

THE INFLUENCE OF HYDROGEN AND ITS DIFFUSION ON FERROMAGNETISM OF 3d-METALS IN THE MODEL OF COVALENT BONDS AND THEIR FLUCTUATIONS

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The equilibrium concentration of hydrogen in ferromagnetic (FM) metal (Me) is calculated by a variational method for covalent and band amplitudes of wave functions of $\text{Me}^{(+)}$ and $\text{H}^{(+)}$ ions. The band spectra and spectra of chemical (covalent) bond fluctuations (CBF) are splitted. It decreases a filling of the conduction band of a Me-H-system. The spin and orbital polarizations of $\text{H}^{(+)}$ -ions change the mean spin, T_c , and FM anisotropy. The contribution of $\text{H}^{(+)}$ in FM anisotropy is large with regard for the spin-orbital bond with rare-earth ions. The contribution of covalent bonds in the diffusion coefficient is found from the motion equation for the complete wave function of an $\text{H}^{(+)}$ -ion. $\text{H}^{(+)}$ diffusion is important in the induction of FM anisotropy.

1. Covalent and Band Electrons. Implantation of Hydrogen $\text{H}^{(+)}$

Since the discovery of large hydrogen absorption by Pd crystals (T.Graham, 1866), numerous theories of metal - hydrogen systems (Me-H) were proposed. That are, as a rule, qualitative models. Each of them interprets some narrow range of experimental data [1, 2]. That are the equation of the mean field (and the classic molecular-kinetic theory of Smirnov et al.), Van der Waals, the spinodal decay, etc., The Mott - Jones band theory (1936) was an important stage. It is actively detalized up to now by modern computer methods (see [1 - 4], etc.). But the insuperable difficulty of the band theory is the necessity to introduce the effective charge Z^* of a hydrogen ion as an experimental parameter (it is different for different Me). So local (covalent and ionic) bonds must be taken into account in addition to metallic collective bonds. The present paper is devoted to this problem.

The changes of properties of a crystal at implantation of hydrogen are large [1, 2]. But they yet are very insufficiently investigated, especially theoretically. The localization of 'dressed' $\text{H}^{(+)}$ ions on defects changes the phase structure (and also strength, local

symmetry, etc.), atomic dynamics, and electronic kinetics [1 - 3]. Only band considerations of interstitials [4] do not allow to take into account $\text{H}^{(+)}$ local bonds (frequently named hydrogenous). The Coulomb repulsion of $\text{Me}^{(+)}$ and $\text{H}^{(+)}$ cations should be taken into account at calculations of the bond energy and the local continual distribution of electronic density. However, the basic influence on the electron localization (and the local spin density of 3d-magnetics) is made by covalent bonds and their fluctuations (CBF) [5]. Hydrogen bonds tend to strengthen the covalency. In a limit of strong hydrogenization (concentration of hydrogen $c_H \sim 1$), it sometimes results in a loss of metallic properties [1, 2].

The sensitivity of hydrogen bonds to the Me-environment has an effect at diffusion. The spatial symmetry of the $\text{H}^{(+)}$ environment in the equilibrium position (in octa-interstice, see Fig. 1,a) is broken, Fig. 1,b. An $\text{H}^{(+)}$ ion passes through a barrier, where the bonds with a pair of $\text{Me}^{(+)}$ ions dominate. Covalent bonds are reconstructed during $r_{el} \ll \tau_D$ (τ_D - diffusion characteristic time). This reconstruction makes easier the $\text{H}^{(+)}$ jump, by strongly decreasing the diffusion activation energy. Just this effect should result in so-called 'quantum diffusion' of $\text{H}^{(+)}$. Its coefficient D_H remains large enough at low temperatures $T \rightarrow 0$ [2].

FM properties of Me-H change both due to spin and orbital polarization of $\text{H}^{(+)}$. The last is connected with $1s - 2p$ transitions. Strong covalent Me-H-bonds should influence a direct exchange Me-Me of the covalent nature, changing the Curie temperature T_c . The $\text{H}^{(+)}$ orbital polarization changes magnetic anisotropy (MA).

