

## Surface effects on valence in rare-earth intermetallic compounds

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It is shown that the electronic properties of the surface of rare-earth intermetallic compounds may differ from those of the bulk whenever the  $4f$  level lies close to the Fermi energy. A surface valence transition is identified in  $\text{YbAu}_2$ .

From the one-electron point of view the well-known valence instability<sup>1</sup> of certain rare-earth elements is described simply by the fact that the  $4f$  level may fall within the immediate vicinity of the Fermi energy. Although pressure-induced valence changes might suggest that the volume available to the rare-earth ion is determinative, it is more accurate to consider the volume to be determined by the valence which in turn depends on electronic factors.

The  $RM_2$  compounds<sup>2-7</sup> ( $R$  is a rare earth,  $M$  is a noble metal) provide an opportunity for further tests of these ideas. The compounds exist in two different structures, orthorhombic  $\text{CeCu}_2$  and tetragonal  $\text{MoSi}_2$ . Lattice-volume and electronegativity effects should be readily separable because Ag and Au have comparable metallic radii but distinct work functions while Cu and Ag have comparable work functions but distinct metallic radii.

A graphic overview of the behavior of these compounds is obtained from the cell volume per formula unit shown in Fig. 1. In the majority of the compounds the rare earth is trivalent, and the smooth trend in the data clearly exhibits the lanthanide contraction. Anomalies are found in the cases of Ce, Eu, and Yb. Cerium shows a tendency to drop below the trivalent curve signalling a trend toward the  $4+$  state, especially in  $\text{CeAu}_2$ .  $\text{CeAg}_2$  appears to be an intermediate-valence compound. Europium compounds are all divalent.

Ytterbium is clearly trivalent in  $\text{YbAu}_2$ , and probably fully divalent in the Cu and Ag compounds. The most interesting observation is that Yb is divalent in the  $\text{YbAg}_2$  whose hypothetical trivalent volume is *greater* than that of  $\text{YbAu}_2$  as well as in  $\text{YbCu}_2$  whose trivalent volume is *smaller*. This argues strongly against lattice volume as a determinative factor. The distinguishing property of Au is its electronegativity. On this basis alone, we would expect greater charge transfer from the rare earth to gold than to copper or silver during alloy formation. Note that the same arguments can also be applied to explain the behavior of Ce which becomes  $4+$  in the gold compound, and remains close to  $3+$  in the copper analog.

The molecular volumes of the compounds which do not fall on the  $3+$  curves do not suffice to define the valence. We know only that those which fall above have a valence lower than  $3+$ , while those which fall below have a valence which is higher. X-ray photoemission spectroscopy (XPS) has previously been used to define the valence of rare-earth compounds<sup>8</sup> and can, in principle, be applied here. It is important to realize, however, that XPS examines a  $\sim 15\text{-}\text{\AA}$  surface layer, so that a substantial fraction of the total signal comes from the outermost layer of atoms. In the case of Sm metal it has recently been shown that the surface atoms have a divalent component, even though the bulk metal is trivalent.<sup>9</sup> In this paper we re-

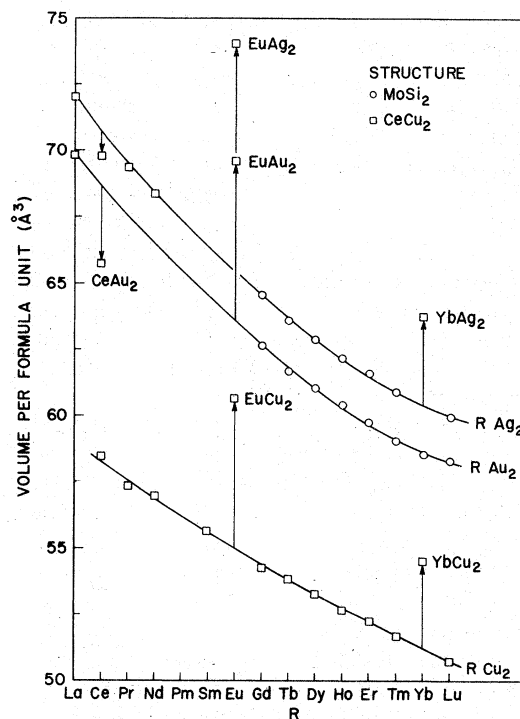


FIG. 1. Cell volume per formula unit in the  $RM_2$  compounds.

port an XPS study of the Yb compounds of the  $RM_2$  series because the large  $4f$  cross section makes it possible to obtain data before surface contamination becomes a serious problem. Data for  $YbNi_5$  are shown because the Yb is known to be trivalent in this compound.

