

Theoretical and experimental investigation of the electronic structure of Ti–Zr–Ni and Ti–Zr–Ni:H alloys

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Abstract

We have calculated the band structure of a model 1/1 approximant of cubic Frank-Kasper type structure of the icosahedral Ti–Zr–Ni quasicrystal. We have shown that the electronic structure is dominated by the metals d bands with a complete mixing of Ti and Zr states. With respect to the pure metal, Ni d states appear to be strongly modified upon alloying. The experimental investigation of the icosahedral alloy shows good agreement with the theoretical calculations for the approximant. We have shown experimentally that dramatic modifications of both occupied and unoccupied states occur in the hydrogenated quasicrystal, due to bonding to H. We have asserted preferential Zr–H rather than Ni–H bonding. We have suggested that Ti–H bonding should also be significant. We interpret the high H/metal ratio by the fact that H bonds to each of the elements in the quasicrystal.

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1. Introduction

Transition metals form hydrides rather easily. Many of them are already used in commercial devices such as power sources for computers. A limitation arises in that the hydrides are often stable and thus, do not allow for H loading–unloading cycles. Quasicrystals belonging to the Ti–Zr–Ni system are promising materials as they are able to reversibly store important amounts of H. Indeed, the as-cast stable $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ approximant Laves phase as well as the stable annealed icosahedral $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ compound accept H up to a H/metal ratio of 1.7 [1].

Therefore one open question relates to H bonding in such materials, requiring that the electronic structure is probed. On the one hand, this can be done theoretically by calculating the band structure and projected densities of electronic states for model structures that mimic the icosahedral order or approximants for which the positions of the atoms are known. On the other hand, various

techniques make it possible to achieve an experimental investigation of the valence and conduction bands of both quasicrystals and their approximants. Here we present a theoretical study of the electronic structure of the 1/1 approximant $\text{W-Ti}_{52}\text{Zr}_{32}\text{Ni}_{16}$ [2], as well as an experimental investigation of valence and conduction states in quasicrystalline $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ and $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}:\text{H}_{1.4}$, respectively. We introduce the theoretical calculations in Section 2, whereas Section 3 recalls the underlying principles of the experimental technique and gives some details about the measurements. The results are reported and discussed in Section 4 and a conclusion is given in Section 5.

2. Band structure calculations

The band structure calculations were done for the 1/1 approximant $\text{W-Ti}_{52}\text{Zr}_{32}\text{Ni}_{16}$ described as a cubic Frank-Kasper type structure consisting of a body centred cubic packing of Bergman clusters with the centre fully occupied [2]. The ab-initio total energy calculations were performed with the Vienna Simulation Package code, the so-called

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VASP [3,4], which is a density functional code using a plane-wave basis and ultrasoft Vanderbilt type pseudopotentials [5,6]. The calculations used the generalised gradient approximation [7] and a plane-wave kinetic-energy cut-off of $E=302.0$ eV to ensure convergence. The pseudopotentials for Ti and Zr involved the usual outer shell states and also the 3p and 4p states, respectively, as valence states. The DOSs were calculated for different tiling structures [2] with an $8 \times 8 \times 8$ k-point mesh resulting in 34 k-points in the irreducible part of the Brillouin zone. Note that the limited size point mesh used for the DOS calculations of the large unit cell structures leads to spiky projected DOSs [8,9]. As our work does not focus on the fine structure of the DOSs but rather on the features on a larger energy scale and since there is a smoothing effect inherent in the experimental technique (see next section), we will not discuss the spiky structure in more detail. The energies given relative to E_F are negative for occupied states (valence band: VB) and positive for unoccupied (conduction band: CB).

3. Experimental techniques: principles and procedure

One technique useful for investigating the electronic structure of a material whatever it is (powder, bulk, crystal, amorphous, metal, insulator...) is X-ray spectroscopy that involves transitions between two different quantum states of the system therefore giving direct insight into the electronic structure [10,11]. There are two complementary techniques: X-ray emission spectroscopy and X-ray photo-absorption spectroscopy, labelled XES and XAS, respectively.