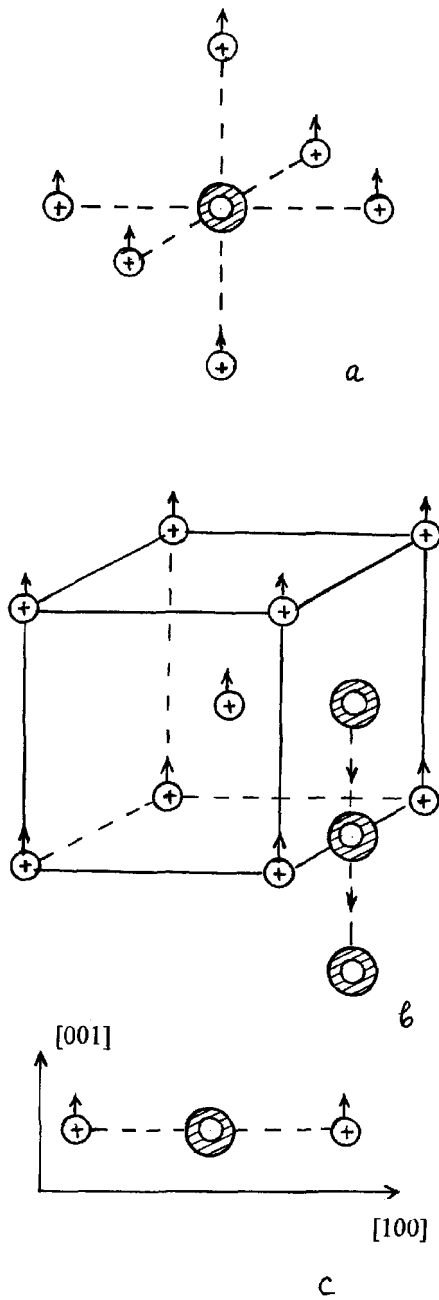


Fig. 1. Covalent bonds Me-H (indicated by dashed lines): *a* - H⁽⁺⁾ position in an octahedral interstice (Me atoms are indicated by circles, arrows are spin directions in the FM phase), *b* - H⁽⁺⁾ jumping through the barrier, *c* - Me-H covalent bonds on the barrier

The account is for one type of interstices \vec{R} . (The generalization of the theory is obvious). The wave function of H⁽⁺⁾,

$$\Psi_{\vec{R}} = \xi_h h_{\vec{R}}^+ + \xi_p \hat{P}_{\vec{R}} \sum \xi_j^2 = 1, N_H = c_H N, \quad (1.1)$$

is composed from band fermions $h_{\vec{R}}$ and multielectronic operator spinors (MEOS) $\hat{P}_{\vec{R}} [\vec{S}]$. N is the density of Me-ions. MEOS contains three factors: coordinate

$$\hat{P}_{\vec{R}} = \{p_{\vec{R}\sigma} c_{\vec{R}\sigma} v_{\vec{R}L}\}, p^+ = \bar{p}, p_{\vec{R}} = p_0 + \sum_{\vec{k}} p_k e^{i\vec{k}\vec{R}},$$

$$p_k = \sum_{\vec{R}} p_{\vec{R}} e^{-i\vec{k}\vec{R}} / N, p_{\vec{R}} \bar{p}_{\vec{R}} = 1, [p_{\vec{k}} \bar{p}_{\vec{q}}]_+ = \delta_{\vec{k}\vec{q}} / N_H, \quad (1.2)$$

spin ($\vec{\sigma}$ - the Pauli matrix) and orbital

$$c_{\vec{R}\sigma}^2 = (1 + \vec{\sigma}\vec{\sigma}_{\vec{R}}) / 2, v_{\vec{R}L}^2 = (1 + \vec{L}\vec{L}_{\vec{R}}) / 3,$$

$$\sigma = 1/2, L = 1. \quad (1.3)$$

Spin ($\vec{\sigma}_{\vec{R}}$) and orbital ($\vec{L}_{\vec{R}}$) H⁽⁺⁾ polarizations are induced by exchange and spin-orbital bonds with local spin $\vec{S}_{\vec{r}}$ of a 3d-ion. Spin polarization of band electrons ($h_{\vec{R}}$ and $f_{\vec{r}}$) is not considered.

Similar to (1.1), the wave function of a Me-ion for 3d- e_g -states ($j=e$, the spin polarization $\vec{s}_{\vec{r}}$), differs from those for 3d- t_{2g} -electrons ($j=t$, local spin $\vec{S}_{\vec{r}}$)

$$\Psi_{j\vec{r}} = \xi_{jd} \hat{D}_{j\vec{r}} + \xi_{jf} f_{\vec{r}}^+ N_{jd} = \xi_{jd}^2 N,$$

$$\sum_i \xi_{ji}^2 = 1, L = 2. \quad (1.4)$$

MEOS for t_{2g} -states are

$$\hat{D}_{t\vec{r}} = \{d_{\vec{r}\vec{S}} c_{\vec{r}\vec{S}} v_{\vec{r}\vec{L}}\}, c_{\vec{r}\vec{S}}^2 = (1 + \vec{S}\vec{S}_{\vec{r}}) / 4,$$

$$S = 3/2 \text{ for Fe}^{(+)}. \quad (1.5)$$

The locality conditions and inequality are

$$d_{j\vec{r}} \bar{d}_{j\vec{r}} = 1, [d_{j\vec{k}} \bar{d}_{j'\vec{q}}]_+ = \delta_{jj'} \delta_{\vec{k}\vec{q}} N_{jd},$$

$$|\sigma_{\vec{R}}|, |s_{\vec{r}}| \ll S. \quad (1.6)$$

All MEOS work in the Fock antisymmetric spaces.

The influence of H⁽⁺⁾ on band spectra is considered by an example of the hybridized bands of 4s - 3d (e_g)-electrons in Section 2. The change of bonds and FM properties are calculated in Section 3. Hydrogen additions to the MA energy and the influence of H⁽⁺⁾ diffusion on MA induction is investigated in Section 4. Section 5 is devoted to

$H^{(+)}$ diffusion. The comparison with experiment and conclusions are given in Section 6.