The intermetallic compounds were prepared by arc melting and/or rf melting in argon using dense recrystallized  $Al_2O_3$  crucibles. The cleanliness of the ingots were checked by x-ray powder diffraction studies and the lattice constants compared to the published values.

The data were taken in an HP5950A spectrometer modified for ultrahigh-vacuum (UHV) operation by substitution of a magnetic motion feedthrough for the differentially pumped sliding seal system. Sample surfaces were prepared in a vacuum of  $\sim 1 \times 10^{-9}$  Torr by removing a finite surface layer with a tungsten carbide blade. Oxygen contamination of the surface remained small for periods of up to 1 h, making it possible to obtain valence band as well as core level data. After several hours a spectrum typical of trivalent Yb oxide could be resolved, requiring renewed surface preparation.

The valence-band data for the four intermetallic compounds are shown in Fig. 2.  $YbCu_2$  and  $YbAg_2$  exhibit only divalent Yb which appears as the spin-orbit doublet just below the Fermi energy. The Cu and Ag  $d$  bands are also readily identified.  $YbNi_5$  exhibits a typical trivalent Yb spectrum starting 5 eV below  $E_F$  with the Ni  $d$  band at  $E_F$ . The structure of the trivalent spectrum is due to the final state multiplets produced by removing one electron from  $4f^{13}$ , and resembles the XPS data of isoelectronic  $Tm^{2+}$  except for an 8% expansion.<sup>8</sup> Comparison with spectra calculated using known coefficients of fractional parentage<sup>10</sup> and the optical spectrum<sup>11</sup> of  $Tm^{3+}$  are not entirely satisfactory, the  $^1G$  component being too strong and  $^3F_3$  too weak. The rest of spectrum is well reproduced.

Since there is considerable overlap in energy between the Yb- $4f$  and the noble or transition-metal  $d$  spectrum, it is advantageous to examine a shallow Yb core level as an indicator of valence. Figure 3 displays the  $5p$  spectra of the samples in Fig. 2. The spectrum of  $YbCu_2$  is characteristic of  $Yb^{2+}$ , that of  $YbNi_5$  of  $Yb^{3+}$ . There is an appreciable shift to greater binding energy and an indication of broadening with increased valence. The latter is attributed to unresolved multiplet splitting due to the coupling between  $4f^{13}$  and  $5p$ .<sup>5</sup> It is of course absent in the divalent  $4f^{14}$  case. The spectrum of  $YbAg_2$  exhibits a small trivalent signal due to surface oxide, typical of a sample surface several hours old. Both the energy of this

