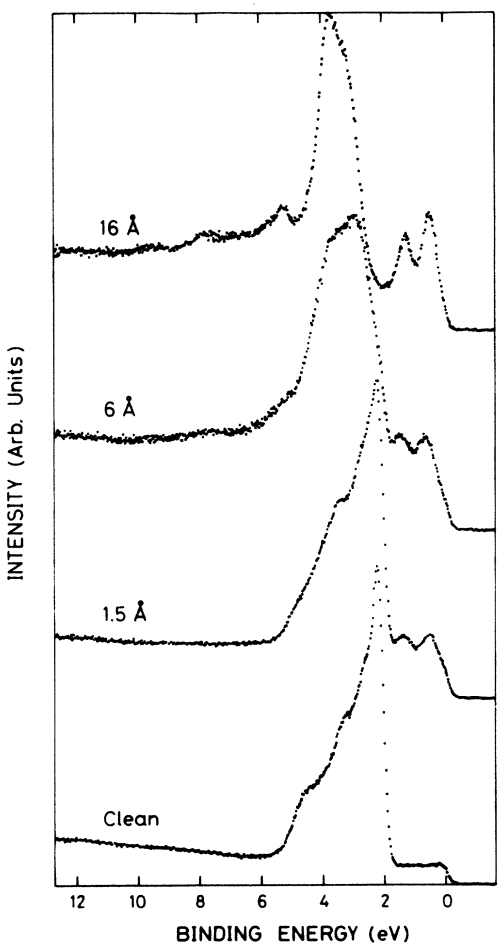

FIG. 2. Photoemission spectra of the valence region for clean and Sm-covered Cu(100) surfaces. $h\nu = 60$ eV. The extra features at lower binding energy than the Cu 3*d* are due to divalent Sm, those at higher binding energy to trivalent Sm.

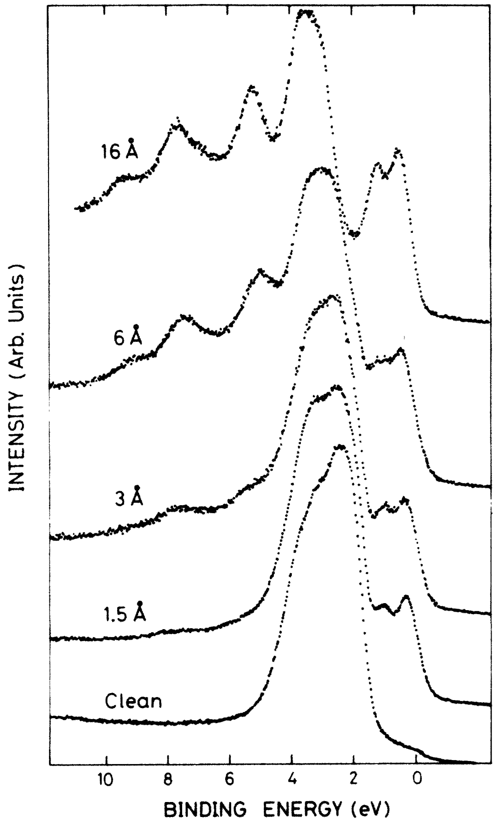

FIG. 3. As Fig. 2 but $h\nu = 141$ eV.

to increase slightly as is to be expected for a layer of isolated Sm atoms. The increase in Sm $4f$ binding energy between 3 and 6 Å coverage indicates the formation of either a Sm-Cu alloy or a pure Sm layer underneath the divalent surface Sm. Similar behavior has been observed for the Yb/Ni(100) system where a compound layer develops.[16,17,25]

The measured binding energy of the highest-lying multiplet term does not meet even the very relaxed requirement for homogeneous mixed valence of being smaller than 0.4 eV. It should further be noticed that the 60-eV photon energy spectra of Fig. 2 show only small amounts of trivalent Sm. If the surface layer of Sm was in a homogeneous mixed-valence state with a valence of larger than say 2.5, as is claimed for large coverages in Ref. 19, a much larger trivalent signal should result. We must conclude, therefore, that the mixed valence is heterogeneous and not homogeneous in contrast with the claim of Ref. 19.

The heterogeneity of the mixed valence is most likely caused by an intermixing between the Sm and the Cu substrate leading to a divalent surface layer and a trivalent bulk layer of Sm that has reacted with Cu.[26] At large coverages also the growth of a clean Sm overlayer with a trivalent bulk and a divalent surface on top of the interface could very well occur. Such behavior has been observed in similar systems[14-17] and is also expected from theoretical considerations.[10,22,23] The large increase in the ratio between the divalent and the trivalent signals when changing the photon energy from 141 eV to the more surface-sensitive 60 eV, Figs. 2 and 3, seems to support this interpretation. However, it should be kept in mind that the resonance of the $4f$ emission at 141 eV changes the ratio between the di- and trivalent cross sections which to some extent will interfere with the mean-free-path considerations. Further, one of the LEED patterns observed suggests that a reaction occurs. At 6 Å coverage the LEED pattern is that of a slightly distorted hexagonal structure with two orthogonal domains (we believe this to be the hexagonal structure reported in Ref. 19) a structure which is also seen on Yb/Ni(100) (Refs. 16 and 17) under conditions where reaction has occurred. Also, the narrowing and shift to higher binding energy of the Cu $3d$ band suggest that a reaction has occurred between the Sm and the Cu. Finally we note that little trivalent Sm is seen in the spectra of Fig. 3 for coverages below 3 Å indicating that a certain threshold coverage has to be reached before reaction starts to occur, as in the Yb/Ni(100) system. The existence of such a threshold coverage has also been reported for Sm on semiconductor surfaces.[27]

We believe that the same conclusion concerning the heterogeneity of the mixed valence of the Sm layers also applies in the case of Sm on Al(111). An ultraviolet photoemission spectroscopy (UPS) spectrum of Sm on Al(111) showing the region close to the Fermi level [Fig. 6(c) in Ref. 21] reveals that the binding energy of the Sm multiplet term closest to the Fermi level is larger than 0.7 eV. Hence, the requirement for homogeneous mixed valence is not satisfied in this case either.

Assuming that intermixing between Sm and the substrate is the cause of the heterogeneous mixed valence also in the case of Sm on Al substrates would explain some of the findings of Refs. 18, 20, and 21. In the case of Al(111) it is reported[21] that thick (3–10 monolayers) annealed films of Sm always exhibit the valence 3 instead of about 2.6 as would be expected from a thin Sm film.[2] For submonolayer annealed films it was found that Sm is trivalent.[21] The authors state that they are unable to explain this result, but the problem is due to their assumption of no intermixing. Clearly, these results could be explained by a reaction between the Sm and the Al(111) substrate, the annealing being necessary in order to provide sufficient mobility. In the case of Sm on Al(100) (Refs. 18 and 20) mainly trivalent Sm is observed after annealing. Furthermore, it is reported that the annealing of thick Sm films leads to a reappearance of the Al $2p$ XPS peaks and to a reduction of the Sm $3d$ intensity which is explained as being due to an agglomeration of the Sm film. However, exactly the same behavior would result if intermixing took place. Such interdiffusion would explain the increased excitation of bulk plasmons by the emitted Sm $3d$ photoelectrons in annealed films compared to unannealed ones.[20]

In summary, we have demonstrated that the mixed valence of Sm on Cu(100) is of heterogeneous type. Based on a published[21] UPS spectrum the same conclusion was reached for the mixed valence of Sm on Al(111) and we suggest that the same also applies for Sm on Al(100). The heterogeneity results from a divalent surface layer and a trivalent intermetallic compound.

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