

THE CORRELATION BETWEEN IONICITY OF METAL-HYDROGEN BONDS IN HYDRIDES AND THEIR THERMAL FIRMNESS

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Numerous investigations of correlations between thermodynamic, hydrogen-sorption characteristics of metal hydrides and parameters of their electron structure point to the existence of binder accumulating the abilities of metal-hydride, the stability of its atomic structure with peculiarities of electron structure of valence zone, character of metal-hydride bonds in hydride and the value of transferred charge from metal atoms to hydride atoms (and contrary) as well. One of these bonds has been determined by us [1,2] at investigation of electron structure of hydrides of IV -group metals and intermetallic hydrides of AB and AB₅ composition by the X-ray spectrum analysis. By the direct X-ray spectrum analysis according to the shift of absorption spectrum of metal-components of hydride forming compounds at the transition to their hydrides the correlation between the value of transferred charge from metal to hydrogen and the value of equilibrium, corresponding to the isotherm plateau, pressure, thermal stability of hydride has been established. We can conclude that correlation between the ionicity of metal-hydrogen bonds in the hydrides investigated and their hydride-sorption and thermodynamic properties have been found. As a result of carried out experiments we can note that metal-hydrides which equilibrium pressure at ambient temperature is close to atmospheric and which have low thermal stability and dissociate at rather low temperatures, show practically full lack of ionic part of metal-hydrogen bond, the latter were of covalent or covalent-metallic character. X-Ray investigation of TiFeH_{1,8} and LaNi₅H_{6,9} metal-hydrides, which are widely used nowadays, prove this. In fact, we can see in fig.1 a,b, that at the transition from TiFe to TiFeH_{1,8} there is no shift of K-absorption spectra of titanium and iron within the limits of error. It testifies that titanium and iron have the same charge state in intermetallic compound and its hydride and allows to say that hydrogen atoms at formation of Me-H bond do not give any visible part of the charge to titanium and iron. It means that there is practically no ionic component of metal-hydride bonds in TiFeH_{1,8} hydride. At the same time this hydride has the equilibrium pressure close to atmospheric and low dissociation temperature.

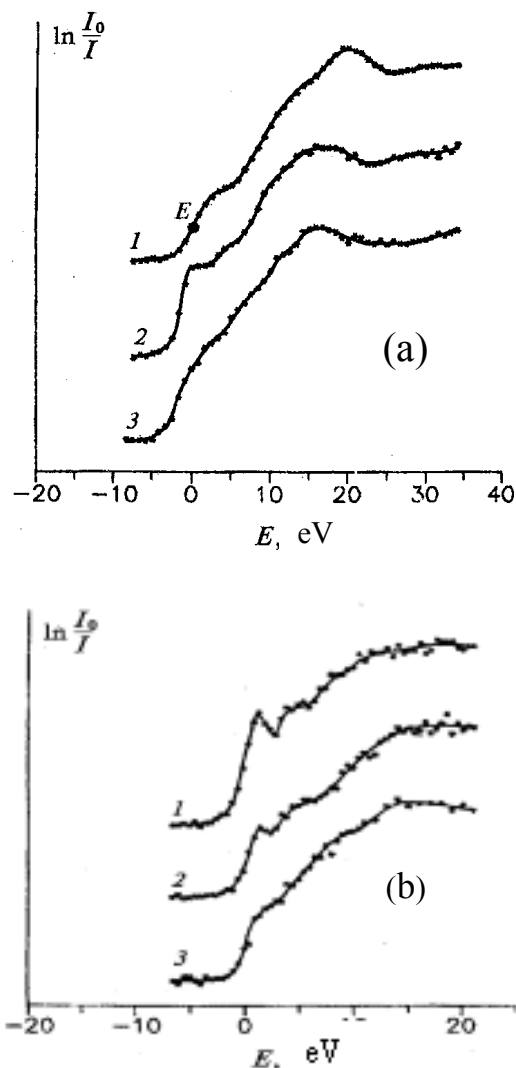


Fig. 1. K-absorption spectra of Fe (a) and Ti (b) in metal-1, TiFe-2, TiFeH_{1,2}-3.

