PHYSICAL REVIEW B VOLUME 43, NUMBER 15 15 MAY 1991-II

Photoemission-spectroscopy investigation of the chemical-pressure effect in $Yb_{1-x}M_xAl_2$ ($M=Ca,Sc$)

E. Vescovo, L. Braicovich, B. De Michelis, and A. Fasana
Istituto di Fisica del Politecnico, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

R. Eggenhöffner
Dipartimento di Fisica dell'Universitá, via Dodecaneso, Genova, Italy

A. Iandelli, G. L. Olcese, and A. Palenzona
Istituto di Chimica Fisica dell'Universitá, Corso Europa, Genova, Italy

(Received 9 August 1990; revised manuscript received 8 January 1991)

We present photoemission results with uv and with x rays from a family of pseudobinary compounds obtained by partial substitution of Yb, with Ca or Sc, in the reference compound $YbAl_2$. The substitution with Ca gives rise to a decompression and the one with Sc a compression of the lattice. Ultraviolet photoemission shows the perturbation of the electron states due to chemical substitution; Sc introduces a *d* character extending up to about 3 eV below the Fermi level. The weights of the Yb^{3+} and Yb^{2+} multiplets given by x-ray photoemission are compared with the results from x-ray absorption; the two spectroscopies agree in $YbAl_2$ while the relative weights Yb^{3+} versus Yb^{2+} from x-ray photoemission are definitely below the x-ray-absorption values in the compounds heavily substituted with Sc; this is interpreted as a photoemission final-state effect connected with the *d* character introduced by the substitution.

I. INTRODUCTION

The study of valence fluctuations in rare-earth (RE) compounds with modern spectroscopic techniques is becoming increasingly important;[1] in this connection the study of chemical substitution is still an open field. As shown by crystallographic techniques a suitable chemical substitution can induce a compression or a decompression around the RE atom giving rise to the so-called "chemical pressure,"[2] and photoemission can be very useful to point out the modifications of the valence states thus giving new information on the problem.[3]

Here we present a photoemission investigation[4] of a family of Yb compounds in which the valence is changed via chemical pressure, i.e., the pseudobinary compounds derived by partial substitution for Yb in $YbAl_2$ either with Ca (lattice expansion) or with Sc (compression) already studied extensively with x-ray diffraction.[5] We give the intensity variation of Yb^{2+} and Yb^{3+} multiplets across the family seen with x-ray-photoemission spectroscopy (XPS) and the effect of the substitution on the chemical bond seen with ultraviolet photoemission (UPS). We discuss the results in connection with x-ray absorption (XAS) in the case of chemical pressure[6] and in $YbAl_2$ under physical[7] pressure. In particular we suggest that final-state effects in photoemission become relevant at increasing substitutions with Sc so that XPS multiplets do not give the valence of the ground state but only a lower value in heavily substituted systems.

The paper is organized as follows. Experimental techniques and sample features are described in Sec. II. The results and discussion are given in Sec. III, the Yb^{2+} and Yb^{3+} XPS multiplets in Sec. III A, the effect of substitution on valence states in Sec. III B, the comparison with XAS under chemical pressure in Sec. III C, and with XAS under physical pressure in Sec. III D. The results are summarized in Sec. IV.

II. EXPERIMENT

A. Sample preparation and structure

Polycrystalline samples were prepared by melting stoichiometric amounts of pure species in sealed tantalum crucibles after argon purging and were annealed to obtain homogeneity. The structure was checked by x-ray diffraction;[4] extra phases were less than 3%.

For convenience we summarize some structural information (see also Refs. 2, 5, and 8 and references quoted therein). The $YbAl_2$ structure is of the $MgCu_2$ type. Each Yb atom has 12 Al nearest neighbors forming a cage with Yb in the center, as shown in the inset of Fig. 1 (not to scale). The structure is a stack of these cages so that there are four Yb atoms second neighbors to each Yb. The Yb-Yb distance is only 5% greater than the Yb-Al distance since the large faces of the cage are much greater than the smaller ones. The Ca or Sc atoms go randomly in place of Yb in any proportion maintaining the same structure and originating the pseudobinary compounds $Yb_{1-x}M_xAl_2$ ($M=Ca$ or Sc). The effect can be described, within the accuracy of the present diffraction experiments, as a uniform variation of the lattice parameter induced by the different dimensions of the substituent ions.[9] Scandium induces a lattice compression and Ca an expansion; the Yb atoms maintain their first coordination shell, while the second neighbors are statistically occupied by substituent atoms. Thus all Yb

