

# THE BAND SPECTRUM ROLE IN H ABSORPTION IN 4f-METALS

Mitsek A.I.

Department of Solid State Theory, G.V. Kurdyumov Institute for Metal Physics, N.A.S.U.,  
36 Academician Vernadsky Blvd, UA-03680 Kyiv-142, Ukraine

Факс: +(380) 44 4242561 E-mail: amitsek@yahoo.com

The problem of H absorption in rare-earth metals (REM) must take into account both change of local (covalent) Me-H bonds and change of electrons (conduction) band spectrum. H-ions inclusion in covalent bonds hybridizes their wave functions

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

and many-electron operator spinors (MEOS)  $P_{r\sigma}$  localize hydrogen electron on covalent bonds (sites  $\mathbf{r}$ ). Localization condition defines  $P_r$  in the Fock fermion spaces, and also band fermions  $f_r$ . Me-ion wave function

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

is composed from MEOS ( $F_r$ ) of local 4f-electrons and MEOS ( $D_r$ ) for 5d-electron. Electron ( $\xi_b$ ) of H-ion passes in conduction band ( $f_r$ ). The band electron density ( $n_k$ ) and the Fermi surfaces change (the Fermi energy  $\varepsilon_F$ ).

The change of band spectrum influences also on covalent bonds. Localization of band electrons (or delocalization of covalent electrons) is described by hybrid terms (MEOS  $D_r$  and fermions  $f_r$ ) in the representation of chemical (covalent) bond fluctuations (CBF) for  $\text{MeH}_x$  system [1,2]

$$\begin{aligned} D_r &= D_0 + \sum D_k e^{ikr}, \\ D_k &= \sum D_r e^{-ikr} / N \xi_D^2, P_k = \sum P_r e^{-ikr} / N \xi_L^2, \end{aligned} \quad (3)$$

where  $N$  is Me-ions density. Anticommutators are

$$[D_k, \bar{D}_q]_{\pm} = \delta_{kq} / N \xi_D^2, [P_k, \bar{P}_q]_{\pm} = \delta_{kq} / N \xi_L^2. \quad (4)$$

The MEOS Fourier images represent CBF branches (main (Me)  $E_k^+$  and admixture  $E_k^-$ ). Crossing of CBF and band branches changes the Fermi surfaces at H absorption.

The spectral part of the exchange Hamiltonian of band and covalent electrons

$$\begin{aligned} H_k^{(2)} &= \Gamma_k^{DD} D_k \bar{D}_k + x(\Gamma_k^{PD} D_k \bar{P}_k + \text{H.c.}) + \\ &+ x\Gamma_k^{PP} P_k \bar{P}_k + x(\gamma_p P_k f_k + \text{H.c.}) + \tilde{\varepsilon}_k f_k^+ f_k \end{aligned} \quad (5)$$

quantizes spectrum by the Bogolyubov Green functions' method

$$G_k^{f,P,D} = \langle\langle f_k(\bar{P}_k, \bar{D}_k) | f_k^+ \rangle\rangle. \quad (6)$$

The motion equations

$$\begin{pmatrix} (E - \tilde{\varepsilon}_k) & x\gamma_p & 0 \\ \gamma_p & (E - \Gamma_k^{PP}) & \Gamma_k^{PD} \\ 0 & x\Gamma_k^{DP} & (E - \Gamma_k^{DD}) \end{pmatrix} \begin{pmatrix} G_k^f \\ G_k^P \\ G_k^D \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (7)$$

are solved, taking into account CBF spectra renormalizing owing to H-Me covalent bonds. All spectra parameters are examined further in a square approximation

$$\begin{aligned} \Gamma_k &= \Gamma k^2, \gamma_p = \gamma k^2, \\ \tilde{\varepsilon}_k &= \varepsilon_k - \varepsilon_F, \varepsilon_k \equiv k^2 / 2m^*. \end{aligned} \quad (8)$$

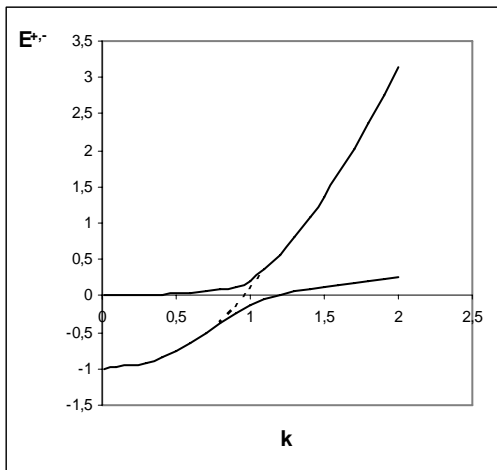
Renormalized main CBF spectrum (matrix metal spectrum)  $\tilde{\Gamma}_k^{DD}$  is chosen. Then solutions (7) are received in a form of two branches

$$E_k^{+,-} = \left\{ \tilde{\varepsilon}_k + \Gamma_k^{PP} \pm \left[ (\tilde{\varepsilon}_k - \Gamma_k^{PP})^2 + 4|\gamma_p|^2 \right]^{1/2} \right\} / 2. \quad (9)$$

The solutions (9) are shown on figure in approximation (8). Number calculation is realized for function

$$E^{+,-}(k) = \left\{ 1, 1k^2 - 1 \pm \left[ (0,9k^2 - 1)^2 + 0,1k^4 \right]^{1/2} \right\} / 2. \quad (10)$$

The result is shown on figure. Above abscissa  $E^+$  corresponds to band spectrum, below abscissa – branch  $E^-$ .



The branch, which depends on  $k$  weakly, corresponds to admixture (hydrogen) CBF. Band branches near the Fermi surface ( $\varepsilon_k \cong \varepsilon_F$ ) are joined by approximation line  $E = A k - 2,4$ ,  $A = 2,5$ . That (linear) part of band spectrum plays the major role at approximation of electron properties (electrical conductivity, the Hall effect, optics etc.). The density of band electron states in that region is

$$\text{DOS}(E) \sim (\partial E / \partial k)^{-1} \sim 1/A \sim 1/x \quad (11)$$

and it is small, when coefficients  $A$  are large enough. That is corresponds to electrical conductivity decrease, what is often observed in hydrides.

Besides that, deformed part of the Fermi surface must influence essentially on heat properties. Their

contribution into t.d.p. can be estimated by band energies integral in linear part of spectrum. The estimation gives

$$\Delta\Phi^b \sim (AT) \sim xT\xi_b^2. \quad (12)$$

That value can be comparable with covalent parts of band energy. But at strong localization of hydrogen electrons ( $\xi_b^2 \ll 1$ ) band part of bond forces is small in comparison with covalent part. So the local models of hydrogen absorption in metals [3] are adequate enough.

### Conclusions

- 1) The interaction of band spectra and collective modes (CBF) deforms the Fermi surfaces.
- 2) Linear ( $E^b \sim k$ ) character of band spectrum near the Fermi level  $\varepsilon_F$  leads to essential linear contribution into thermodynamical potential (t.d.p.). It is more than contribution of the "Maxwell tail" of pure metal fermion spectrum, but it small in comparison with CBF contribution into t.d.p.

### References

1. Mitsek A.I., Pushkar V.N. Metallofiz. Noveishie Tekhnol. 2008, **30**(12):
2. Mitsek A.I. Uspehi Fiz. Met. 2005, **6**(3): 233.
3. Smirnov A.A. The theory of interstitial alloys (Moscow: Nauka: 1979).