XES probes the radiative recombination of a core hole of the sample. One interesting channel is the transition of an electron from the VB towards the inner vacancy. In XAS, a core electron is promoted towards the normally empty CB states. Both processes leave a remaining hole in the outermost band of the solid: they must obey dipole

selection rules, namely $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$; hence, XES and XAS are partial probes. Because of the overlap between the localised initial state with the rather extended final state (the remaining hole in VB or CB), XES and XAS are also local probes. The energy distribution curves reflect the product $|M|^2 N(\epsilon) * L(\epsilon)$ where $N(\epsilon)$ is the analysed partial DOS and $L(\epsilon)$ is a Lorentzian energy distribution whose FWHM is the energy width of the inner level involved in the X-ray transition. Accordingly, VB and CB states of chosen spectral character around each component of a system can be analysed separately. The variation with energy of the transition probability is usually negligible over the width of a band. Hence, there is a direct relationship between the spectral distributions and the investigated $N(\epsilon)$ and changes in the shape of the spectral curves of a definite element from one sample to another one are directly related to modifications in the probed partial VB or CB DOSs.

We used several samples prepared according to Ref. [12]. The X-ray transitions that were probed are indicated in Table 1 together with a few experimental details. The VB Zr and Ni d-s states were examined with a vacuum spectrometer fixed with a crystal bent under a radius of 50 cm; the excitation of the spectra was produced by incoming photons and the sample was kept at liquid nitrogen temperature so as to avoid H escaping from i-TiZrNi:H while measuring. The unoccupied p and d states were scanned at the synchrotron radiation facility of LURE (Orsay, France) at lines SA32 in the yield mode (Y) or EXAFS 13 in the transmission mode (T) [13]. The final instrumental energy resolutions were ~ 0.5 eV in all cases.

As the XES and XAS techniques do not provide absolute DOS values, the experimental curves shown here, that are given in the X-ray transition energy scales (different from one transition to another), are all normalised to their maximum intensity after accounting for an appropriate background. This is taken as linear for the XES spectra. In XAS, the intensities are obtained from the ratios I/I_0 or $\log I/I_0$ in the Y and T modes, respectively. I_0 is the intensity of the incident photon beam; I is either the

Table 1
X-ray transitions

X-ray transition	Probed states	Investigated energy range (eV)	Experimental technique	Monochromator
Zr $L\beta_{2,15}$: VB \rightarrow Zr $2p_{3/2}$	4d-5s*	2200–2240	XES	Beryl 100
Ni $L\alpha$: VB \rightarrow Ni $2p_{3/2}$	3d-4s*	840–860	XES	Beryl 100
Zr L_{III} : Zr $2p_{3/2} \rightarrow$ CB	s-d	2215–2250	XAS (Y)	Si 111
Ni L_{III} : Ni $2p_{3/2} \rightarrow$ CB	s-d	845–875	XAS (Y)	Beryl 100
Zr K: Zr $1s \rightarrow$ CB	p	17950–18040	XAS (T)	Si 311
Ti K: Zr $1s \rightarrow$ CB	p	4950–5030	XAS (T)	Si 311
Ni K: Zr $1s \rightarrow$ CB	p	8310–8410	XAS (T)	Si 311

The transition probability favors d states against s states. Consequently, in these measurements, there is no view of s states contribution to the spectra that mainly reflect the VB d states.

yield current intensity or the intensity of the transmitted photon beam.