2. Band Spectra and their Crossings with CBF

The fermion spectra of band and covalent electrons are calculated by the Bogolyubov - Zubarev method for two-time quantum Green functions. There are one covalent electron of $H^{(+)}$ ion and one electron of the $4s - 3d (e_g)$ -subsystem of $Me^{(+)}$. We are limited by binary Hamiltonians. For the band subsystem, we have

$$\begin{aligned}
 H^b = & \sum_{j\vec{k}} \tilde{\varepsilon}_{jk} f_{jk}^+ f_{jk}^- + \sum_{j\vec{r}} E_j \xi_{jf}^2 f_{j\vec{r}}^+ f_{j\vec{r}}^- \\
 & + \xi_h^2 E_H \sum_{\vec{R}} h_{\vec{R}}^+ h_{\vec{R}}^- - \xi_h \sum_{j\vec{r}\vec{R}} \xi_{jf} [t_j(|\vec{r}\vec{z} \\
 & - \vec{R}|) f_{j\vec{r}}^+ h_{\vec{R}}^- + \text{h.c.}], \quad j = e, t,
 \end{aligned} \quad (2.1)$$

where

$$\begin{aligned}
 \tilde{\varepsilon} = & \varepsilon - \varepsilon_F, \quad \varepsilon_{jk} = t_{jj}(0) - t_{jj}(\vec{k}), \\
 \hat{t}(\vec{k}) = & \sum_{\vec{r}} \hat{t}(|\vec{r}\vec{\gamma}|) e^{i\vec{k}\vec{r}}.
 \end{aligned} \quad (2.2)$$

The Fermi energy $\varepsilon_F \leq |E_H|$. It allows us to neglect the energy of $H^{(+)} - H^{(+)}$ jump for FM metals (especially for a small concentration of hydrogen $c_H \ll 1$). The hybridization of "optical" $4s$ - and $3d (e_g)$ -electrons is considered to be strong enough and already taken into account in $t_{ee}(\vec{k})$.

The covalent Hamiltonian is binary on MEOS (1.1) and (1.5):

$$\begin{aligned}
 H^{\text{cov}} = & - \sum_{j\vec{r}\vec{r}'} \xi_{jd}^2 \hat{D}_{\vec{r}}^j \hat{D}_{\vec{r}'}^j \times \\
 & \times \Gamma^{jj}(|\rho|) - \xi_p \sum_{j\vec{r}\vec{R}} \xi_{jd} (\Gamma^{jH} \hat{D}_{\vec{r}}^j \hat{P}_{\vec{R}}^j + \text{h.c.}) - \\
 & - \sum_{\vec{R}\vec{R}'} \Gamma^{pp}(|\rho|) \hat{P}_{\vec{R}} \hat{P}_{\vec{R}'}, \quad \vec{\rho} = \vec{r} - \vec{r}' \quad (\text{or} = \vec{R} - \vec{R}').
 \end{aligned} \quad (2.3)$$

The delocalization of covalent electrons (transition in a band) is represented by the Hamiltonian

$$\begin{aligned}
 H^{b-c} = & \sum_{j\vec{r}} \xi_{jf} \xi_{jd} (g^{jf} \hat{D}_{\vec{r}}^j f_{j\vec{r}} + \text{h.c.}) + \\
 & + \sum_{j\vec{r}\vec{R}} \xi_h \xi_{jd} (g^{jH} \hat{D}_{\vec{r}}^j h_{\vec{R}} + \text{h.c.}) +
 \end{aligned}$$

$$+ \xi_p \sum_{j\vec{r}\vec{R}} \xi_{jf} (g^{pf} \hat{P}_{\vec{R}} f_{j\vec{r}} + \text{h.c.}). \quad (2.4)$$

The details of account are not given here (detailed description is given in [5, 6]).

The first difference of MeH band spectra from those for pure Me is their splitting. For $4s - 3d (e_g)$ -subsystems, we have

$$E_{ek}^{+,-} \approx \tilde{E}_{ek} \pm (|g^{ef}|^2 - 2c_H R_e^h) / |\tilde{E}_{ek} - \Gamma_k^{ee}|, \quad (2.5)$$

where

$$\begin{aligned}
 \tilde{E}_{jk} = & E_j + \tilde{\varepsilon}_{jk} \quad \hat{\Gamma}_{\vec{k}} = \hat{\Gamma}(0) - \hat{\Gamma}(\vec{k}), \\
 R_j^h = & \text{Re} [g^{*if} g^{jh} t_j(\vec{k})] / |E_H|.
 \end{aligned} \quad (2.6)$$

Similar to (2.6), the spectrum of the $3d (t_{2g})$ -subsystem includes the exchange terms in $\tilde{\Gamma}^{tt}(S_T)$ and $\tilde{g}^{tH}(S_T)$. Their renormalization in the FM temperatures region ($T < T_c$) depends on the mean spin S_T [5].