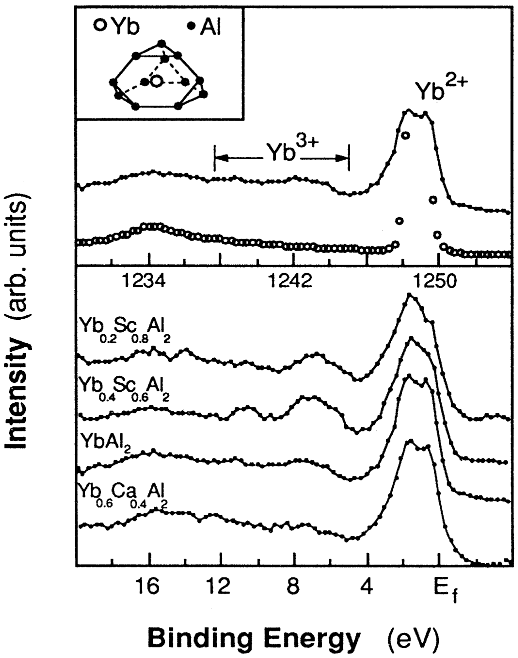

FIG. 1. Lower panel—angle-integrated XPS spectra ($h\nu = 1253.6$ eV) from $YbAl_2$ and pseudobinary compounds obtained via partial substitution of Yb with Ca or Sc. The spectra are normalized to the same height in order to point out shape modification with chemical substitution. Upper panel—energy-loss spectrum of $YbAl_2$ (open circles) used to subtract the background from the photoemission spectrum (also shown). The abscissa is the electron kinetic energy (eV).

sites in each compound are equivalent in terms of first-neighbors coordination, except the atoms in the surface region.

We studied substitution with Sc up to higher values than with Ca because $YbAl_2$ has a valence rather close to 2 (around 2.3 as shown below), so that the increase of the valence due to Sc is seen much better than the decrease due to Ca. Moreover the more interesting case is the substitution with Sc, which has greater *d* occupancy in the valence states. Lattice parameters and atomic distances are summarized in Table I [columns 1, 2, and 3 (from Ref. 5)].

B. Experimental procedures

Most measurements were taken with a conventional XPS-UPS facility equipped with a nonmonochromatized Mg $K\alpha$ source ($h\nu = 1253.6$ eV) and a He I ($h\nu = 21.2$ eV)–He II ($h\nu = 40.8$ eV) lamp with differential pumping. As the synchrotron radiation (SR) source we used beam line 1.1 at the Stanford Synchrotron Radiation Laboratory (SSRL) equipped with the so-called "grasshopper monochromator" (60–600 eV).[10] All spectra were measured with a cylindrical-mirror analyzer equipped with a coaxial electron gun. The instrumental resolution [full width at half maximum (FWHM)] was 0.35 and 1.1 eV for the He and XPS measurement and 0.45 eV for SR measurements. The base pressure was below 1×10^{-10} Torr.

TABLE I. Structural data of $Yb_{1-x}M_xAl_2$ compounds.

M	*x*	Lattice parameter (Å)	Yb-Al distance (Å)	Yb-Yb distance (Å)	XPS valence
Sc	0	7.881	3.267	3.413	2.33±0.033
	0.6	7.668	3.179	3.321	2.49±0.04
	0.8	7.625	3.161	3.302	2.52±0.04
Ca	0.4	7.957	3.299	3.445	2.28±0.03

The samples were cleaned *in situ* by scraping with a diamond file. Immediately before scraping, the manipulator head, including the sample, was covered by evaporation of Mg, which is very visible through 2*p* photoemission and is not a contaminant of the samples as grown. The absence of any Mg signal after scraping guarantees that the whole surface seen by the spectrometer is well scraped. The scraping was carried out up to disappearance of contributions from Mg (2*p*), oxygen (1*s* and 2*p*), and carbon (1*s*).

The sensitivity to oxygen has been checked by exposing a clean sample to a controlled oxygen atmosphere; we could establish that oxygen contamination of our clean surfaces was, if any, below 0.01–0.02 monolayer, i.e., totally negligible for our purposes. The scraper was installed with an isolation valve so that the files could be substituted without breaking the vacuum; a clean file was used after the first coarse scraping.

Scraping is the only feasible way to clean these samples. Sputtering cannot be used due to its well-known selectivity; in principle, fracturing *in situ* could be preferable, but this is not feasible because the samples with heavy Sc substitution are very brittle.

III. RESULTS AND DISCUSSION

A. XPS and the Yb^{2+} and Yb^{3+} multiplet weights

The XPS spectra are shown in Fig. 1 (lower panel); for cross-section reasons the spectra are dominated by 4*f* ionization, while the 3*d* states introduced either by Sc or by Ca are not seen with the present sensitivity. The final-state multiplets[11] coming from ionization of divalent Yb^{2+} 4*f* (Ref. 14) and trivalent Yb^{3+} 4*f* (Ref. 13) show qualitatively the valence modification upon chemical substitution and the Yb^{2+} and Yb^{3+} weights give the "XPS valence" (or "photoemission valence") which is to be regarded as an operative definition. In this case XPS is more convenient to define the valence than UPS, where the *d* signal coming from the substituent atoms (see below) makes the procedure very difficult. Kaindl *et al.*[12] effectively used UPS for nonsubstituted $YbAl_2$; the present results agree with Ref. 12.

