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Photoemission study of the hydrogenation of the intermetallic compounds YFe_3 and YFe_2

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Intermetallic yttrium-iron compounds do have a strong affinity to hydrogen. Exposure to H_2 at 300 K leads to a hydrogen-induced state at 5.3 eV below E_F and a strong reduction of d-like states at E_F. For higher H_2 exposures at 700 K, these hydrides undergo a metal-to-semiconductor transition with an energy gap $E_0=0.3\pm0.1$ eV. In addition to the lowering of d-like states at E_F, a second H_2-induced structure appears at 10 eV.

I. INTRODUCTION

The use of hydrogen as an energy carrier has led to a rapidly growing field of experimental and theoretical studies on its interaction with metals and intermetallic compounds.[1–4] Potential storage materials such as $LaNi_5$ or TiFe can absorb more than twice the density of liquid hydrogen. Their surface segregation and poisoning, however, are still serious problems which limit their use as economical and rechargeable long-term hydrogen absorbers.[4] Moreover, the low hydrogen equilibrium pressure of many binary hydrides AH_2 (with $A=$Y, Zr, Ce, and Ca) excludes them as conventional storage materials.

Technologically more convenient pressure-composition isotherms can be obtained by intermetallic compounds through alloying metals with a high hydrogen affinity (rare earths, Y, Zr, Ti) and $3d$ elements which have nearly no affinity to hydrogen.[5] While the electronic properties of elemental hydrides AH_x (with $A=$Y, Zr, Hf, Er, and Pr) which are formed over a wide compositional range ($x=1$–3) are theoretically and experimentally well studied,[6–8] there is a lack of detailed understanding of the electronic properties of metal-compound hydrides.

The present work reports the first synchrotron radiation investigation on the hydrogenation of YFe_3 and YFe_2. These compounds absorb hydrogen in large quantities after an initial activation obtained at higher temperatures and at a H_2 pressure of 40 atm. Hydrides up to $YFe_3H_{4.8}$ and $YFe_2H_{4.2}$ are formed by absorption of hydrogen at 50 °C.[9] The hydrogenation increases the lattice volume by ~20% but does not change the initial crystal structure which is $PuNi_3$ type for YFe_3 and $HgCu_2$ type for YFe_2.[5] The low hydrogen equilibrium pressure which is less than 10^{-5} atm allows an *in situ* study of the early stages of hydride formation in an ultrahigh vacuum.

II. EXPERIMENTAL

The samples were prepared by arc-melting followed by annealing under vacuum. X-ray diffraction with monochromatized CuK_α radiation was used to determine their crystallographic structure and homogeneity. Samples were exposed to H_2 atmosphere in the 10^{-4}–10^{-7}-Torr range at different temperatures between 300 and 700 K.

The photoemission measurements were performed using synchrotron radiation from the electron storage ring Tantalus of the University of Wisconsin, Madison. The radiation was dispersed with an ultrahigh-vacuum grasshopper monochromator. The base pressure of the vacuum chamber during each run was in the 10^{-11}-Torr range. Photoelectron energy analysis was carried out with a double-pass cylindrical mirror analyzer (CMA) used in the angle-integrated mode. The total energy resolution (monochromator and analyzer) was experimentally determined from the width of the photoemission onset at the Fermi level to be ~0.35 eV.

The samples were cut in the form of plates of $5\times4\times1$ mm^3 and were mounted so that their surface normal was at an angle of 42° with respect to the CMA axis and the angle of incidence at ~30° with respect to the sample surface.