The spin (effective) splitting of the Fermi energy by s - d -exchange [7],

$$\varepsilon_{Fj\sigma} = \varepsilon_F + \sigma S_T A_{j\sigma}, \quad j = e, t, \quad (2.7)$$

is more essential than $\tilde{\Gamma}^{tt}(S_T)$ renormalization. The latter is small: $\sim 10^{-1}$ for $S \leq 3/2$ for Fe, Co, Ni. Splitting (2.7) adds peculiarities in the density of states DOS (E) [7]. However, it plays a smaller role than the crossing of band spectra with CBF spectra near the Fermi surfaces.

The difference in the denominator of (2.5) changes a sign near the Fermi surfaces. The priming CBF energy $\Gamma_{\vec{k}}$ becomes comparable with the relative energy of jumps of band electrons E_{jk} . Result (2.5) of the first approximation for $4s - 3d (e_g)$ -electrons is shown in Fig. 2 by a solid line. Nonmonotonicity of the spectrum near the Fermi surfaces [6] is shown as a peculiarity of DOS (E) in Fig. 2,b for $j = e$ and in Fig. 3 for $j = t$. Maxima and minima on the curves DOS (E) are sharp, as observed experimentally [7].

3. CBF Spectra and Thermodynamic Potential (t.d.p.)

The diagonalization of (2.1) for small $k \ll k_F$ gives (as well as (2.5)) a splitted CBF spectrum

$$E_{jk}^{d+,-} \approx \Gamma_{\vec{k}}^{jj} (|g^{jf}|^2 / \varepsilon_F) + c_H \{ (|g^{jH}|^2 / E_H) -$$

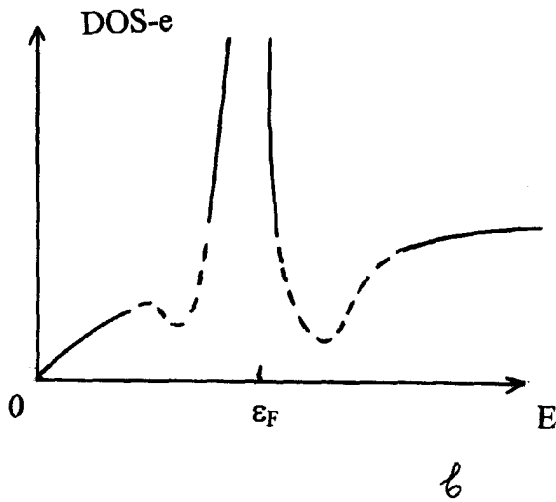
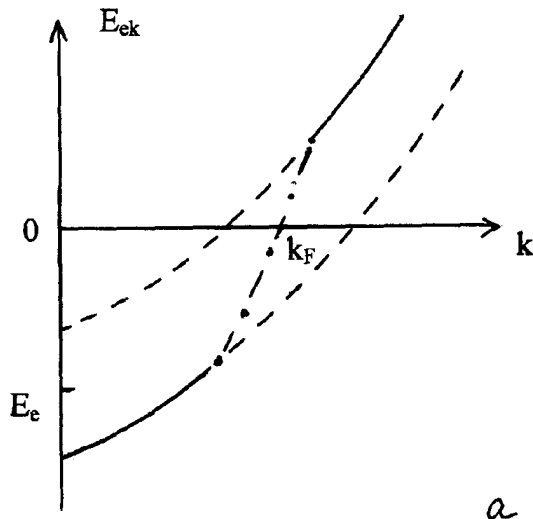


Fig. 2. Energy E_{ek} and DOS-e for the $4s - 3d (e_g)$ -subsystem: $a - E_{ek}(k)$ dispersion for one of the splitted bands higher and lower than the Fermi level (ϵ_F), $b -$ DOS-e dispersion ($k -$ wave number)

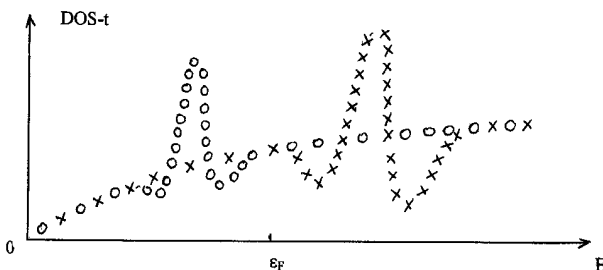


Fig. 3. Spin subbands DOS-t as a function of energy E for the $3d (t_{2g})$ -subsystem (the curves for spins $\sigma = 1/2$ are indicated by circles and for $\sigma = -1/2$ by crosses)

$$- 2 (R_j^h / \epsilon_F) \pm \{ |\Gamma^{jH}|^2 / \Gamma_k^{jj} \}. \quad (3.1)$$

The last term in braces is large enough. It is received for $k \neq 0$ (the Fermi momentum $k_F \sim 1$), and $\Gamma^{pp} \rightarrow 0$. When $c_H \rightarrow 1$, the energy of the lower branch (3.1) sharply decreases. The CBF correlators reach limiting values

$$N \frac{dd}{jk} \approx \langle d_{\vec{k}} \bar{d}_{\vec{k}} \rangle \approx N \frac{pp}{k} \approx 1/2N, \quad (3.2)$$

$$K_{f(j)h(p)} = \langle f_{\vec{r}}^+ (d_{j\vec{r}}) h_{\vec{R}} (p_{\vec{R}}) \rangle,$$

and the initial metal phase is destabilized.