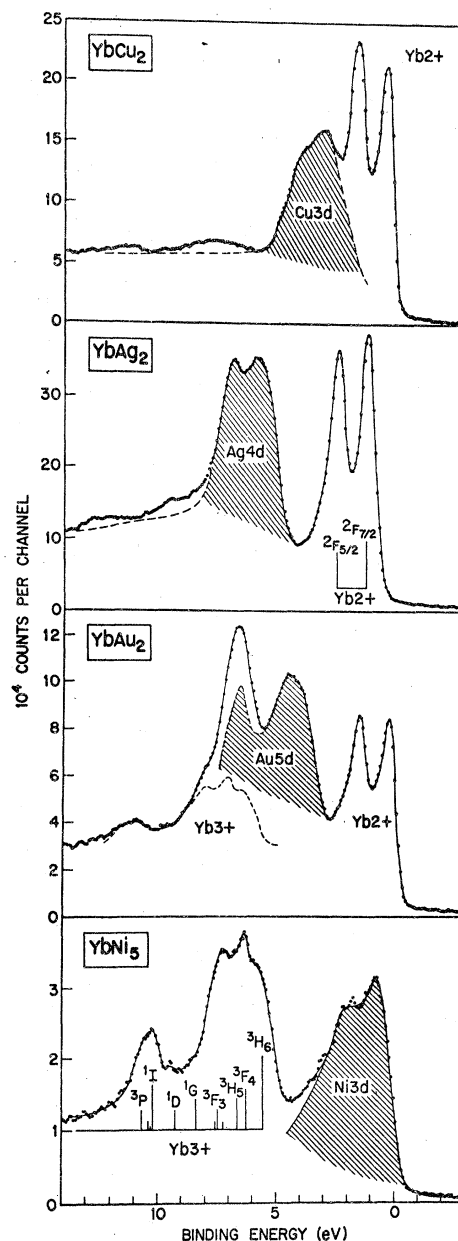


FIG. 2. Valence-band spectra of  $YbCu_2$ ,  $YbAg_2$ ,  $YbAu_2$ , and  $YbNi_5$  obtained by x-ray photoemission. Noble or transition-metal  $d$  contributions are shown shaded.

peak and its growth with time identify it as due to oxide. Indications of surface oxide can also be seen in the valence band peaking at  $\sim 9$  eV, see Fig. 2.

The most interesting observation in Figs. 2 and 3 is the strong divalent component in  $YbAu_2$ , which according to the lattice volume is entirely trivalent.<sup>12</sup> The divalent component in the valence band spectrum of  $YbAu_2$  is located at the Fermi energy,

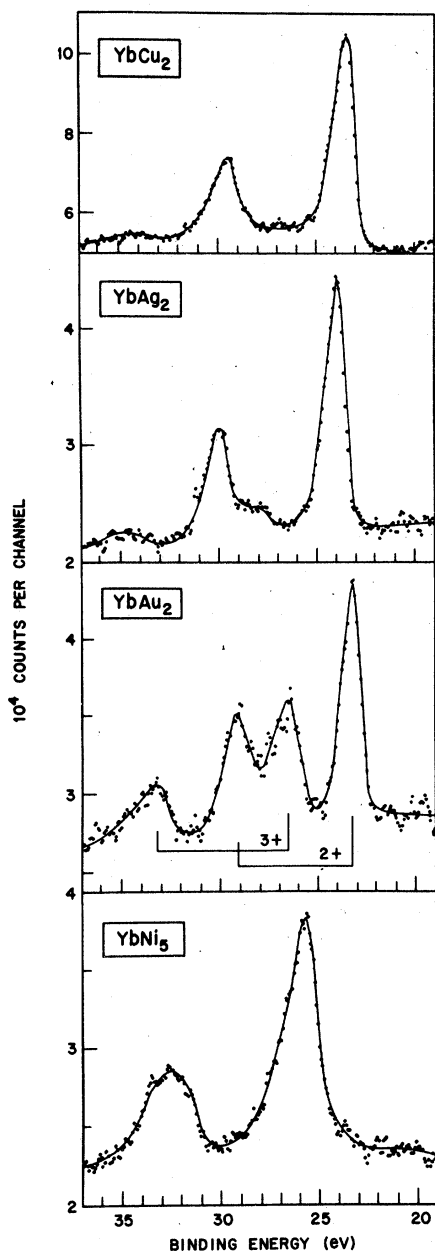


FIG. 3. Ytterbium  $5p$  spectra in the compounds of Fig. 2.

indicative of an intermediate valence system. By taking data as a function of electron take-off angle it was established that the divalent component is a surface feature, i.e., there is a surface valence transition analogous to that found on metallic samarium.<sup>9</sup>

A special difficulty arises upon careful inspection of the Yb- $5p$  spectrum in YbAu<sub>2</sub>, Fig. 3. The divalent contribution contained in this spectrum which has been shown to be due to a divalent com-

ponent in the surface layer clearly exceeds the intensity of the trivalent contribution by about a factor of 2. Decreasing the take-off angle, which diminishes the surface sensitivity of the experiment, increases the trivalent contribution, as is expected if the divalent portion of the spectrum comes from the surface. Increasing the take-off angle on the other hand, which increases the surface contribution to the measured intensity, does not lead to a measurable change in relative intensity. This could mean that at the standard take-off angle of 52° the experiment samples essentially only the surface layer which would then have to be much thicker in YbAu<sub>2</sub> than in Sm metal. It is also possible that the greater surface roughness in the present experiment makes it impossible to achieve a large effective take-off angle. We conclude that the Yb surface atoms in YbAu<sub>2</sub> exhibit an initial-state mixed-valence phenomenon with a 3+ to 2+ ratio of about 0.4. The fact that the valence in the surface layer can be different from that of the bulk clearly requires a reassessment of XPS as a technique for the study of intermediate valence materials.