A plasma loss associated to the Yb^{2+} feature is superimposed to the Yb^{3+} signal; this is shown in the upper panel of Fig. 1 where we report the XPS and electron-energy-loss spectra of $YbAl_2$ measured at the same primary energy in the same experiment. After subtraction of this plasma-loss function,[13] one can recover the bulk 2+ contribution from the whole 2+ region where also signals from the surface and the subsurface regions are present (see also our preliminary work of Ref. 4 on $Yb_{0.6}Ca_{0.4}Al_2$). To this end the instrument response function to a $4f$ doublet has been obtained from the spectra of metallic divalent Yb measured with our apparatus in strictly comparable conditions; thus we have decomposed the XPS (2+) spectra by fitting the upper part of the measured spectrum ending at E_F with a doublet representing the bulk contribution; as it is well known this is closer to E_F than the surface and subsurface signals.[11] With our resolutions the change of line-shape asymmetry from the metal to our compounds due to a possible variation of the Doniach-Šunjić[14] effect is not relevant.

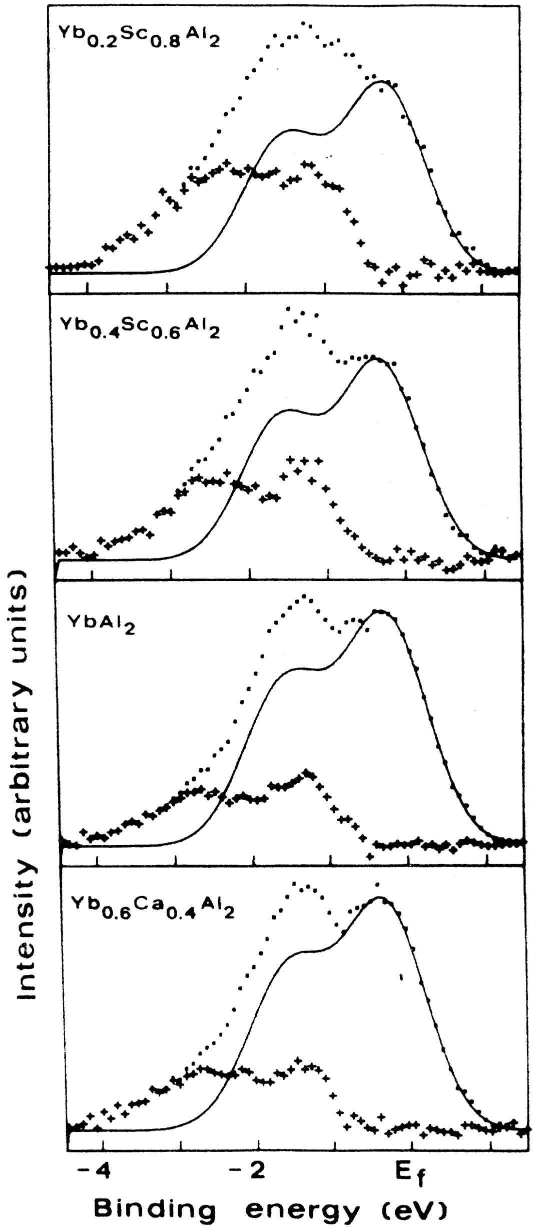

FIG. 2. Expansion of the Yb^{2+} region of the XPS spectra of Fig. 1. The measured spectra are decomposed in bulk (solid line) and surface-derived (crosses) components.

The decomposition of the 2+ region is given in Fig. 2; solid lines show the bulk components and crosses show the difference spectra (i.e., total bulk). The further decomposition in surface and subsurface components is immaterial in determining the XPS valence and has not been done. The error of the XPS valences was obtained with an extensive sensitivity analysis to the parameter changes in the data handling. The measured XPS valences are collected in Table I (column 4).

B. UPS and the effect of Yb substitution on the valence states

The He spectra normalized to the same height in the Yb^{2+} region are given in Fig. 3. With Sc substitution the signature of the Sc $3d$ states is clearly seen near E_F both in He II (lower panel) and in He I (upper panel), where the weight of the $3d$ emission is greater due to cross-section effects.[15] Note that the total width of the Yb^{2+} region in UPS agrees with the above XPS data if one accounts for the resolution.

It is important to recover information on the spectral distribution of the Sc $3d$-derived states. In this connection the data on $Yb_{0.2}Sc_{0.8}Al_2$ measured with SR give simple and direct insight. In Fig. 4 (lower panel) we compare the spectra taken at two energies (65 and 181.5 eV);

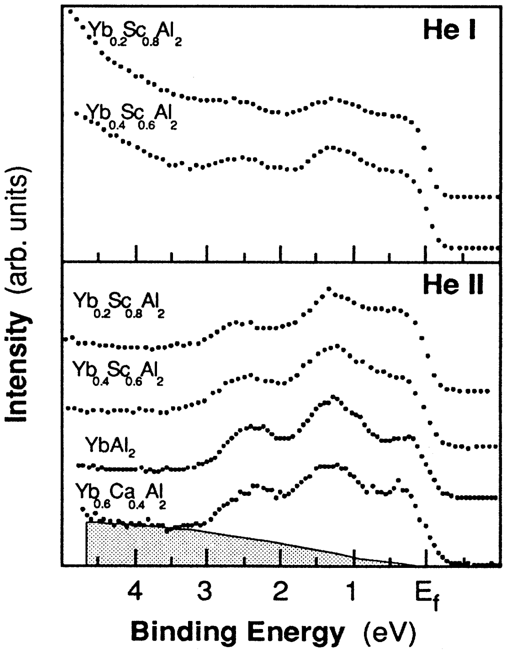

FIG. 3. Lower panel—He II ($h\nu=40.8$ eV) photoemission spectra of $YbAl_2$ and substituted compounds. As an example, the integral background used in the analysis of the data is reported under one of the spectra. Upper panel—He I ($h\nu=21.2$ eV) of two Sc substituted compounds. The Sc $3d$ contribution, just below the Fermi level, is clearly seen.