At appreciable hydrogenization ($c_H \geq 1$), hydrogen $H^{(+)} - H^{(+)}$ bonds are appeared. There are the CBF branches

$$E_{jk}^{CBF} = \Gamma_k^{pp} + c_H |\Gamma^{jH}|^2 / \Gamma_k^{pp}, \text{ when } \Gamma_k^{pp} \gg |\Gamma^{jH}|. \quad (3.3)$$

Their energy (3.3) is more than (3.1) E^{d-} , that indicates the stabilization of a new hydride phase, which can be not metal if splitting (2.5) will become large enough. Then the low ('valent') band will be strongly lowered. And a high band ('the conduction band') will appear too highly. Spectra (3.1) are used for account of t.d.p. Correlators (3.2) $N \frac{jj}{k}$ are received as the Fermi functions with zero chemical potential [5, 6]. The t.p.d., received in this way, is used for variational account of amplitudes $\hat{\xi}$. At $T = 0$, we have

$$\Phi = \sum_j \{ (U_j \xi_{jf}^4 / 2) - \tilde{E}_j \xi_{jf}^2 - c_H \tilde{t}_j \xi_{jf} \xi_h - \Gamma^{jj} \xi_{jd}^2 - c_H \xi_p \xi_{jd} \tilde{\Gamma}^{jH} \} + c_H E_H \xi_h^2 + U_H (\xi_h^4 + \xi_p^4) c_H / 4 + \sum_j \Phi_j^{CBF}, \quad j = e, t, \quad (3.4)$$

where

$$\tilde{\Gamma}^{jH} \approx \Gamma^{jH} K_{jp}, \quad \tilde{E}_j = |E_j| - \epsilon_F > 0, \quad \tilde{t}_j = t K_{jh}. \quad (3.4')$$

T.d.p. (3.4) is varied on three independent variable (amplitudes) ξ_h and ξ_{jf} . At $U_H \rightarrow \infty$, there is

$$\xi_h^2 \approx 1/2, \quad \xi_{jf}^2 = [\xi_{jf}^{(0)}]^2 + c_H R_j^- / U_j + \delta_{je} / 2, \quad [\xi_{jf}^{(0)}]^2 = (\tilde{E}_j - \Gamma^{jj}) / U_j, \quad (3.5)$$

where

$$R_j^\pm = (\tilde{t}_j / \xi_{jf}^{(0)}) \pm (\tilde{\Gamma}^{jH} / \xi_{jd}^{(0)}), j = e, t. \quad (3.6)$$

The account of CBF (the last terms in (3.4)) gives the phase diagram (c_H, T). If the covalent MeH bond dominantes ($R_e^- < 0$) and $|R_e^-| > U_e$, the band amplitudes (3.5) quickly decrease with growth in c_H .

The contribution of $H^{(+)}$ to t.d.p.,

$$\Delta E_c = \Delta\Phi / c_H \approx U_H / 8 - |E_H| / 2 - E_H^2 / U_H - R_e^+ / 2\sqrt{2} - \sum_j [\xi_{jf}^{(0)}]^2 R_j^-, \quad (3.7)$$

is compared with the energy $E(H_2)$ of generation of molecules of the gas leaving a crystal. Whence the equilibrium concentration of dissolved $H^{(+)}$ is found to be

$$E(H_2) = -c_H^2 E_{2H} \geq \Delta\Phi(c_H), \quad \text{Sup } c_H \approx |\Delta E_c| / E_{2H}, \quad \Delta E_c < 0. \quad (3.8)$$

Transition metals with strong covalent bonds and strong Hund exchange should have $\text{Sup } c_H \sim 1$ in agreement with (3.7) - (3.8). This conclusion is proved by good hydrogen solubility in rare-earth (RE) metals, where the strong Hund exchange creates a large local moment $J \geq 1$.

A spin of Hamiltonian (2.1) is selected. It is varied on spin polarization. The operator of $H^{(+)}$ polarization,

$$\vec{\sigma}_{\vec{R}} \approx f_H \sum_{\vec{r}} (\tilde{\Gamma}^{tH} / U_H) \vec{S}_{\vec{r}} \\ \sigma_T \approx (f_H \tilde{\Gamma}^{tH} z_{tH} / U_H) S_T, \quad f_H \sim 1, \quad (3.9)$$

gives the contribution $\sigma_T \sim S_T$ to magnetization after averaging. We substitute (3.9) in the Hamiltonian and get the addition to the Heisenberg exchange parameter

$$\Delta A_H(|\vec{r} \hat{z} \vec{r}'|) \approx c_H (f_H^2 / U_H) \times \\ \times \sum_{\vec{R}, \vec{R}'} \tilde{\Gamma}^{tH}(|\vec{r} \hat{z} \vec{R}|) \tilde{\Gamma}^{tH}(|\vec{r}' - \vec{R}'|) > 0. \quad (3.10)$$

In this approximation, addition (3.10) raises $T_c(c_H)$ that also is sometimes observed experimentally [2].