4. Results and discussion

The calculated DOS for the 1/1 W-approximant is dominated by a wide d-band complex, which is structured into a number of subbands. E_F lies more or less in a valley of the DOS. In order to understand the origin of the different subbands, site projected densities of states were calculated and are presented in Fig. 1a–c for the partial s, p and d DOS of Ti, Zr and Ni, respectively. In the pure elements the VB states are dominated by the d states that extend over ~ 4 eV below E_F [14], s states of quite low intensity are present at about -3 eV for Ti and Zr and below -4 eV for Ni. In the alloy, this is still true as far as Ti and Zr states are concerned: the d states display two onsets of peaks centred around $E_F - 0.8$ and $E_F - 3$ eV. Let us mention that for binary transition metal alloys, the hybridisation effects lead to a transition from a common-band regime, for small differences in the energies of the atomic d-states of the constituents, to a split-band regime at increasing differences in the d levels [15]. This effect is observed here. The Ti and Zr d DOSs have a similar shape, show a complete mixing (hybridisation) and exhibit major contributions around E_F whereas the Ni d DOSs differ significantly and are mostly located at energies below -2 eV. This indicates a large charge transfer from the Ti and Zr atoms to the Ni atoms, consistent with the higher electronegativity of Ni (1.75) as compared to Ti (1.32) and Zr (1.22) [16]. The DOSs show a local minimum near E_F , with the smallest value of the DOS at about -0.1 eV. In general, one expects a reduction of the DOS near E_F to provide a stabilising contribution to the electronic energy [17]. Indeed, the stabilising effects of a Fermi-level gap are apparent in covalently bonded materials, that have both strong bonds and band gaps. Such a full gap does not exist in metallic compounds like those discussed here, however, the ‘pseudogap’ at the Fermi level contains in partial fashion the stabilising effect of the gap. The Ti and Zr empty states in the W-crystal show that, like in the pure elements [14], there is a strong contribution of d states over $E_F + 2$ eV with some contribution of p states. For Ni, the d states are once more pushed beyond about $E_F + 1$ eV whereas they are at E_F and just above in the pure metal. So, the first Ni empty states are mixed p-d states. Altogether, our data are in good agreement with the results of a calculation of the band structure of a 1/1 approximant of nominal composition $Ti_{46}Zr_{37}Ni_{17}$, performed using the TB-LMTO method. This calculation pointed out the presence of a deep pseudogap whose minimum is slightly shifted from E_F [18]. Note that we have measured the binding energies of Ti, Zr and Ni 2p states in $i-Ti_{53}Zr_{27}Ni_{20}$ owing to photoemission experiments. The

sample was rather oxidised. Accordingly, the spectra were dominated by the oxide signal for Ti and Zr for which, within a precision of ± 0.5 eV, we did not observe any shift with respect to the pure elements. On the contrary, with respect to pure Ni, we measured a shift of ~ 0.8 eV for Ni, thus confirming the strong changes of Ni DOSs upon alloying with Ti and Zr.

Because of the broadening of the DOSs by the inner level involved in the X-ray transitions and the spectrometers instrumental functions, one expects rather smooth shapes for the experimental energy distribution curves. Indeed, this is what we observe in Figs. 2–4 for the $i-TiZrNi$ and $i-TiZrNi:H$ compounds. In Fig. 2, we display the CB p-states distribution curves for Ti, Zr and Ni, respectively, in the pure elements and in the $i-TiZrNi$ and $i-TiZrNi:H$ compounds. Upon alloying, the pre-peak P due to s-p states at the edge of Ti decreases in intensity and features A and B beyond E_F are smeared out and shifted towards high energies. In contrast, the shape of the Zr p states is hardly modified: there is only a smoothing of features A, B and C above the absorption edge. For Ni, the feature just above the edge is more marked in the alloy than in pure Ni, peak A is shifted towards low transition energies and B and C are hardly noticeable. Upon hydrogenation, for all elements, the edges are shifted towards high energies and structures A, B and C are usually more marked than in the i-compound. Zr p states are more significantly repelled from the energy position of the edge in pure Zr. For Ni, and Ti, there are some additional states as shown by an arrow on the figure. With respect to $i-TiZrNi$, peak A of the Ni curve is pushed to high energies whereas it is found at lower energies in Ti. We ascribe all these changes to modifications in p-s hybridised states upon alloying in $i-TiZrNi$ and, in $i-TiZrNi:H$ we suggest it is due to mixing with H s states.

One expects stronger changes in d-s states distributions as s states are more extended in character than the p states. We show in Fig. 3, the distributions of Zr and Ni d states in pure metals and in $i-TiZrNi$. For Zr, upper panel, by referring to the DOS of pure Zr [14], we ascribe features A and C mainly to the contribution from t_{2g} and s orbitals, whereas feature B should come from both t_{2g} and e_g orbitals. In $i-TiZrNi$, structure A decreases appreciably, therefore the balance between the occupation of t_{2g} and e_g orbitals favors the latter ones. This is even more marked in the hydrogenated sample where there is a depletion of states in the energy range of feature B and an inversion in the intensities of features B and C with respect to $i-TiZrNi$. This suggests d-e_g states are dominant. Note that in the pure metal as well as the i-alloy the d states are present in this energy range. In the hydrogenated compound, some enhanced contribution from s states arising from mixing with s states from H can also be invoked to interpret this inversion of intensity. The absorption jump considered between the foot of the curves before the maximum at the