Surface contamination has been removed by bombardment with Ar ions at an energy of 500 eV. After several hours of cleaning, well-developed oxide-free core lines of Y and Fe have been measured at $E_B(\mathrm{Y}\,4p_{3/2})=26.1(3)$ eV, $E_B(\mathrm{Fe}\,3p)=52.8(3)$ eV, and $E_B(\mathrm{Fe}\,3s)=91.8(3)$ eV. The valence band spectra showed, however, small amounts of Ar $3p$ emission at 11 eV which could be re-

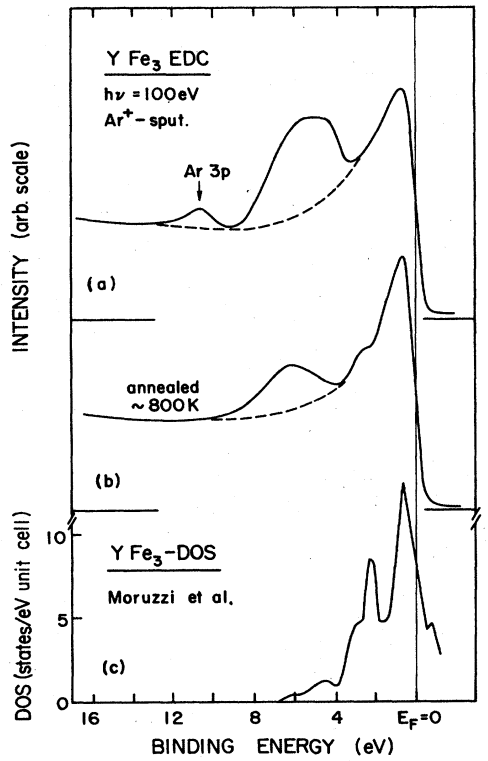

FIG. 1. (a) Valence band photoemission spectra of YFe_3 obtained at $h\nu = 100$ eV after sputtering with Ar ions of 500 eV kinetic energy. (b) Valence band EDC after annealing at 300 K for 10 min. (c) Total density of states of YFe_3 from Ref. 10.

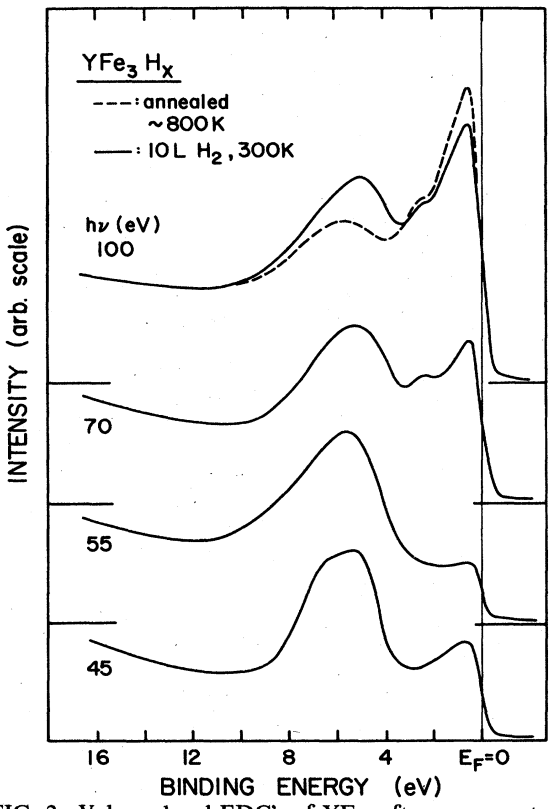

FIG. 2. Valence band EDC's of YFe_3 after exposure to 10-L H_2 at 300 K obtained with different photon energies. [1 langmuir (L) $\equiv 10^6$ Torr sec.]

moved by an annealing of the samples for 15 min at ~600 K.

III. RESULTS AND DISCUSSION

A. Hydrogen-induced features: Low coverage

The valence band energy distribution curves (EDC) of YFe_3 obtained at $h\nu = 100$ eV are shown in Figs. 1(a) and 1(b) after each step of the cleaning procedure. The annealing of the sample narrows and reduces the intensity of the broad structure of ~5.3 eV of binding energy and, moreover, makes a new feature at ~2.5 eV appear. Since the ratio of intensities of Y 4p and Fe 3p core lines does not change with prolonged sputtering, a preferential sputtering mechanism leading to a substoichiometric surface composition can be excluded.