According to (3.10), exchange hardness $D_{ex}(c_H, T)$ changes. Its changes are connected with CBF singularities near the Fermi surfaces [5, 6]. The role of singularities is characterized (in particular) by

sharpness of DOS (E) extrema, Figs. 2, 3. It is necessary to expect the increase of $D_{ex}(T)$ and $S_T(T)$ anomalies. This phenomenon should have an effect on critical FM properties in a vicinity of $T_c(c_H)$.

4. Magnetic Anisotropy of MeH and (REH)-intermetallides

The hydrogen implantation influences a spin lattice symmetry [8]. It is observed as the induction of uniaxial MA. Here, we do not consider the nature of a uniaxial symmetry of a ferromagnet. The model of a crystal field is used and spin-orbital bands of $Me^{(+)}$ and $H^{(+)}$ ions are taken into account. For a 3d-metal, we have

$$H^{CF} = \sum_{\vec{R}, \vec{r}} A_{20}(|\vec{\rho}|) L_{\vec{r}}^z J_{\vec{R}}^z \\ H^{SO} = -\sum \Lambda_H(|\vec{\rho}|) \vec{S}_{\vec{r}} \vec{L}_{\vec{R}}, \quad \vec{\rho} = \vec{r} \hat{z} \vec{R}. \quad (4.1)$$

The intraionic Hamiltonian (2.1) is added to (4.1). Its part dependent on orbital moments $Me^{(+)}$ - ($L_{\vec{r}}$) and $H^{(+)}$ - of ions ($l_{\vec{r}}$) is as follows:

$$\Delta H^i = \tilde{U}_H \sum_{\vec{R}} \vec{l}_{\vec{R}}^2 / 2 + \tilde{U}_t \sum_{\vec{r}} \vec{L}_{\vec{r}}^2 / 2 - \lambda_t \sum \vec{S}_{\vec{r}} \vec{L}_{\vec{r}}. \quad (4.2)$$

Only covalent t_{2g} -electrons are taken into account, and the dependence on amplitudes $\xi(T)$ is taken into account in parameters (4.2).

Defreezing of orbital moments in the FM phase of a spin lattice

$$\vec{L}_{\vec{r}} = (\lambda_t / \tilde{U}_t) \vec{S}_{\vec{r}} \vec{l}_{\vec{r}} = \sum_{\vec{r}'} \lambda_H(|\vec{\rho}|) \vec{S}_{\vec{r}'} \tilde{U}_H \quad (4.3)$$

is substituted in (4.1). The addition ΔK_1 to the MA parameter of pure Me-ferromagnet, K_1 , gives

$$H^{MA} = \sum_{\vec{r}, \vec{r}'} (K_1 + \Delta K_1) S_{\vec{r}}^z S_{\vec{r}'}^z, \quad \vec{r} = \vec{r} \hat{z} \vec{r}' \quad (4.4)$$

where

$$\Delta K_1(|\vec{\rho}|) = c_H (\lambda_t / \tilde{U}_t \tilde{U}_H) \sum_{\vec{R}} A_{20}(|\vec{R} - \vec{\rho}|) \lambda_H(|\vec{R}|). \quad (4.5)$$

The sign and value of (4.5) depend on the signs of spin-orbital parameters and A_{20} . At the different signs

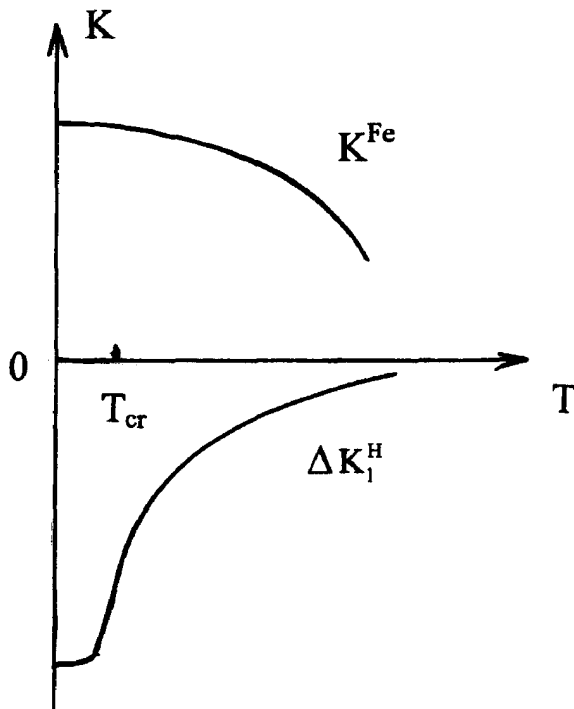


Fig. 4. T -dependences of the contributions of the $\text{Me}^{(+)}$ -lattice (K^{Fe}) and addition from the $\text{H}^{(+)}$ subsystem (ΔK_1^{H}) to the uniaxial magnetic anisotropy constant K_1 . The point of the orientational phase transition $T = T_{\text{cr}}$ is indicated for rare-earth intermetallide RE-Me-H

of K_1 and ΔK_1 , the hydrogen implantation can result in orientational phase transitions (OPT) [8].