Before we can give an interpretation of the origin of the surface valence transition it is essential to understand why YbAu<sub>2</sub> is trivalent when YbCu<sub>2</sub> and YbAg<sub>2</sub> are divalent. We adopt a one-electron point of view, and consider the charge transfer and Fermi level changes which accompany alloy formation. Ytterbium metal is divalent,  $4f^{14}$ , with its  $f$  level 1.2 eV below  $E_F$ . (The location of the  $f$  level is defined by the energy required to remove an electron from the  $f$  shell to  $E_F$ , i.e., it is the energy called  $\Delta_-$  by Herbst *et al.*<sup>13</sup>) In order to make Yb trivalent in an alloy it is clearly necessary to lower the Fermi energy below the  $f$  level. In principle this can be accomplished by alloying with an element of greater electronegativity. Admittedly we are here dealing not with alloys but with ordered intermetallic compounds, but the energy associated with the ordering process is relatively small.<sup>14</sup> At fixed atom ratio, in YbM<sub>2</sub>, the greater the electronegativity of the  $M$  atom the lower the Fermi energy in the alloy is expected to be. The work function of Au is about 1 eV larger than that of Cu or Ag. The conclusion drawn from the molecular volume that Yb is trivalent in YbAu<sub>2</sub> but not in YbAg<sub>2</sub> or YbCu<sub>2</sub> can be understood in terms of this model.

It is not necessary to assume, however, that the formation of trivalent Yb requires substantial charge transfer from Yb to Au. The  $4f$  charge may go into Yb  $5d$  states.<sup>15</sup> Core-electron binding-energy shifts provide important information on this and other points. In Table I we summarize the binding energies measured relative to the

TABLE I. Core-electron binding energies in  $\text{YbM}_2$  compounds.

Material	Core level	Binding energy (eV)	Shift
Cu	Cu 3p $3/2$	74.9	...
$\text{YbCu}_2$	Cu 3p $3/2$	75.4	+0.5
Ag	Ag 3d $5/2$	368.2	...
$\text{YbAg}_2$	Ag 3d $5/2$	368.8	+0.6
Au	Au 4f $7/2$	84.0	...
$\text{YbAu}_2$	Au 4f $7/2$	84.6	+0.6
Ni	Ni 2p $3/2$	852.4	...
$\text{YbNi}_5$	Ni 2p $3/2$	852.7	+0.3
Yb	Yb 5p $3/2$	24.3	...
$\text{YbCu}_2$	Yb 5p $3/2$	23.3	-1.0
$\text{YbAg}_2$	Yb 5p $3/2$	23.7	-0.6
$\text{YbAu}_2$	Yb 5p $3/2$	23.2	-26.3 <sup>a</sup> -1.1
$\text{YbNi}_5$	Yb 5p $3/2$	...	25.7 <sup>a</sup> ...

<sup>a</sup>  $\text{Yb}^{3+}$ .

Fermi energy in the intermetallic compounds considered here and their constituents. It is, of course, well known that the binding energy depends not only on charge transfer but also on the shift of the Fermi level. This presents a problem since the work function of alloys and intermetallics are generally not known.

The importance of Fermi energy changes emerges clearly from the well-established differences in work function between Au (5.1 eV) and Yb (~3 eV). An inspection of Table I shows that in every case the binding energy of the noble metal core level increases by an amount between 0.5 and 0.6 eV, i.e., in a direction indicative of loss of valence electrons if it were due to a charge transfer alone. (Even in  $\text{YbNi}_5$ , where the Yb is trivalent, the shift is in this direction.) However, the necessity of establishing a common Fermi energy upon compound formation also causes a shift of the core level because binding energies in XPS are measured relative to the Fermi energy. If we assume that the Fermi energy of the compound is somewhere between that of the constituents, then the Fermi energy of the low work-function component is lowered and that of the higher work-function component raised, leading to a decrease and an increase of the core level energies, respectively. In  $\text{YbAu}_2$  the adjustment of the Fermi energies produces an increase of core binding energies in Au and a decrease of those in Yb, both qualitatively in agreement with observations (cf. Table I). If we assume the work function changes to be roughly proportional to the reciprocal composition ration,<sup>16</sup> we find a nearly quantitative agreement of the observed 5p core level shifts with those estimated from a proper adjustment of the Fermi energies. Consequently, we are

tempted to conclude that the core electron binding energy shifts arise largely from changes in the Fermi level which assumes a position between those of the constituents in the intermetallic compound.