At LaNi₅H_{6,9} hydride formation the charge state of nickel and lanthanum atoms practically does not change and is the same as in LaNi₅. Practically the same position of point "A" on the caves of K-absorption spectra of nickel in LaNi₅ and LaNi₅H_{6,9} and on the caves of L₁₁₁- absorption spectra of lanthanum in these compounds shown in Fig. 2 testify that. This result allows to ascertain the lack of charge transfer from lanthanum and nickel atoms to hydrogen atoms at LaNi₅→LaNi₅H_{6,9} transition and to say about the

lack of ionic component of La-H and Ni-H metal-hydrogen bonds and to characterize these bonds as essentially covalent or covalent-metallic as well. We must confirm that $\text{LaNi}_5\text{H}_{6.9}$ hydride as well as studied $\text{TiFeH}_{1.8}$ hydride decomposes at low temperature and its equilibrium pressure at ambient temperature is close to atmospheric

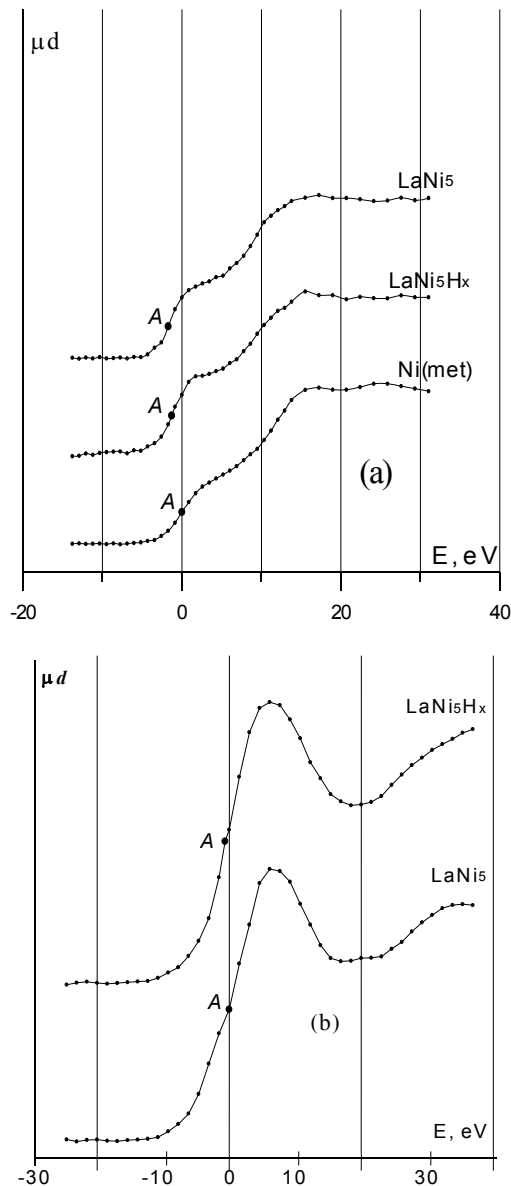


Fig. 2. K-absorption spectra of Ni (a) and L111-absorption spectra of La (b) in LaNi_5 and $\text{LaNi}_5\text{H}_{6.9}$.

The data on character of chemical bonds in binary hydrides of Ti, Zr, Hf [2] and yttrium obtained by us by X-Ray electron spectroscopy testify about the existence of correlation between the degree of ionicity of Me-H bonds in hydrides and their thermal stability. Titanium-hydrogen bonds in $\text{TiH}_{1.83}$ hydride (γ -phase), which

thermally more stable than $\text{TiFeH}_{1.8}$ and $\text{LaNi}_5\text{H}_{6.9}$ and its decomposition temperature is higher than 500°C , and its equilibrium pressure at ambient temperature is lower than atmospheric, cannot be estimated as pure covalent bonds according to X-Ray results (fig. 3). Taking account of 0,9eV shift of K- titanium absorption edge of $\text{TiH}_{1.83}$ comparing with its position in metallic titanium, we can make a conclusion about the transmission by titanium atoms part of their covalent electrons to hydrogen atoms, i.e. about partly ionic character of Ti-H bonds, which have mainly covalent character. The same conclusion can be made at analysis of the character of Me-H bonds in zirconium and yttrium hydrides.

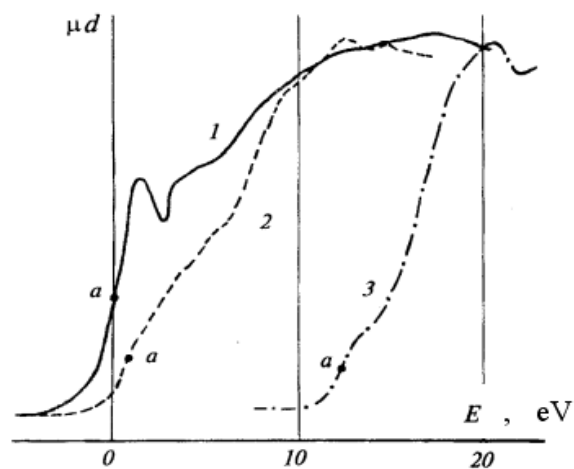


Fig. 3. K-absorption spectra of Ti in metal-1, $\text{TiH}_{1.83}$ -2, TiO_2 -3

Consequently, the study of charge transfer in metal-hydrides, the role of hydrogen charge ion in the formation of their hydrogen-sorption properties allow not only understand better the chemical nature of these compounds but better forecast and rule by their sorption characteristics, for example by doping and so on.

References

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