Such OPT are observed in intermetallides $(\text{RE})\text{Fe}_{11}\text{TiH}_2$ [9] ($\text{Re} = \text{Er}, \text{Ho}$) at hydrogen implantation. The strong hydrogen influence is explained by the influence of the angular moments $\vec{J}_{\vec{r}}$ of RE-ions on the crystal field

$$H^{CF}(\text{RE}) = \sum_{\vec{r}} A_{20}^{\text{H}}(|\vec{\rho}|) l_{\vec{r}}^z L_{\vec{r}}^z$$

$$\vec{L}_{\vec{r}} = (2 - g) \vec{J}_{\vec{r}} \quad \langle \vec{J}_{\vec{r}} \rangle = \vec{J}_T \quad (4.6)$$

The nonfrozen orbital moment of a RE-ion ($\vec{L}_{\vec{r}}$) and the constant Lande factor g (4.6) give the amendment of the first approximation to K_1

$$\Delta K_R^{\text{H}} = c_{\text{H}} b_R J_T / S,$$

$$b_R = (2 - g) \sum_{\vec{r}} A_{20}^{\text{H}}(|\vec{r}|) \lambda_{\text{H}}(|\vec{r}^z \vec{\rho}|) / \tilde{U}_{\text{H}} \quad (4.7)$$

Value (4.7) is much more than the amendment of the second approximation on spin-orbit (4.5). The value

$\Delta K_R^{\text{H}}(|\vec{\rho}|)$ is large and practically does not depend on T at $T < T_{\text{ex}}$. Its fast decrease with increase in T [7, 8] looks like (Fig. 4)

$$\Delta K_R^{\text{H}}(T) \sim J_T, \quad J_T \approx T_{\text{ex}} / T, \quad \text{when } T > T_{\text{ex}} \quad (4.8)$$

At $c_{\text{H}} = 0$, the contributions of RE-ions to K_1 are also of the first order. By the form, it is similar to (4.7), but instead of $l_{\vec{r}}^z$ it is proportional to the small defrozed orbital moment of a $3d$ -ion. According to data [9], the signs of the contributions of the first order are alternative to the sign of $K_1 < 0$ of the $\text{Fe}^{(+)}$ sublattice.

The presence of RE-ions causes OPT in some $(\text{RE})\text{Fe}_{11}\text{Ti}$ [12]. The $\text{H}^{(+)}$ implantation strongly displaces the OPT temperature $T_{\text{cr}}(c_{\text{H}})$. OPT from a state with an easy magnetization axis into a state with a cone of easy magnetization axes occurs even in intermetallides that have no OPT at $c_{\text{H}} = 0$. The total MA constant of a pure intermetallide is designated as K_R . The critical concentration of OPT occurrence is derived from (4.7) as

$$c_{\text{H}}^{\text{cr}} \approx K_R / |b_R| J, \quad c_{\text{H}} > c_{\text{H}}^{\text{cr}} \quad (4.9)$$

The expression for the OPT critical temperature follows easily from (4.8). The induction of uniaxial MA under hydrogen implantation is calculated on the basis of this theory at the given distribution of defects of a cubic lattice.

5. The Quantum Theory of Hydrogen Diffusion

The diffusion of 'dressed' protons $\text{H}^{(+)}$ is connected with heterogeneity of covalent bonds, Fig. 1. Displacement of $\text{H}^{(+)}$ ions (Fig. 1,b) changes the wave function $\psi_{\text{el}}(R)$ (1.1). The proton factor of the wave function ψ_+ is

$$\psi(\vec{R}) = \psi_+(\vec{R}) \psi_{\text{el}}(\vec{R}), \quad d\psi/dt = 0, \quad (5.1)$$

that takes into account the Coulomb repulsion (the Madelung energy) of $\text{Me}^{(+)}$ - and $\text{H}^{(+)}$ -ions. The motion equation (5.1)

$$\dot{\psi}_+(\vec{R}, t) \psi_{\text{el}} + \psi_+ \dot{\psi}_{\text{el}}(\vec{R}, t) +$$

$$+ \vec{R} \cdot [(\vec{\nabla}_{\vec{R}} \psi_+) \psi_{\text{el}} + \psi_+ (\vec{\nabla}_{\vec{R}} \psi_{\text{el}})] = 0 \quad (5.2)$$

includes the Heisenberg equations for band ($\hbar\vec{R}$) operators and MEOS ($\hat{P}_{\vec{R}}$). The partial derivative with respect to time t is shown by a point from above.

The probability density of protons is expressed through the concentration c_H

$$W_+ = \Psi_+ \Psi_+^+, N_H W_+ = c_H(\vec{R}, t) N. \quad (5.3)$$

The operator form of (5.2)

$$\hat{A} c_H = F = -c_H \hat{A} \ln(\Psi_{el} \Psi_{el}^+), \hat{A} = \partial/\partial t + \dot{R} \vec{\nabla}_{\vec{R}} \quad (5.4)$$

is reduced to the diffusion equation. The Fick law [3] is postulated,

$$\dot{\vec{R}} c_H = -D_0 \vec{\nabla}_{\vec{R}} c_H, \text{ when } \hat{A} = 0, D_d = D_0 + D_{cov}, \quad (5.4')$$

which takes into account only the Coulomb repulsion when $H^{(+)}$ penetrates through a barrier (Fig. 1,c).

