

MAGNETIC PROPERTIES AND H ABSORPTION IN THE LOCAL-COVALENT MODEL OF 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

Usual control methods of MeH_x composition of H solution in metal (Me) (weight and other) can be insufficient, when it is necessary to take into account heterogeneous H distribution. The Mössbauer effect gives good results (dependence of superfine field etc. on number of H neighbors near Me-ion). But magnetic methods are often more simple. Experimental data show essential dependence of MeH_x phase diagram (temperature of phase transition (T_c, metal-helicoid, T_N, ...), critical fields (H_c, EA-EP, metamagnetism, ...) and other characteristics) on x, and also on H-ions distribution on sample depth. The magnetic data interpretation requires detailed quantum theory. It is convenient to give such theory on the base of covalent-local model of 4f-5d-system of Me-ion electrons.

The wave function of H and Me-ions in the MEOS representation [1,2] is

$$\begin{aligned} \Psi_H^+ &= P_r, \quad \Psi_{Me}^+(\mathbf{r}) = \xi_F F_r + \xi_D D_r, \\ P_r &= \{P_{r\sigma}, c_{r\sigma}\}, \end{aligned} \quad (1)$$

where

$$\begin{aligned} D_r &= \{a_{r\sigma}^+, c_{r\sigma}\}, \quad F_r = \{F_{r\sigma L}, c_{r\sigma}, v_{rL}\}, \\ c_{r\sigma}^2 &= (1 + \bar{\sigma} \bar{S}_r) / 2, \end{aligned} \quad (2)$$

and spin and orbital MEOS factors ($\bar{\sigma}$ and \bar{L} - spin and orbital matrixes)

$$\begin{aligned} c_{r\sigma}^2 &= (1 + \bar{\sigma} \bar{S}_r) / 2, \quad v_{rL}^2 = (1 + \bar{L} \bar{L}_r) / 7, \\ J_r &= S_r \pm L_r \end{aligned} \quad (3)$$

Define moment J_r of Me ion. Factor

$$\begin{aligned} F_{r\sigma L} &= \prod_{\mu=1}^n a_{r\sigma L}^+, \quad D_r = D_0 + \sum D_k e^{ikr}, \\ [D_k, \bar{D}_q]_+ &= \delta_{kq} / N \xi_D^2, \end{aligned} \quad (4)$$

is formed of local fermions $a_{r\sigma L}^+$. MEOS anticommutators ($\bar{D}_k = D_k^+$) take part in calculations of chemical (covalent) bond

fluctuations (CBF) spectra. Me-ions covalent bonds are realized through 5d-electrons (D_r).

Exchange bond of 4f-shells (and their moments J_r) is realized indirectly through 5d-electrons excitation

$$\begin{aligned} H^{\text{cov}} &= -\sum \Gamma D_r F_r \bar{F}_r \bar{D}_r - \\ &- x \sum (\gamma F_r D_r \bar{P}_r \bar{F}_r + \text{H.c.}) \end{aligned} \quad (5)$$

and arises from spin part of (5). Spin $c_{r\sigma}$ and orbital v_{rL} factors are expanded in operators \bar{S}_r and \bar{L}_r

$$c_{r\sigma} \cong (1 + \frac{\bar{\sigma} \bar{S}_r}{2}) / \sqrt{2}, \quad v_{rL} = (1 + \bar{L} \bar{L}_r / 2) / \sqrt{7} \quad (6)$$

and spin and orbital parts of the exchange Hamiltonian are received in usual form [3]

$$H^{\text{ex}} = -\sum A_S(\mathbf{r}-\mathbf{R}, \mathbf{T}) \bar{S}_r \bar{S}_R - \sum A_L \bar{L}_r \bar{L}_R - \dots \quad (7)$$

Exchange parameters are

$$\begin{aligned} A_S &= Z_S \{ \Gamma(\mathbf{r}-\mathbf{R}) \langle D_r \bar{D}_R \rangle + x [\gamma \langle D_r \bar{P}_R \rangle + \gamma^* \langle P_r \bar{D}_R \rangle] \} = \\ &= Z_S \tilde{\Gamma}(\mathbf{r}-\mathbf{R}, \mathbf{T}) \end{aligned} \quad (8)$$

and

$$A_L = Z_L \tilde{\Gamma}(\mathbf{r}-\mathbf{R}, \mathbf{T}), \quad \tilde{A} = (\tilde{Z}_S + \tilde{Z}_L) \Gamma(\mathbf{r}-\mathbf{R}, \mathbf{T}) \quad (9)$$