After several cleaning cycles, the Y 4p core line spectrum does not show additional oxide structures. Since the photoemission cross section at low photon energy is bigger for O 2p than that of Y 4p and Fe 3p, we still cannot completely rule out the possibility that the 5.3-eV feature is related to O 2p emission. Reduction of the surface oxide by heating the samples at elevated temperatures in a H_2 atmosphere did not remove this valence band structure but increased it further. Since the intensity of the 5.3-eV structure increased with H_2 exposures, it is more likely a H_2-induced feature. Moreover, this structure is not related to YFe_3 valence band emission as can be seen by comparison with theoretical calculations.[10]

The total density of states (DOS) of pure YFe_3 calculated by Moruzzi *et al.*,[10] shown in Fig. 1, reproduces the peaks at 0.5 and 2.5 eV below E_F whereas the structure at 5.3 eV has no counterpart. However, it is close to the bottom of the valence band and the theoretical DOS exhibits a weaker third structure around 4—6.5 eV below E_F. The small DOS in this region is due to s-p-like bands while the high DOS around E_F arises mainly from electrons having d-band character. Thus the different partial photoionization cross sections for s-p- and d-like states should produce a much less intense emission around 6 eV.

Although the theoretical comparison has been limited to YFe_3, it can also be extended to YFe_2 since band structure calculations[11] using a tight binding approximation reveal a total d-band DOS for YFe_2 which is similar to that of YFe_3.

The high affinity of Y-based 3d compounds to hydrogen supports further the conclusion that the 5.3-eV structure is related to hydrogen-derived bands. Similar structures have been observed in synchrotron radiation[6] and x-ray photoemission experiments[7,8] on d-band metal hydrides. Small H_2 contaminations of the vacuum system which cannot be avoided easily do result in an early stage of the formation of YFe_3 hydrides.

The reaction of hydrogen with YFe_3 is shown in the upper part of Fig. 2. In comparison with the annealed sample, exposure to 10-L H_2 leads to a reduction of d-

state emission at E_F and to a further increase of the 5.3-eV structure.

B. Resonance effect

Valence band photoemission spectra taken at different photon energies do show similar structures but with different relative intensities (Fig. 2). At $h\nu=55$ eV the intensity of the peak at 0.5 eV below E_F goes through a minimum. The shoulder at ~ 2.5 eV below E_F weakens and cannot be resolved at photon energies below $h\nu<70$ eV.

Intensity modulations of the valence band emission are quite common and have been observed for d- and f-band metals.[12–14]

The effect of resonant photoemission can be used as a spectroscopic tool to determine the angular character of the local valence band DOS.[15] The strong resonant reduction of emission at E_F can be used to investigate the changes in the d-like DOS at different stages of hydrogenation. For compounds containing $3d$ metals the excitation of a $3p$ core level gives rise to a discrete excited $3p^5 3d^{N+1}$ state which may decay, via a super-Coster-Kronig (SCK) transition, into a continuum $3p^6 3d^{N-1}\,\epsilon_f$ final state. Since the direct valence band photoemission $3p^6 3d^N + h\nu \rightarrow 3p^6 3d^{N-1}\,\epsilon_f$ leads to the same final state both channels may interfere and give rise to resonances or antiresonances in the photoemission cross section.[16]

Figure 3 shows the resonance effect at $h\nu\sim 55$ eV for the YFe_3 which had been exposed to 10-L H_2 at room temperature. The intensities of the valence band structure at initial energy $E_i=0.5$ eV below E_F, which had been normalized with respect to the intensity of the EDC's at 15 eV, shows a well-developed dip at $h\nu\sim 55$ eV. The choice of the reference point at 15 eV of binding energy has been used since it is not affected either by valence band structures or the onset of additional Auger emission. Thus it can be used to correct the valence band intensities against the monochromator response function.

The normalized EDC intensity at $E_i=5.3$ eV shows an analogous but weaker resonant effect. The amplitude of the EDC at $E_i=5.3$ eV has been corrected against the inelastic background by assuming a linear increase from E_F up to the tail of secondary electrons.

Since both initial states ($E_i=0.5$ and 5.3 eV) resonate around the Fe $3p$ threshold they have to be of d symmetry. The weaker resonance at $E_i=5.3$ eV can be explained by a less-pronounced d-like character of the hydrogen-induced EDC structure.