the cross-section ratio σ_{3d}/σ_{4f} is smaller at higher energy,[16] and the spectra are fitted to the same values around 2.5–3 eV where the Sc 3*d* contribution is, if any, negligible due to the low *d* occupation. Thus the shape of the difference spectrum is that of the Sc 3*d*–derived states. Note that this procedure gives information on the Sc contribution *in the presence* of Yb, i.e., in the real compound under discussion with the real lattice spacing we are interested in.

The Sc 3*d* component given in Fig. 4 is qualitatively confirmed by the trend of the He I spectra of Fig. 3 (upper panel) showing a departure of the spectrum from the secondary electron background around 3 eV below E_F with a very tiny 4*f* contribution. Another completely independent confirmation of the Sc 3*d* shape comes from the decomposition of the He II spectra presented in Appendix A.

The Sc 3*d* distribution is compared in Fig. 4 (upper panel) with the He II spectrum of Sc metal,[17] which is dominated by the *d* contribution. The close similarity of the two spectra is clear evidence of a relevant lateral interaction of the Sc 3*d* states in our compounds consistently with structural data.[2,5,8] In hcp Sc metal each atom has 12 nearest neighbors at 3.177 Å (we neglect the small departure of the *c*/*a* ratio from the ideal value); in our case a Sc atom sees 12 Al neighbors at a comparable distance (3.161 Å when $x = 0.8$) and four sites of the Yb type at slightly greater distance (3.302 Å), where other substituents are likely to be found. Thus the Sc interaction with first and second neighbors is important, and this explains the shape of the *d* contribution. In fact, also the interaction with Al is expected to give a tail in the *d* character extending down to several eV as suggested by electron-state calculations of the aluminides of other early transition metals.[18] Thus the interpretation of the spectroscopic properties of these pseudobinary compounds must consider the perturbation due to the *d* states of the substituent atom. This is consistent with the heavy substitution needed to change the lattice parameter; the 1% reduction of the lattice parameter implies the substitution with about 50% of Sc.

For the Ca 3*d* distribution the situation is qualitatively similar, but the influence of the *d* contribution is expected to be smaller due to the lower *d* occupation (see Fig. 3, lower panel). Also in Ca aluminides a *d* tail (narrower than in the Sc case) is found as shown by the calculations of Ref. 19 for Ca-Al glassy metals.

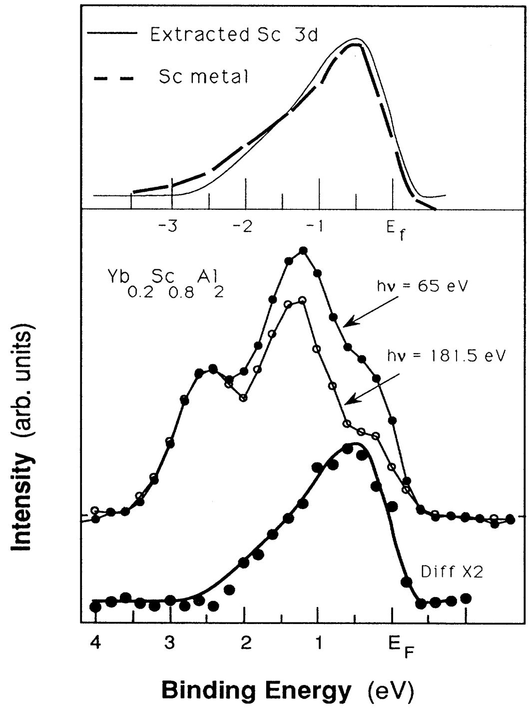

FIG. 4. Lower panel—two photoemission spectra of $Yb_{0.2}Sc_{0.8}Al_2$ in the Yb^{2+} region are compared. The spectra are normalized to the same height at about 2.5–3 eV below E_F, where the Sc 3*d* density of state is expected to be negligible. Due to cross-section effects the difference of the two spectra reflects directly the Sc 3*d*–derived states. Upper panel—the Sc 3*d* contribution in $Yb_{0.2}Sc_{0.8}Al_2$ is compared with the He II spectrum of Sc metal from Ref. 17 (a small vertical offset is given to the 3*d*-extracted spectrum to make the figure more understandable).

C. The meaning of the XPS valence and the comparison with XAS

The above traditional definition of the XPS valence has given values in reasonable agreement with dilatometric and low-excitation methods in a variety of Yb compounds. This approach assumes that the relative weights of 2+ and 3+ configurations are not modified in the final 4*f* ionization state due to the interaction with the solid, for example, by the hopping of an extra electron jumping into the 4*f* hole. Due to the contraction of the Yb 4*f* shell with respect to light rare earths, this assumption is more reasonable here than in Ce, where the coupling between the 4*f* states and the solid is crucial in the interpretation of photoemission spectra.[20] In our case the presence of a strong *d* contribution in the substituted systems raises the question of the meaning of the XPS valence since a new hopping channel is opened when Sc atoms replace Yb and a 3*d* contribution is inserted in a fraction of Al cages.

