



ELECTRONIC STRUCTURE OF Mg_2FeH_6 AND Mg_2CoH_5 HYDRIDES AND BINDING ROLE OF HYDROGEN IN THEM

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Participation of d and p symmetry valence electrons of iron and cobalt in metal-hydrogen bonding in the Mg_2FeH_6 and Mg_2CoH_5 hydrides has been investigated on the basis of X-ray emission spectroscopy data. An additional charge acquired by iron and cobalt atoms in the hydrides has been measured and the role played by hydrogen atoms as a binding component in the investigated hydrides has been explained.

Ternary Mg_2FeH_6 and Mg_2CoH_5 hydrides synthesized in the last few years, apart from a high hydrogen storage capacity, exhibit a unique feature which resides in a fact that Mg_2Fe and Mg_2Co alloys don't crystallise without hydrogen. Thus, hydrogen atoms manifest themselves as a binding component of the compounds. Investigation of the crystal structure of these hydrides [1-3] has shown that hydrogen atoms are located at the vertices of an octahedron (incomplete in the case of Mg_2CoH_5) around and immediately adjacent to the transition metal atoms at a distance of 1.5 Å. The interaction with alkali-earth Mg is supposed to be of a distinct ionic nature and therefore terms "pyramidal" and "quadratic-pyramidal" ions have been introduced [1-3], but the charge state of atoms in the hydrides was not investigated. Theoretical calculations of the electronic structure of Mg_2FeH_6 and Mg_2CoH_5 [4-6] have revealed a covalent interaction Fe-H and Co-H. However, X-ray spectral investigation of Mg_2CoH_5 [5] didn't prove the presence of the hybrid states of cobalt and hydrogen, which is not in agreement with the calculation results.

Synthesis of the ternary hydrides was carried out in a high-pressure apparatus with a net volume of 0.23 cm³ and 21.5 mm in diameter. The starting materials were Mg hydride and powders of chemically pure iron and cobalt. Preliminary tests showed that for synthesis of Mg_2FeH_6 a $MgH_2:Fe$ blend should be used taken in proportion 3:1 respectively. Metallic Mg which separates out during the reaction settles in the surface layer of the sample in the high-pressure chamber and readily separates from the hydride preform.

A sample preform 5.5 mm in diameter and 7 mm high is placed in a holder and positioned on centre of a turbular graphite heater. The sample

holder was made of sodium chloride of boron nitride pressed on a special press-mould. Optimum values for synthesis of the said ternary hydrides are the following: pressure is (30 to 40)*10³ bar, temperature is 600 to 800 °C and synthesis time is 5 min.

Ternary Mg_2FeH_6 hydride crystallizes in the cubic structure with a lattice spacing being $a=6.41$ to 6.43 Å (Fm3m space group), and the Mg_2CoH_5 hydride crystallizes as a tetragonal lattice at room temperature with a lattice spacing being $a=4.45$ to 4.48 Å, $d=6.57$ to 6.60 Å (P4/mmc space group).

Fe and Co X-ray L emission spectra were obtained with the use of an ultrasoft spectrometer with secondary excitation of X-ray spectra, with mica being used as a spectrum analyser having a (100) reflecting plane and a resolving power of 0.2 to 0.3 eV. RbAP spectrum analyser was used for measuring the relative integral intensity of $FeL_{d_{1,2}}$ emission, with a resolving power of 0.3 eV. Fe and Co X-ray K emission spectra were obtained using a spectrometer with secondary excitation of X-ray spectra and a photographic recording. Quartz having a reflecting plane (1340) and a resolving power of 0.2 to 0.3 eV was used as a spectrum analyser. Deviations in measuring relative integral intensities did not exceed 6%.

Shown in Fig. 1 are the Fe and Co $L_{d_{1,2}}$ emission spectra (3d-2p transition), which represent the energy spectrum of the d-symmetry valence electrons of these metals. As can be seen from the figure the hybrid subband, which is not present in a pure metal, is observed at the edge of the low-energy branch of the emissions at a distance of 3 to 4 eV from the energy maximum of $L_{d_{1,2}}$. This subband indicates the participation of valence d electrons of transition metals in formation of the subband of