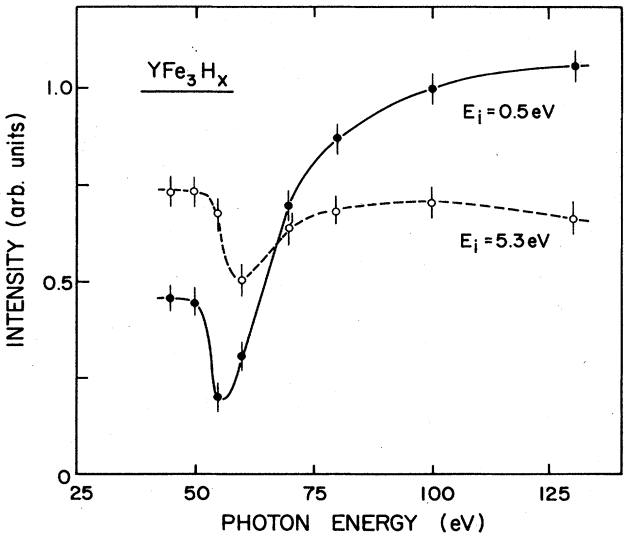

FIG. 3. Photon energy dependence of the emission at $E_i=0.5$ and 5.3 eV below E_F for YFe_3 exposed to 10-L H_2 at 300 K.

C. Metal to semiconductor transition

The effects of higher hydrogen exposures to YFe_2 are shown in Fig. 4. Valence band EDC's are taken around the resonance energy at $h\nu=55$ eV and at $h\nu=100$ eV. The spectra are very similar to those obtained for YFe_3 after the equivalent H_2 exposure as expected from the similarity of the main features[10,11] between YFe_3 and YFe_2 DOS's.

Room-temperature adsorption is saturated after an exposure to 10 L of H_2. A further change in the valence band EDC can be obtained by exposures at higher temperatures. The 5.3-eV peak sharpens and increases considerably after an exposure at 10^3 L of H_2 at 700 K while the emission due to the region close to E_F is strongly re-

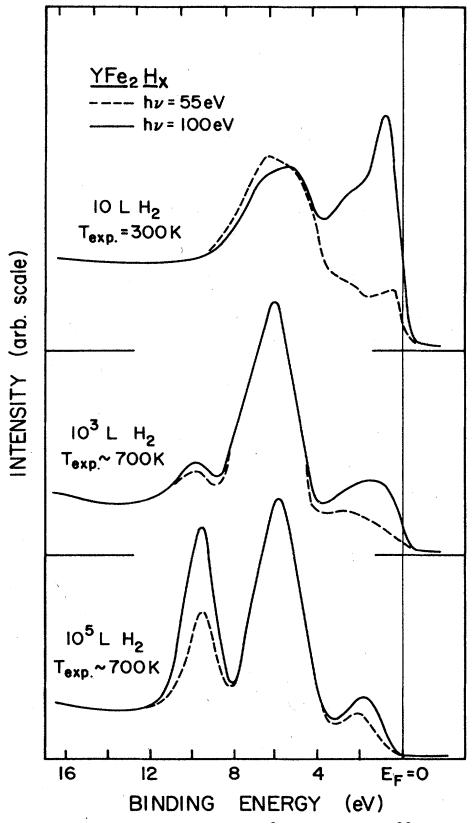

FIG. 4. Valence band EDC's of YFe_2 at different stages of hydrogenation obtained at photon energies of $h\nu=55$ eV (dashed line) and $h\nu=100$ eV (solid line). T_{exp} indicates the temperature at which the sample has been exposed to hydrogen.

duced and a new structure arises at 10 eV of binding energy. The comparison between the spectra taken around the resonance energy ($h\nu=55$ eV) and out of resonance ($h\nu=100$ eV) show that d-like states have been drastically removed from E_F. Both effects, the decrease of d-like state at E_F and the filling of a new state at ~ 10 eV, increase further with higher hydrogen exposures.