As a pictorial indication we consider the atomic wave functions[21] in two nearby sites. This is done in Fig. 5 by comparing the 4*f*-4*f* overlap (no substitution, lower panel) and the 3*d*-4*f* overlap (Sc substitution, upper panel); this is a strong support for a considerable increase of the hopping upon substitution, although it neglects the Al cage which surely reduces the hopping with respect to this simple atomic scheme. Thus we cannot discard *a priori* a possible influence of the *d* contribution on the hopping probability.

In the ground state the substitution could originate in differences between chemically and physically compressed systems due to the different hopping in situations with the same lattice parameter. In the final photoemission state the XPS valences could also be biased by hopping, and this process should be more efficient than the hopping in the ground state due to the attractive hole

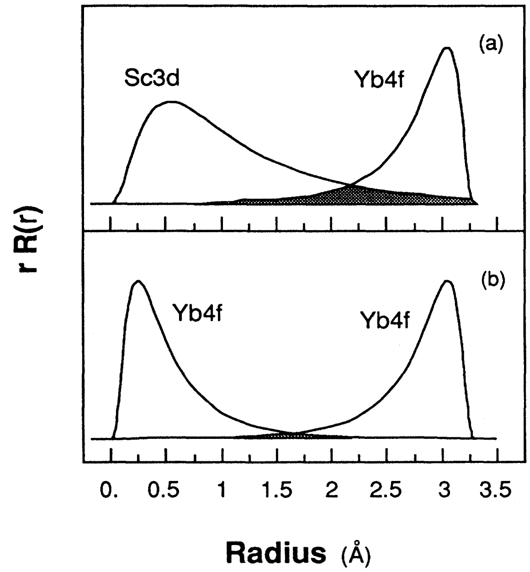

FIG. 5. Comparison between the radial part $[rR(r)]$ of the Sc $3d$ and Yb $4f$ atomic wave functions (from Ref. 18). The origins of the two wave functions are displaced by 3.302 Å, which is the interatomic Yb-Yb (Yb-Sc) distance in $Yb_{0.2}Sc_{0.8}Al_2$.

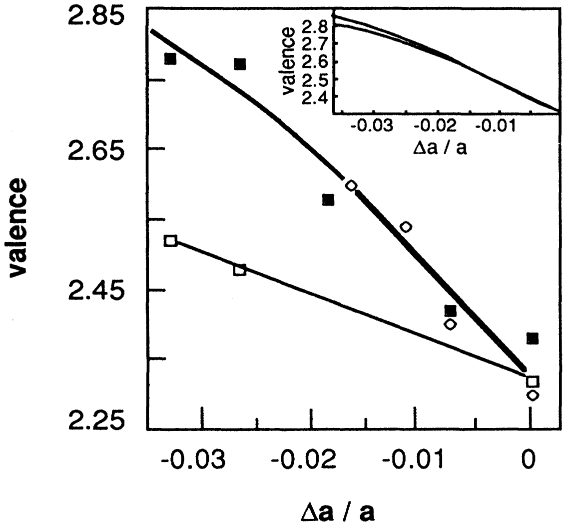

FIG. 6. Plot of Yb mean valence measured with different methods vs relative variations of the lattice parameter Yb $L_{\rm III}$ XAS in the presence of physical (open circles) or chemical (solid squares) pressure (from Ref. 5) and XPS spectra (open squares). The inset gives the curves obtained with the model described in Appendix B.

potential. These arguments are *a priori* valid also in other compounds, but here we have the specific circumstance that chemical pressure may introduce a bias which, if relevant, is *variable and nonmonotonic along* the sequence of the substituted compounds. In fact both compression and decompression are obtained via chemical pressure by introducing an extra d contribution (stronger in Sc).

With these precautions in mind we consider the data collection of Fig. 6, where the XPS valences (open squares) and the XAS valences (solid squares) are plotted versus the fractional variation of the lattice parameter in the case of compression (for the other information given in Fig. 6, see Sec. III D below). The XAS valences in $L_{2,3}$ absorption were measured on the same samples and are taken from Ref. 6, where the XAS analysis is carefully presented. The increase of the XPS is definitely smaller than in XAS. In the reference compound ($YbAl_2$) the two approaches give the same value within the experimental accuracy, and consistent application of the *same* data handling to the other compounds shows a strong difference which is thus to be attributed to a different response of the system to the two spectroscopies in the compounds heavily substituted with Sc.

Besides the above mechanisms affecting XPS, we must also consider that shakeup and shakedown can take place in XAS. A shakedown due to the L core hole would decrease the XAS valence but should be less efficient than that due to a $4f$ hole which is less screened. On the other hand, an overestimation of the valence in XAS could be originated by a shakeup of a $4f$ electron due to the repulsion with the excited $5d$ electron created in L absorption. The relative roles of the possible mechanisms able to modify the XAS valence with respect to the XPS valence is surely very much dependent on the detailed nature of the system due to the trade off between different aspects, such as localization of the $5d$ states, screening capability, and hopping integrals. Probably there is no general answer to this problem, which deserves future theoretical work at least in model systems.