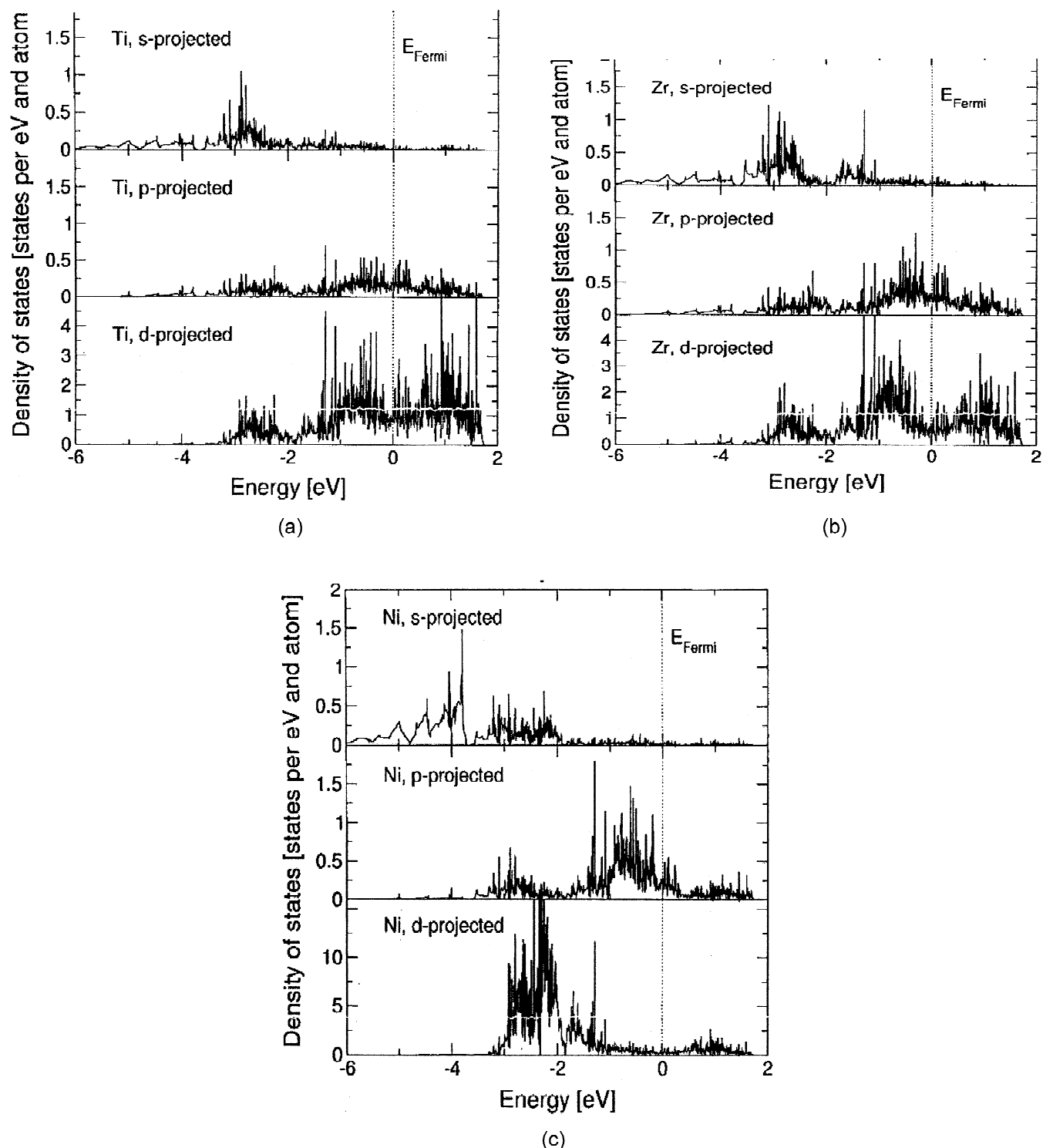


Fig. 1. (a) Ti projected calculated DOS. (b) Zr projected calculated DOS. (c) Ni projected calculated DOS.

edge and the curve quite far from it decreases from pure i-TiZrNi to i-TiZrNi:H. This gives an indication that the localised character of the empty d states increases upon hydrogenation. Ni d states in i-TiZrNi are strongly modified with respect to pure Ni. In the pure metal, the spectrum shows an intense peak above the edge, due to d

states, followed by two structures denoted Σ and σ , due to s states. In addition there is a faint absorption jump. In i-TiZrNi, the peak after the edge is noticeably broadened and Σ is no longer visible whereas σ is pushed towards increasing energies; the absorption jump is rather significant. This means that d states above the edge are mixed to