Further qualitative insight is provided by the approach illustrated in Fig. 4 in which we plot the 4f level of Yb (see Refs. 17 and 18) and the 4f and 5d band of Au schematically. The work function of the compound is placed at the weighted average of Yb and Au. (Density of states are assumed to be similar; volume changes neglected, etc.) We then find that the 4f level of Yb lies above the Fermi level of the compound and that the d band of gold actually shifts very little from Au to  $\text{YbAu}_2$ . The core level shifts are consequently more likely to be due to changes in the Fermi energy, rather than to charge transfer. A small shift of the gold 4f level to smaller absolute binding energy, as one would expect for charge transfer to gold does emerge from this analysis. A similar diagram drawn for  $\text{YbAg}_2$  leaves the Yb 4f level below the Fermi energy accounting for the divalent character.

The close proximity of the empty Yb 4f level to  $E_F$  in  $\text{YbAu}_2$  is a necessary condition for a surface valence transition. Any change in electronic structure which raises  $E_F$  at the surface makes it divalent. A mechanism which could be responsible for this phenomenon has been discussed in connection with the case of Sm metal.<sup>9</sup> It is the narrowing of the band structure at the surface due to the reduced coordination number. This raises the  $E_F$  in the partially occupied 5d band and populates the 4f level.

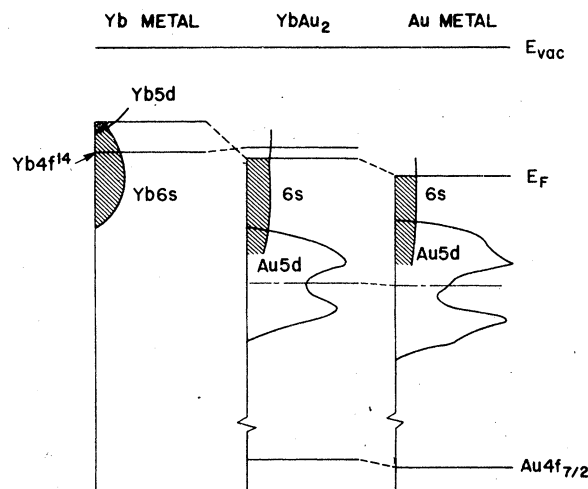


FIG. 4. Schematic presentation of the electronic structure of Yb, Au, and  $\text{YbAu}_2$ .

These observations raise basic questions regarding the utility of XPS in the study of metallic intermediate valence systems. In such systems the  $f$  level is within  $kT$  of  $E_F$  (at least in a one-electron virtual-bound-state model). Significant changes in the average valence at the surface can be anticipated in every case. Only in the rare case in which the escape depth is much larger than the thickness of the surface layer will bulk information be obtained. In general, the surface valence may be anticipated to be lower than that of the bulk, the opposite of what is expected from surface oxidation. This observation serves to clarify certain problems encountered in other ex-

periments. For example, in the study<sup>19</sup> of  $\text{YbAl}_3$ , a second divalent component was found well below  $E_F$ , i.e., not involved in the mixed valence behavior. Although surface oxidation to  $\text{YbO}$  was initially suggested as the source of this phenomenon, measurements in UHV have given similar results, casting some doubt on this explanation. The present study suggests that it may simply represent a stable divalent surface layer wholly electronic in origin. A similar problem, encountered<sup>19</sup> in  $\text{EuCu}_2\text{Si}_2$ , may have the same explanation. It thus appears that metallic intermediate valence compounds may quite generally have stable divalent surface layers.

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<sup>1</sup>See, for example, *Valence Instability and Related Narrow Phenomena*, edited by R. D. Parks (Plenum, New York, 1977).

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<sup>12</sup>The lattice constants of the sample used in this investigation were in good agreement with published values.

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<sup>15</sup>The one-electron model cannot describe this aspect of the electronic behavior because loss of an  $f$  electron perturbs the  $5d$  band.

<sup>16</sup>We here follow the approach of R. E. Watson, J. Hudis, and M. L. Perlman, *Phys. Rev. B* **4**, 4139 (1971).

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