In the present case, the evidence of a considerable lateral interaction of the Sc d states strongly suggests the hopping into the photoemission hole as the more important process. In this case the XPS valence would be an underestimation of the valence in the ground state. We will show in Sec. III D that the present knowledge about physical pressure conspires in the same direction.

The present experimental results can also stimulate further work on the coupling of $4f$ states with solid states. In this connection also, low-excitation work will be useful to fit the photoemission results with more advanced models. This future work will have the chance of use an Anderson Hamiltonian approach as already done extensively for Ce compounds.[20] In some Yb compounds simpler than the present ones, this approach has been already fruitful;[22] the application to this case is at present premature but can be very interesting in the future.

D. Chemical versus physical pressure

The available XAS valences of $YbAl_2$ under physical pressure taken from the recompilation done by Sancrotti *et al.*[6] are also given in Fig. 6 (open circles). They cover about half of the compression range explored with chemical pressure. The deviation, if any, between chemical and physical pressure is negligible, showing that the added d

component has little influence on the XAS valence in this subrange.

Figure 6 suggests that the trend under physical pressure gives valences much closer to the XAS than to the XPS values. This can be put on a better basis by means of a reasonable extrapolation of the available data. To this end we note that the energy separation between the 2+ and the 3+ configurations changes drastically with the compression as shown by the atomic calculations by Herbst and Wilkins.[23] Thus this effect should be definitely more important than the hybridization variation, and the valence change would be basically determined by the energy dependence of the partition function. In this case an accurate description of the hybridization variation is not needed, and a thermodynamic model of the type suggested by Sales and Wohlleben[24,25] has a good chance of correctly reproducing the trend as discussed in detail in Appendix B (Ref. 26). Appendix B gives the details of the extrapolation represented by the darker line in Fig. 6.

This extrapolation gives some confidence on the similarity of the XAS valences under physical and chemical pressure in the whole range covered in Fig. 6, although the accuracy of the data and the use of a model cannot show small differences. On the other hand, the XPS results under chemical pressure are definitely below the other data. One can thus guess that the introduction of the *d* contribution typical of chemical pressure is much more important in the excited states due to 4*f* photoemission than in the ground state. This does not exclude that final-state effects are also present in XAS but strongly supports the argument of the previous paragraph that the most relevant contribution to the discrepancy between XAS and photoemission is a final-state effect due to the opening of a 4*f* hole in the presence of the *d* states introduced by substitution.

IV. CONCLUSIONS

We have presented a photoemission study (XPS-UPS) of a typical family of pseudobinary compounds obtained by partial substitution for Yb atoms in the reference compound $YbAl_2$ with Sc (compression) and with Ca (decompression). The UPS results give evidence of the electron states' modification due to chemical substitution; this is particularly evident with Sc which introduces a *d*-character distribution extending to about 3 eV below the Fermi level. The effect of these *d* states cannot be neglected in the study of a Yb mixed valence. In systems with heavy Sc substitution the valence obtained from the weights of final-state multiplets in XPS is definitely smaller than the XAS value which is not far from available information on $YbAl_2$ under physical pressure. On the contrary XPS and XAS give consistent results in the reference compound $YbAl_2$. This is interpreted in terms of final-state effects in XPS which lower the weight of the Yb^{3+} terms due to the interaction with the *d* states introduced by substitution. Thus the present work gives evidence of the interplay between chemical substitution and the perturbation due to the high-energy spectroscopy used to investigate the system.

ACKNOWLEDGMENTS

The authors would like to thank E. Puppin for allowing the use of the spectra of Fig. 4 prior to publication. This work was supported by the Ministero della Ricerca Scientifica e dell' Universita' through the Consorzio Istituto Nationale di Fisica della Materia.

APPENDIX A: EVALUATION OF THE *d* CONTRIBUTIONS TO THE DENSITY OF STATES IN THE SUBSTITUTED COMPOUNDS FROM He II SPECTRA

We have already obtained the Sc 3*d* partial density of states by using the energy dependence of the cross sections in SR photoemission. Here, as a confirmation, we extract this contribution from the He II spectra. This extraction does not pretend to be a quantitative analysis, which is not needed for the present discussion. Our analysis is as follows.

(i) The spectrum of the reference compound ($YbAl_2$) is decomposed in the traditional way as in Ref. 12 by Kaindl *et al.* after background subtraction [Fig. 7(a)]; we neglect in first approximation the *sp* contribution, which