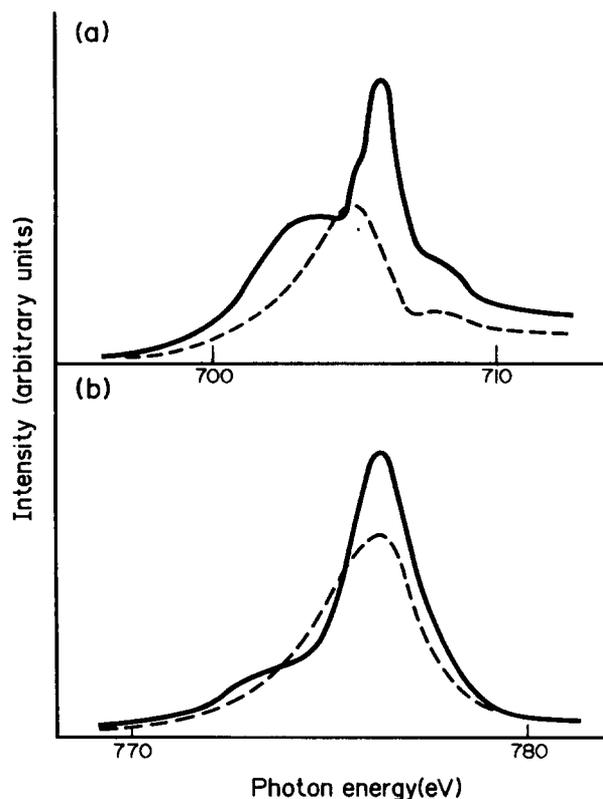


Fig. 1. $L\alpha_{1,2}$ emission spectra in hydrides (full line) and pure metals (broken line): curve a, Fe; curve b, Co. All spectra are normalized to equal intensity of L_1 line.

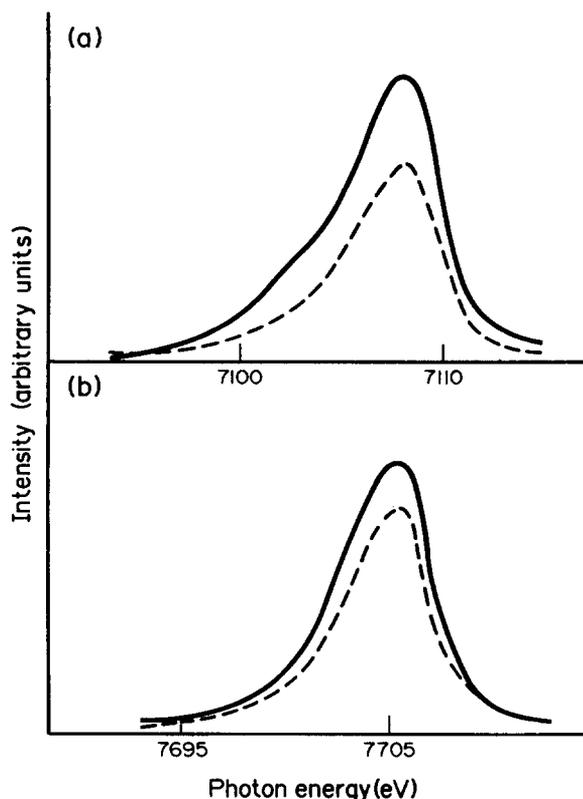


Fig. 2. $K\beta_5$ emission spectra in hydrides (full line) and pure metals (broken line): curve a, Fe; curve b, Co. All spectra are normalized to equal intensity of $K\beta_1$ line.

metal-hydrogen bonding. The intensity of the hybrid subband of the $FeL\alpha_{1,2}$ emission is higher than that of the hybrid subband of the $CoL\alpha_{1,2}$ emission. The energy position of the $CoL\alpha_{1,2}$ emission intensity maximum remains unchanged as compared with a pure cobalt, while in the case of the $FeL\alpha_{1,2}$ emission it shifts in the direction of increasing energy by 0,7 eV. The relative integral intensity of the emissions is increasing in going from metals to hydrides.

Fig. 2 shows Fe and Co $K\beta_5$ emission spectra ($4p-1s$ transition) representing the energy spectrum of p symmetry valence electrons. However, in contrast with the Fe and Co $L\alpha_{1,2}$ emission spectra there are no pronounced changes in the shape of their $K\beta_5$ emission in hydrides compared with a pure metals. Only a little hump reflecting the metal-hydrogen states appears on the low-energy branch of the $FeK\beta_5$ emission. It means that p symmetry valence electrons of iron and cobalt almost do not participate in covalent bonding with hydrogen. The relative integral intensity of the $K\beta_5$ emission in hydrides increases and the energy position of the emission maximum remains practically unchanged.

The charge state of Fe and Co atoms in the Mg_2FeH_6 and Mg_2CoH_5 hydrides was determined on the basis of measurement of the relative integral intensities of the valence emission spectra and the inner lines. A relative change in the number of d symmetry valence electrons of

metal atoms in a hydride as compared to a pure metal was determined from the following equation [8]:

$$R_L = \frac{(IL\alpha_{1,2}/IL_1)_{\text{hydride}}}{(IL\alpha_{1,2}/IL_1)_{\text{metal}}}$$

where $IL\alpha_{1,2}$ and IL_1 are the relative integral intensities of the $L\alpha_{1,2}$ emission and of the core L_1 line respectively which are formed as a result of transition to one and the same inner 2p level of an atom of transition metal. Thus, the change in the number of d symmetry valence electrons in hydride in comparison with a pure metal Δn_d can be determined as follows:

$$\Delta n_d = n_d(R_L - 1)$$

where n_d is the number of d symmetry valence electrons of Fe and Co atoms in a pure metal, determined from self-consistent band calculations [9].