The electronic properties of the sample changed with increasing hydrogenation from metallic to semiconductor behavior. Extrapolating from the top of the valence band emission, we obtain an energy gap $E_0=0.3\pm0.1$ eV for the highest H_2 exposure by assuming that E_F is located at the bottom of the conduction band.

A metal to semiconductor transition[2,17] has been predicted for the system YH_x with $x\sim2.8$ by Switendick.[2] Since there is the lack of proper theoretical calculations of intermetallic compound hydrides we will use arguments in analogy to those describing the electronic properties of elemental hydrides.[2,3,17–19]

These theories predict that each H atom which is inserted into the unit cell will form a new band below the bands with predominant metal d character. Due to the hybridization of these hydrogen-induced states with metal d states, these new bands will have also some d character. Thus for the dihydrides, two hydrogen-induced bands form below the d bands and accommodate four of the five valence electrons. Since the fifth valence electron partially fills the metal d bands, the dihydride is metallic. Consequently, the trihydride will have a semiconductor behavior because the three-hydrogen-induced bands accommodate all of the six valence electrons.

The hydrogen-induced effects, the removal of d-like states around E_F, and the formation of a new structure at ~ 5.3 eV below E_F, which are seen in the valence band spectra of YFe_2 and YFe_3 during the different stages of hydrogenation, are similar to those of elemental hydrides whereas the appearance of a third peak at 10 eV below E_F seen for higher exposures has no counterpart in elemental hydrides.

Since elemental hydrides do undergo different phase transitions with different hydrogen occupation sites, whereas yttrium-iron hydrides do not change their crystal structure, it may not be appropriate to compare the electronic structure of these two systems at least for higher hydrogen concentrations.

For the understanding of these problems a detailed theoretical analysis seems to be necessary. The ability of yttrium-iron compounds to form stable hydrides up to $YFe_2H_{4.8}$ around room temperature cannot easily be explained either by the high H_2 affinity of Y or by its contribution to the electronic properties of the compound. Actually, local density-of-states calculations[11] of YFe_2 do show only a negligible amount of Y d states within the first few eV below E_F.

IV. CONCLUDING REMARKS

Ternary hydrides of the type MFe_2H_x were obtained for various hydrogen concentrations by Viccaro *et al.* and their magnetic properties studied by ^{57}Fe Mössbauer spectroscopy.[20] Their results showed that H_2 absorption leads to an increase in the Fe magnetic moment up to a H_2 concentration of $x\sim3.7$. For $x>3.7$ the magnetic moment decreased drastically. The result of the present photoemission study correspond closely to this behavior since the prerequisite for the formation of the $3d$ moment, i.e., the high d-like density of states at E_F, was shown to be absent in the case of high H_2 exposures.

However, the pressure composition isotherms of YFe_2H_x and YFe_3H_x are such that the bulk hydrogen content must be considered to be low under the present experimental condition.[21] For this reason we are led to the conclusion that features observed in the valence band spectra reflect mainly hydrogen-induced changes close to the surface region of the samples.

Besides the theoretically expected behavior of a metal to semiconductor transition with increasing H_2 content we observed a new strong feature at ~ 10 eV below E_F in the valence bands of YFe_2 and YFe_3 after high H_2 exposures.

The appearance of a second hydrogen-induced metal band cannot be explained within the anion model proposed by Switendick[2] to explain the band structure of binary hydrides. It seems that at higher H_2 contents the so called proton model which assumes charge transfer from the hydrogen to metal d states, and as a result of this a splitting of metal states, is more appropriate to describe the electronic structure of ternary hydrides. It should be recalled that the hydrogen content of the ternary hydrides ($YFe_2H_{4.2}$ and $YFe_3H_{4.8}$) when expressed as the number of H atoms per Y atom is considerably larger than that of YH_3 for instance.

Further experiments are planned including an investigation of the core line shifts during the hydrogenation stages as well as the quantitative determination of the absorbed hydrogen. Studies will also focus on the so-called activation treatment of the compounds. Since this is generally a procedure necessary to initiate the high room-temperature H_2 uptake, it seems to be a crucial step controlling the H_2 dissociation at the surface and diffusion into the bulk.

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