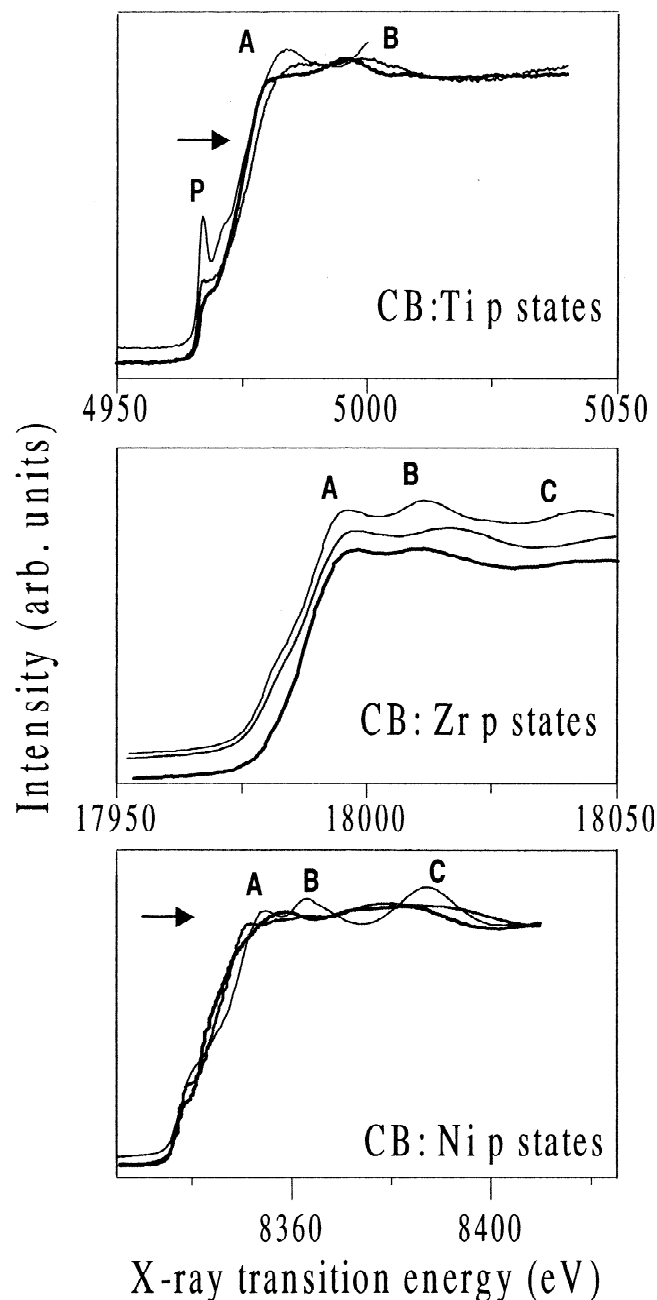


Fig. 2. Experimental p states distribution curves for Ti (upper panel), Zr (middle panel) and Ni (lower panel). The thin lines correspond to pure metals, the thick lines are for the elements in the i-sample and the thicker lines (lower lines in each panel) are for the same elements in the hydrogenated i-compound.

s states and therefore the localised d character is less marked in the alloy than in the pure metal. No measurements have been made to date for i-TiZrNi:H.

The Zr and Ni occupied d states in i-TiZrNi and i-TiZrNi:H are presented in Fig. 4 upper and lower panels, respectively. For clarity, the spectral curves for the pure elements are not shown as their shapes are similar as in the alloys. Both curves for the hydrogenated samples exhibit a feature labelled as S on the low energy side of the bands.