A relative change in the number of p symmetry valence electrons of transition metals in hydrides with respect to pure metals was determined in a similar manner:

$$R_K = \frac{(IK\beta_5/IK\beta_1)_{\text{hydride}}}{(IK\beta_5/IK\beta_1)_{\text{metal}}}$$

where $IK\beta_5$ and $IK\beta_1$ are the relative integral intensities of the $K\beta_5$ emission and of the core $K\beta_1$ line respectively, formed as a result of transition to one and the same inner 1s level. In this case change in the number of p symmetry valence electrons of Fe and Co in hydrides with respect to pure metals Δn_p can be expressed as follows

$$\Delta n_p = n_p(R_K - 1)$$

where n_p is the number of p symmetry valence electrons of Fe and Co in pure metal [9].

The results of measurements of the charge state of Fe and Co atoms in hydrides are shown in the table below:

Table 1. The change in the number of valence d and p electrons of Fe and Co atoms in hydrides as compared to pure metal

	R_L^*	R_K^*	Δn_d^{**}	Δn_p^{**}
Mg_2FeH_6	1.59+0.09	1.41+0.06	3.66+0.56	0.16+0.02
Mg_2CoH_5	1.29+0.06	1.22+0.07	2.22+0.46	0.07+0.02

* arbitrary units

** electrons per atom

As can be seen from the table, atoms of transition metals in Mg_2FeH_6 and Mg_2CoH_5 hydrides have a negative charge. Thus, in the said hydrides a charge transfer to Fe and Co atoms takes place. Hydrogen atoms being located in the first coordination sphere of transition metal atoms and intensely interacting therewith, take part in the charge transfer. However, it is

difficult to suggest that an excessive negative charge on the Fe and Co atoms depends only on the charge transfer from the hydrogen atoms, since in such a case the ionization degree thereof would be too high. Besides, a chemical bond "transition metal - hydrogen" in the investigated hydrides has a pronounced covalent component, which is evidenced by the presence of hybrid states. Mg atoms are also supposed to take place in formation of the excessive negative charge of the Fe and Co atoms. Unfortunately, it is impossible to conduct X-ray spectral investigation of the participation of magnesium atoms in the charge transfer, since the X-ray transition from the 3s level of magnesium is not present.

Thus, the role of hydrogen atoms as binding component in the Mg_2FeH_6 and Mg_2CoH_5 hydrides resides in the fact that they form a chemical bond of a covalent nature with atoms of both the transition metals and magnesium [4-6], thereby contributing to ion interaction, during which they give a portion of their electron density to transition metal atoms. However, Mg-Fe and Mg-Co interaction alone is not sufficient to form stable compounds, and therefore Mg_2Fe and Mg_2Co alloys don't crystallize. As the 3d shell in the transition metal series is occupied the interaction between a transition metal and hydrogen in hydrides decreases (Fig. 1), which is indicative of the fact that the role of interaction between a transition metal and magnesium increases. In the case of Ni the latter is quite sufficient for a stable Mg_2Ni intermetallic compound to exist, which can be formed without hydrogen.

References

1. J.J.Didisheim, P.Zolliker, K.Yvon, P.Fischer, J.Schefer, M.Gubelmann & A.F.Williams, Inorg. Chem., 23 (1984) 1953.
2. P.Zolliker, K.Yvon, P.Fischer & J.Schefer, Inorg. Chem., 24 (1985) 4177.
3. D.Noreus, K.Jansson & M.Nygren, J. Phys. Chem. (BRD), 146 (1985) 191.
4. M.Gupta, J. Less-Common Met., 103 (1984) 325.
5. E.Belin, M.Gupta, P.Zolliker & K.Yvon, J. Less-Common Met., 130 (1987) 261.
6. E.Orgaz & M.Gupta, J. Less-Common Met., 130 (1987) 293.
7. S.G.Porutsky & E.A.Zhurakovsky, J. Less-Common Met., 120 (1986) 273.
8. A.Wenger, G.Burri & S.Steinemann, Solid State Commun., 9 (1971) 1125.
9. V.V.Nemoshkalenko, A.T.Timoshevsky & V.N.Antonov, Dokl. Akad. Nauk U.S.S.R., 253 (1980) 11; A.A.Lisenko, V.L.Bekenev, T.A.Kiyashchenko et al, Preprint Inst. Materials Science Problems Ukr. S.S.R. (Kiev) 15 (1985).