The influence of the electronic (covalent) structure on the diffusion coefficient $D_d[\hat{\xi}]$ is got from the right part of Eq. (5.4). $H^{(+)}$ movement is assumed to be slow enough on comparison with the time of reorganization of the electronic structure ($\tau_d \gg \tau_{el}$). Therefore, the solution of the Heisenberg equation for MEOS is beforehand taken into account in the concentration of band n_b and covalent n_c electrons. With the account of the covalent electrons' locality, the product of electronic wave functions in (5.4) is

$$W_{el} = \xi_p^2 + \xi_h^2 \hat{n}_b \vec{R} + \xi_p \xi_n (D_{\vec{R}} \hbar \vec{R} + \text{h.c.}). \quad (5.5)$$

The electronic density (5.5) is averaged, and nondiagonal correlators are neglected. (The latter can rather easily be taken into account). Expression (5.5) is expanded in the displacement \vec{l}_2 :

$$\xi_p^2(\vec{R}) = \xi_p^2(\vec{R}_0) + \vec{l}_2 \vec{\nabla}_{\vec{R}} \xi_p^2(\vec{R}), \vec{R} = \vec{R}_0 + \vec{l}_2, \quad (5.6)$$

where \vec{R}_0 is the $H^{(+)}$ equilibrium position (Fig. 1,a), \vec{l}_2 - distance up to a barrier (Fig. 1,c). (5.6) is substituted in (5.4). We obtain

$$F = -c_H \dot{\vec{R}} \{ \xi_p^2(\vec{R}_0) n_c + n_b \}^{-1} \otimes \vec{l}_2 \cdot \vec{\nabla}_{\vec{R}}^2 [\xi_p^2(\vec{R}) n_c]. \quad (5.7)$$

The roughening, similar to the Fick law, gives

$$\vec{\nabla}_{\vec{R}}^2 \xi_p^2(\vec{R}) \approx -\eta_1 (\vec{\nabla}_{\vec{R}}^2 c_H) / c_H. \quad (5.8)$$

The coefficient η_1 is a functional of wave functions (amplitudes ξ_p , etc.). According to (5.8), the amendment to the diffusion coefficient (a - lattice parameter),

$$D_{cov}(\xi_p) = (a^2/\tau_d) \eta_2 n_c / (\xi_p^2 n_c + n_b), \eta_2 \sim \eta_1, \quad (5.9)$$

is small enough, when n_c/n_b is small. However, when $n_b \rightarrow 0$ quantum amendments (5.9) are defined by η_2 and can be large enough. As the η_2 sign is not determined in this theory, $H^{(+)}$ diffusion in transition metals can become easier due to effect (5.9), or become more difficult. In the latter case, effect (5.9) stabilizes a hydrogenized state of metal.

6. Comparison with Experimental and Conclusions

The comparison of any theory of Me^-H diffusion with experimental data is hampered by the fact that the latter [1 - 3], are not in agreement with each other, in contrast to magnetic data (MA and others). Result (5.9) of our theory allows one to draw some total quantitative conclusions when comparing with experiment. For simple metals ($n_c \ll n_B$), addition (5.9) is small. In them, $H^{(+)}$ diffusion is defined by the activation energy of passage through a barrier and by the value D_0 . In transition metals (especially in REM), $n_c \gg n_B$, and, when $\eta_2 < 0$, the large addition (5.9) decreases more strongly than D_d (5.4). It is possible in them that $c_H \geq 1$. On the contrary, when $\eta_2 > 0$, a weak dependence $D_d(T)$ is possible in transition metals at $T \rightarrow 0$, i.e., the effect of quantum diffusion is revealed.

The different stability of hydrogenized state in both pure metals and alloys [1 - 3] confirms the importance of the account of effect (5.9). The theory connects the observable high diffusion coefficient of hydrogen with a large contribution to it of covalent bonds. The theory is confirmed also by the effect of fast relaxation of the ferromagnetic anisotropy [8]. General conclusions of the theory:

1. Hydrogen solubility in transition metal is defined by the covalent bonds of $H^{(+)}$ - and $Me^{(+)}$ -ions.
2. Me^-H band spectra are splitted. The splitting value $\Delta E_H \sim c_H$ and can result in the transition to a nonmetallic state, when $c_H \rightarrow 1$.
3. Splitting of CBF spectra results in a new nonmonotonicity (peaks) of the band states' density.
4. Spin polarization of $H^{(+)}$ changes the magnetization and $T_c(c_H)$.
5. Orbital polarization of $H^{(+)}$ changes the value (and sometimes the sign) of MA constants $K_n(c_H)$ and the magnetic phase diagram.

6. $H^{(+)}$ diffusion coefficient depends on the amplitude of covalency ξ_p .

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