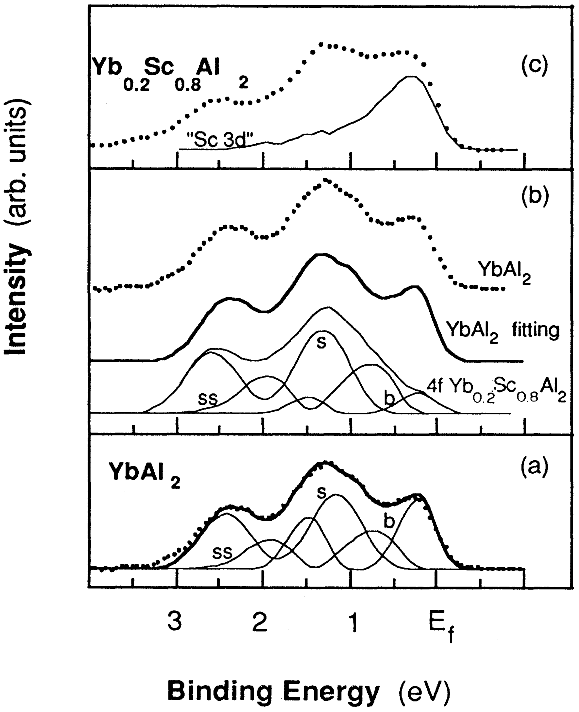

FIG. 7. (a) Best-fit analysis of the 4*f* (Ref. 13) final-state multiplet spectrum ($h\nu=40.8$ eV) of $YbAl_2$. Three doublets with slightly asymmetric components represent the emission from bulk *b*, surface *s*, and subsurface *ss*; (b) synthesized 4*f* part of $Yb_{0.2}Sc_{0.8}Al_2$ spectrum by means of properly weighted *b*, *s*, and *ss* components; (c) photoemission spectrum of $Yb_{0.2}Sc_{0.8}Al_2$ ($h\nu=40.8$ eV) and Sc 3*d* contribution obtained after a subtraction of the synthesized 4*f* part.

is small due to cross-section reasons.[27] The surface component is broader, since a variety of sites is present.

(ii) The thickness of the surface region containing divalent Yb is enhanced in the Sc substituted compounds, as shown in XPS (Fig. 2). This attenuates the bulk component in the UPS spectra of $Yb_{0.2}Sc_{0.8}Al_2$; by assuming a typical escape depth around 2 monolayer the bulk 2+ component should be attenuated by about a factor of 0.3. With this attenuation and with the $4f$ surface and subsurface components of the reference case, one synthesizes the total $Yb\,4f^{2+}$ contribution in the substituted system shown in Fig. 7(b) ($4f$ $Yb_{0.2}Sc_{0.8}Al_2$). The difference between the measured spectrum (after background subtraction) and the total $4f$ contribution gives the Sc $3d$ contribution shown by the solid line in Fig. 7(c). The close similarity of the d distribution with that obtained with SR measurements is evident. This evaluation is very reliable since the value of the bulk attenuation is by no means critical.

APPENDIX B: THE EXTRAPOLATION OF THE XAS VALENCES OF $YbAl_2$ UNDER PHYSICAL PRESSURE

Herbst and Wilkins[23] calculated the ionic energies as a function of the Wigner-Seitz (WS) cell radius. By assuming the fractional variation of the lattice parameter as a measure of the variation of the WS radius, one can use the energies by Herbst and Wilkins in a partition-function model as that suggested by Sales and Wohlleben.[24,25] In this model the effective temperature T^* used in the partition function is defined as $(T^2+T_f^2)^{1/2}$, where the fluctuation temperature T_f takes into account phenomenologically the quantum transitions between the two configurations. Under physical pressure the change of the quantum-transition rate is basically due to the variation of the hybridization originated by the lattice parameter modification. The most rapidly varying term is the hybridization between nearby f-d states depending roughly on the sixth power of distance.[28] Thus, as an upper extreme, we adopt distance dependence for the whole hybridization; this is done with the ansatz that T_f has the same power dependence on the distance.

Within these assumptions it is straightforward to write the valence v appropriate for Yb as

$$v = 2 + \{8/[8+\exp(E_x/kT^*)]\} ,$$

where $E_x = E(4f^{n-1}) - E(4f^n)$.

By fitting the value of $v = 2.33$ ($YbAl_2$) at zero compression, one obtains $E_x/kT^* = 2.8$. The physical pressure is introduced by varying the energy E_x according to the calculations by Herbst and Wilkins[23] and by accounting for the hybridization variation with a new $T_f' = AT_f$, where T_f is the fluctuation temperature without compression and A depends on the lattice parameter as

$$A = (1+|\delta a/a|)^6 .$$

Here we have only one free parameter (T_f) instead of two (T_f and E_x) as in the traditional formulation, and this reduces the ambiguities in the use of the model. The value of T_f is obtained by fitting the XAS valences under physical pressure, and the analytical expression is used to extrapolate the trend toward higher compressions.

We used the model with and without the pressure dependence of the hybridization. The results (Fig. 6 inset) correspond to $T_f = 1170$ K (fixed hybridization, upper curve) and to $T_f = 1100$ K (variable hybridization, lower curve) and show that the trend is basically due to the E_x dependence of the partition function, so that an accurate description of the hybridization is immaterial to fit the physical pressure data. This justifies the use of the simple model as done in Fig. 6, where we used the variable hybridization since it is conceptually more satisfactory.

The XPS valence of $YbAl_2$ at 80 K measured by us in comparable conditions is about 2% smaller than that at room temperature. The present model, used without compression and with variable temperature, fits our result of 2% with $T_f = 900$ K in good qualitative agreement with the value used above.