Temperature dependence arises through the MEOS correlators. The effective Hamiltonian is received

$$\begin{aligned} H^{\text{ex}} &= -\sum \tilde{A} J_r J_R, \quad \tilde{Z}_S = Z_S (g-1)^2, \\ \tilde{Z}_L &= Z_L (2-g)^2, \quad T_c(x) \sim \tilde{A} \end{aligned} \quad (10)$$

spin and orbital contributions into exchange parameter are expressed through the Lande factor g. Hydrogen influence (the second term in brace (8) for $\tilde{\Gamma}$) is expressed through pair MEOS correlators of 5d-1s-electrons. Dependence on H-ions concentration (x) enter both directly and through coordination numbers of Me-H

neighborhoods. So dependence $T_c(x)$ for MeH_x FM phases is sometimes nonlinear

$$\begin{aligned} T_c(x) &\cong T_c(0)[1 + x\gamma K_{\text{DP}}(x)/\Gamma], \\ K_{\text{DP}} &= 2\text{Re}\langle D_r \bar{P}_R \rangle \end{aligned} \quad (11)$$

H influence on magnetic phase diagram lower T_c (or T_N) must depend strongly on $\tilde{\Gamma}(\mathbf{r}-\mathbf{R})$ inhomogeneity. Even if CBF influence (i.e. T) is neglected. That aspect can become apparent in experimental data difference for various sample treatment. But influence of Me-H correlators on magnetic phase stability is more interesting. The metamagnetic transition ferromagnet (FM)-helicoid is of interest. Some theories connect it with magnon spectrum peculiarities (with presence of linear term in magnon energy $E^m(\mathbf{k})$). The dispersion calculation of exchange integral (8) at $x=0$ gives in our model

$$\begin{aligned} A(\mathbf{k}) &= \phi \left\{ \Gamma(\mathbf{k})\rho^2 + \sum_q \Gamma(\mathbf{k}+\mathbf{q})N_q^D \right\}, \\ \rho^2 &= \langle D_0 \bar{D}_0 \rangle, N_q^D = (e^{\beta \Gamma_q} + 1)^{-1} \end{aligned} \quad (12)$$

where CBF density N_q^D is approximated by the Boltzmann factor at low temperature $T \leq 10^2 \text{ K}$ at $\Gamma \sim 1 \text{ eV}$. Expansion $\Gamma(\mathbf{k}+\mathbf{q}) \cong \Gamma(\mathbf{q}) + \Gamma'(\mathbf{k}\mathbf{q})$ for small \mathbf{k} gives the law of magnon dispersion

$$\begin{aligned} E^m(\mathbf{k})/2J &= A(0) - A(\mathbf{k}) + \mu_B B_0 = \\ &= Ak^2 + (\tilde{\Gamma}_1 \Gamma^2) \tilde{\mathbf{k}} + \mu_B B_0, \Gamma_1 \sim \Gamma'/\Gamma^2, B_0 \sim B_A + B \end{aligned} \quad (13)$$

Helicoid vector \mathbf{k} is defined by $E^m(\mathbf{k})$ minimum and depend on linear term (13). B_A is anisotropy

field, B is external field.

H absorption renormalizes also exchange dispersion (8). The calculation, analogous to (13), renormalizes $A(\mathbf{k}, x, T)$

$$\Delta A(\mathbf{k}) = x \sum \gamma(\mathbf{k}+\mathbf{q}) K_{\text{DP}}(\mathbf{q}), \langle D_q \bar{P}_q \rangle = K_{\text{DP}}(\mathbf{q}) \quad (14)$$

Magnon energy (13) is also renormalized. Linear term

$$\begin{aligned} \Delta E^m(\mathbf{k}, x) &= \\ &= \text{const. } x \tilde{\mathbf{k}} \tilde{\Gamma}_1(x), \hat{\gamma}'_k(x) \sum \tilde{\mathbf{q}} K_{\text{DP}}(\tilde{\mathbf{q}}, x) = \tilde{\Gamma}' \end{aligned} \quad (15)$$

receives essential addition. Owing to that fact helicoid wave vector $\mathbf{k}_0(x, T)$ and its period are renormalized.

Conclusions

- 1) The change of $T_c(x)$ at hydrogen absorption is caused by 1s-electron localization on covalent Me-H bonds.
- 2) Magnetic phase diagram (creation helicoid phase and other) is deformed, in particular, owing to changes of exchange (magnon) energies dispersion.

References

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