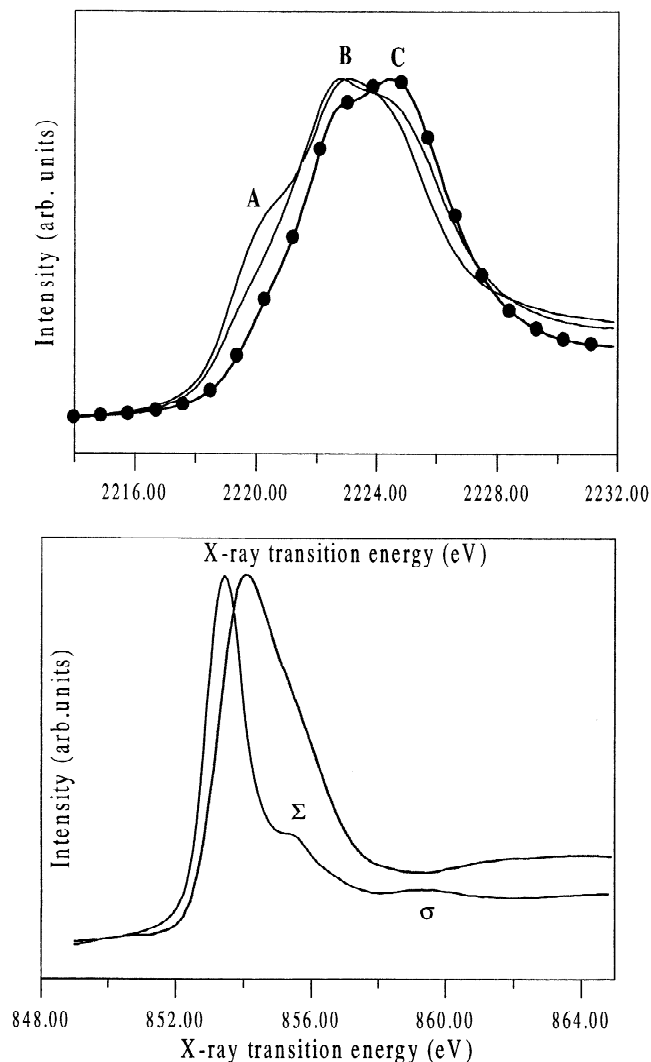


Fig. 3. Upper panel: Zr L_{III} spectra in pure Zr (thin line), i-TiZrNi (thick line) and i-TiZrNi:H (thick line with symbols). Lower panel: Ni L_{III} spectra in pure Ni (upper line) and i-TiZrNi (thick line).

A previous investigation of Pd:H, by theoretical as well as experimental means [19], has shown that additional states due to hybridisation between Pd d states and H s states are present on the low energy wing of the Pd 4d band. Here, by analogy, we ascribe the additional states corresponding to bump S as resulting from transitions to the Zr or Ni core holes from metal d states mixed to H s states. The differences in intensity of bump S in Zr and Ni bands suggests H bonds preferentially to Zr although bonding with Ni also exists. This result confirms our interpretation of the modifications pointed out in the empty Zr d-s states that should arise from states hybridised to H-s states.

5. Conclusion

In this work we aimed at investigating the effect of hydrogenation on the electronic structure of i-TiZrNi

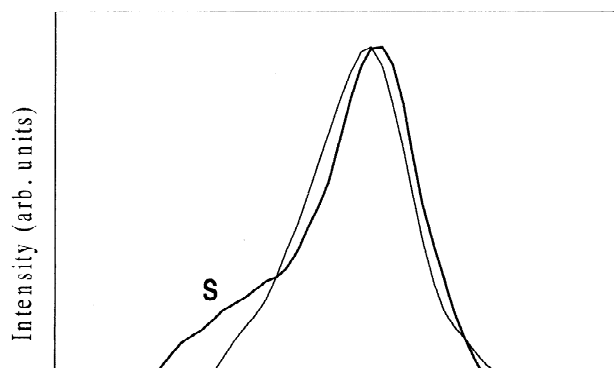


Fig. 4. Upper panel: Zr 4d states in i-TiZrNi (thin line) and i-TiZrNi:H (thick line). Lower panel: Ni 3d states in i-TiZrNi (thin line) and i-TiZrNi:H (thick line).

quasicrystal. We have calculated the band structure of a model approximant of the icosahedral intermetallic and have shown that the electronic structure is dominated by the metals d bands. We have stressed a complete mixing of

Ti and Zr states that lie close to E_F and in the centre of the VB whereas Ni states pushed far below E_F . The experimental investigation of the icosahedral alloy shows good agreement with the theoretical calculations for the approximant. From the investigation of the unoccupied states of p and d-s character and occupied states with d-s character, we have pointed out dramatic modifications of both VB and CB states induced by bonding to H. We have shown that H bonds preferentially to Zr rather than Ni atoms. Similarity between changes of the unoccupied Ni and Ti states of p character suggests that Ti–H interaction should also be significant. On the other hand, the fact that H bonds to all the elements in the quasicrystal is in line with the high H/metal ratio.

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