---

[1] *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981); *Handbook on the Physics and Chemistry of Rare Earth*, edited by K.A. Gschneider, Jr., LeRoy Eyring, and S. Hufner (North-Holland, Amsterdam, 1987), Vol. 10.

[2] A. Iandelli and G. Olcese, J. Less Common Met. **29**, 293 (1972); W. C. M. Mattens, J. Aarts, A. C. Moleman, and F. R. de Boer, in *Valence Instabilities*, edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982).

[3] Hereafter we will adopt the expression "chemical pressure" for simplicity.

[4] On this family only very limited and preliminary photoemission information is available: I. Abbati, B. De Michelis, A. Fasana, M. Sancrotti, A. Iandelli, G. L. Olcese, and R. Eggenhöffner, Solid State Commun. **65**, 743 (1988).

[5] A. Iandelli and G. L. Olcese, J. Less Common Met. **111**, 145 (1985).

[6] M. Sancrotti, I. Abbati, E. Puppin, Z. X. Shen, I. Lindau, R. Eggenhöffner, A. Iandelli, and G. L. Olcese, Solid State Commun. **74**, 1131 (1990); R. Eggenhöffner, M. Sancrotti, I. Abbati, E. Puppin, Z. X. Shen, I. Lindau, A. Iandelli, and G. L. Olcese, *ibid.* **74**, 1009 (1990).

[7] J. Röhler, G. Krill, J. P. Kappler, M. F. Ravet, and D. Wohlleben, in *Valence Instabilities* (Ref. 2); E. Beaurpeaire, J. P. Kappler, and G. Krill, Solid State Commun. **57**, 145 (1986).

[8] J. H. Wernick, in *Intermetallic Compounds*, edited by J. H. Westbrook (Wiley, New York, 1967).

[9] A. Iandelli and A. Palenzona, in *Handbook on the Physics and Chemistry of Rare Earth* (Ref. 1), 1980, Vol. 2.

[10] The Synchrotron radiation data will be presented more extensively elsewhere. L. Braicovich, B. De Michelis, A. Fasana, E. Puppin, M. Sancrotti, E. Vescovo, R. Eggenhöffner, A. Iandelli, G. L. Olcese, and A. Palenzona (unpublished); E. Puppin and I. Lindau (unpublished).

[11] T. Penney, B. Reihl, R. A. Pollak, B. Barbara, and T. S. Plaskett, J. Appl. Phys. **55**, 1975 (1984); S. J. Oh, J. W. Allen, M. S. Torikachvili, and M. B. Maple, J. Magn. Magn. Mater. **52**, 183 (1985).

[12] B. Kaindl, B. Reihl, D. E. Eastman, R. A. Pollak, N. Mårtensson, B. Barbara, T. Penney, and T. S. Plaskett, Solid State Commun. **41**, 157 (1982).

[13] This has been suitably broadened to simulate the effect of the width of the Yb^{2+} peak. We do not report the loss spectra from the other compounds since they are similar.

[14] S. Doniach and M. Šunjić, J. Phys. C **3**, 285 (1970).

[15] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[16] In purely atomic terms this cross-section ratio decreases by a factor of 21 (according to Ref. 15).

[17] F. L. Battye, H. Schulz, A. Goldmann, S. Hüfner, D. Seipler, and B. Elschner, J. Phys. F **8**, 709 (1978).

[18] Jian-hua Xu and A. J. Freeman, Phys. Rev. B **40**, 11 927 (1989).

[19] S. R. Nagel, U. M. Gubler, C. F. Hague, J. Krieg, R. Lapka, P. Oelhafen, J. Güntherodt, J. Evers, A. Weiss, V. L. Moruzzi, and A. R. Williams, Phys. Rev. Lett. **49**, 575 (1982).

[20] See, for example, O. Gunnarson and K. Schönhammer, in *Valence Fluctuations of Solids* (Ref. 1), and references quoted therein.

[21] F. Hermann and S. Skillmann, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1973).

[22] F. Patthey, J. M. Imer, W. D. Schneider, Y. Baer, B. Delley, and F. Hulliger, Phys. Rev. B **36**, 7697 (1987); R. Monnier, L. Degiorgi, and D. D. Koelling, Phys. Rev. Lett. **56**, 2744 (1986); A. Fujimori, T. Shimizu, and H. Yasuoka, Phys. Rev. B **35**, 8945 (1987).

[23] J. F. Herbst and J. W. Wilkins, Phys. Rev. B **29**, 5992 (1984).

[24] B. C. Sales and D. K. Wohlleben, Phys. Rev. Lett. **35**, 1240 (1975).

[25] B. C. Sales, J. Low Temp. Phys. **28**, 107 (1977).

[26] This simple model is open to criticism when used to fit properties depending on a balance of tiny contributions as in the magnetic susceptibility versus temperature; the situation is different here and the use of the model is justified as shown in Appendix B.

[27] R. Niholm, Ib. Chorkendorff, and J. Schmidt-May, Surf. Sci. 143, 177 (1984).

[28] J. W. Allen, S. J. Oh, O. Gunnarsson, K. Schönhammer, M. B. Maple, M. S. Torikachvili, and I. Lindau, Adv. Phys. **35**, 275 (1986).