

THE BAND-COVALENT MODEL OF (4f) METAL–HYDROGEN SYSTEM. BONDING FORCES. H ABSORPTION

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The strong H absorption by rare earth 4f-metals (REM) attracts theorist's attention. The special interest arose lately to magnetic properties (T_c , magnetic anisotropy etc. as a function of H concentration). The local-covalent theory of REM magnetism [1] gives the key for solution of magnetic problem of REM-H systems. But the H influence on electric (and magnetoelectric, optic and other) properties is of the same interest. The latter requires more careful analysis of MeH_x band spectra. This problem is discussed in the secondary quantization: the representation of band fermions f_r and many-electron operator spinors (MEOS) for magnetic local (F_r) and covalent (D_r) electrons in sites r [1]. The wave function of H-ion

$$\begin{aligned} \Psi_H^+(\mathbf{r}) &= \xi_b f_r^+ + \xi_L P_r, \\ \sum \xi_j^2 &= 1, \quad N_{r\sigma} = P_{r\sigma} \bar{P}_{r\sigma} \end{aligned} \quad (1)$$

takes into account the transition of valent electron into conduction band (ξ_b) and on covalent bonds (MEOS on its P_r can correspond to both 1 and 2 electrons, the latter gives $H^{(-)}$ in some interpretations).

The local-covalent wave function is

$$\begin{aligned} \Psi^+(\mathbf{r}) &= \xi_D D_r + \\ &+ \xi_F F_r, \quad \{\phi_{r\sigma L}^{(n)}, c_{r\sigma\sigma}, v_{rL}\} = F_r, \quad 0 < n < 7, \end{aligned} \quad (2)$$

coordinate ϕ_r , spin $c_{\sigma r}$ and orbital v_{rL} factors are defined in [1]. The Hamiltonian of bond forces of MeH_x system

$$\begin{aligned} H &= -\sum \Gamma^{DD} D_r \bar{D}_r \xi_D^2 + \sum \tilde{\xi}_k f_k^+ f_k - \\ &- \xi_D x \sum (\Gamma^{DP} D_r \bar{P}_r + \text{H.c.}) + x \sum (\gamma P_r f_r + \text{H.c.}) - \\ &- t_H \xi_b^2 x + x \sum (\omega F_r f_r^+ \bar{P}_r \bar{F}_r + \text{H.c.}) + \\ &+ \sum (\Theta F_r D_r \bar{P}_r \bar{F}_r + \text{H.c.}) \xi_D + \frac{C}{2} u_H^2 \end{aligned} \quad (3)$$

takes into account the covalent bond Me-H (Γ^{DP}), the band-covalent bond (γ), and H influence on magnetic electrons (ω) through the band spectrum too.

The transition into the k-representation gives for interionic bond forces [2]

$$H = H_0 + \sum_k H_k^{(2)} + \dots \quad (4)$$

The intraionic Hamiltonian (taking into account localization of covalent electrons) is also added [2]

$$\begin{aligned} H_i &= H_i^{\text{Me}} + x H_i^H, \quad H_i^H = \\ &= \frac{U_H}{2} \xi_L^4 N_{r\sigma} N_{r,-\sigma} = \frac{U_H}{2} \xi_L^4, \quad \xi_D^2 \ll 1 \end{aligned} \quad (5)$$

where

$$H_i^{\text{Me}} = \frac{U_D}{2} \xi_D^4 + A(\xi_D \xi_F)^2 \sum F_{rS} D_{r\sigma} \bar{D}_{r\sigma} \bar{F}_{rS}. \quad (6)$$

The last term in (6) corresponds to the Hund exchange.

The varying of the sum of H_i and the Hamiltonian, separated from (3),

$$H_0 = -\Gamma \xi_D^2 - x \xi_D \xi_L \Gamma^{\text{DP}} + x \xi_D \Theta K_{\text{FDP}} \xi_L - x t \xi_b^2 \quad (7)$$

on amplitudes of wave functions ξ_i of Me (2) and H (1) ions gives the change of covalent 5d-electrons' density

$$\begin{aligned} \xi_D^2 &= \{ \Gamma^{\text{DD}} + x(\xi_L / 2\xi_{D0}) (\Gamma^{\text{DP}} - \Theta K_{\text{FDP}}) \} / \\ &/ U_D, \quad K_{\text{FDP}} = \langle F_0 D_0 \bar{P}_0 \bar{F}_0 \rangle, \end{aligned} \quad (8)$$

which increases, when direct covalent Me-H bonds $\Gamma^{\text{DP}} > 0$ predominate. The density of 1s-electrons, passing from H ions to covalent bonds, is defined by the same bond

$$\xi_L^2 \cong (\Gamma^{\text{DP}} - 2t_H) / 2U_H > 0$$

at

$$\Gamma^{\text{DP}} \gg 2t_H, \quad \xi_L^2 \rightarrow 1. \quad (9)$$

It is supposed, that the part of 1s-electrons which pass into conduction band, is small. Strengthening of covalent bond leads to the change of Me-H system properties, in particular of magnetic properties.

Deformation $u_H = gx$ is created by hydrogen.

$C_H = Cg^2$ is introduced and H_0 is varied on x . The equilibrium concentration of dissolved H is received

$$\begin{aligned} x &\cong \xi_D \xi_L (|\Gamma^{DP}| - \Theta K_{FDP}) / C_H, \Delta\Phi_0(x) \cong \\ &\cong -x|\Gamma^{DP}|^2 / 2C_H, \end{aligned} \quad (10)$$

which depends on amplitudes of covalent electrons (8) and (9). At $(\xi_D, \xi_L) \rightarrow 1$ H solution is almost completely defined by localization of 1s-electrons of H ions on covalent bonds. When energies of those bonds are $\Gamma^{DP} \sim 1 \text{ eV} \sim C_H$, $x \sim 1$ is received, which is in agreement with experiment.

The influence of temperature T on H solution is taken into account calculating the thermodynamic potential (t.d.p.) $\Phi(x, T)$. $H_k^{(2)}$ is quantized, introducing the MEOS Fourier-images (D_k and P_k) [1,2]. Calculated spectra of chemical (covalent) bond fluctuations (CBF)

$$\begin{aligned} E_D &= \Gamma^{DD} + xR, R = |\gamma|^2 / \Gamma^{DD}, E_p = \\ &= \Gamma^{PP} - xR \end{aligned} \quad (11)$$

give the contribution into t.d.p., whose part strong dependent on x , is

$$\Delta\Phi(x, T) = \alpha_p \Gamma^{5/2} / \tilde{T}_p^{3/2}, k_B \tilde{T}_p = \Gamma^{PP} - xR. \quad (12)$$

Comparison of (10) and (11) gives the critical temperature of H desorption from solution

$$T > T_0 = \left[\tilde{T}_p^{3/2} |\Gamma^{DP}|^2 / C_H \alpha_p \right]^{2/5}. \quad (13)$$

Conclusions

1) The band-local-covalent model of MeH_x for 4f-metals calculates the bond energy as a function of local and covalent amplitudes of wave functions of 4f-electrons.

2) The covalent bonds give the main contribution into t.d.p. in the approximation of small probability of hydrogen electrons transition into the conduction band.

3) The estimation of equilibrium value $x \sim 1$ (for covalent parameter $\Gamma \sim 0,1 - 1 \text{ eV}$) and also of temperature dependence $x(T)$ agrees with experiment.

References

1. Mitsek A.I., Pushkar V.N. Metallofiz. Noveishie Tekhnol. 2005, **27**(12): 1591.
2. Mitsek A.I. Uspehi Fiz. Met. 2005, **6**(3): 233.