

THE COVALENT-BAND DESCRIPTION OF γ -RESONANCE IN 3d- AND 4f-FERROMETALS

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The hybridization of ns -shells with covalent and band electrons is calculated in the multielectronic operator spinors (MEOS) representation. The density of ns -electrons on a nucleus $\rho(0)$ is dependent on covalent bonds. The hyperfine field (HF) B_{HF} is expressed through the spin polarization of ns -electrons. The Hund exchange of an ion Fe^{57} gives $B_{\text{HF}} \sim S_T$, where S_T is the mean spin. In heavy rare earth metals (REM), the spin-orbital $ns^{-4} f$ -contribution is added. It causes a large B_{HF} and the dependence on temperature T as $B_{\text{HF}}(T) \sim J_T$, where J_T - angular moment of an RE ion. Chemical (covalent) bond fluctuations (CBF), responsible for Fe polymorphism, define a linear dependence on T for the chemical shift of a line of γ -resonance in α -Fe and iron compounds. The large energy gap in CBF spectra stabilizes the hcp lattice of heavy REM. The received results interpret experimental data.

1. Spin Polarization of Hybridized ns -Shells of the Mossbauer Ions

The densities of electrons and their spins functionally define properties of ferromagnetic (FM) materials [1, 2]. Their experimental local indicator is a γ -resonance [1-3]. Inhomogeneities of a spin lattice create local (hyperfine) fields B_{HF} on the nuclei of Mossbauer ions (for example, Fe^{57}). The local bonds of an atomic lattice change the density of ns -electrons on nucleus $\rho(0)$. It is measured as the chemical shift of a γ -resonance line. The weak spin polarization of band electrons and their practical homogeneity in good metal (alloy) allow one to neglect their influence on the dependence of $B_{\text{HF}}(T)$ and $\rho(0, T)$ on temperature T in zero approximation.

However, experimental γ -resonance lines were interpreted up to now on the basis of one-electron theories. The temperature dependence of $\rho(0)$ (which is sometimes strongly enough) was interpreted differently (on the basis of the phonon Debye theory). The theory of hyperfine fields stood by itself. Their values were formed from the own field of a radioactive magnetic ion and fields of surrounding ions at sites \mathbf{r} in the Heisenberg model of localized electrons. These contributions are defined by their moments (spins $\mathbf{S}_{\mathbf{r}}$). Spin decompensation of electron densities on a nucleus was taken into account phenomenologically. The combination of these points of view and the united

theory of γ -resonance in magnetics is not created up to now.

In our opinion, it is connected with the fact that covalent bonds were not taken into account. The interaction of ns -electrons with covalent electrons is no less important than the bond with band electrons. The CBF role is also more important in many cases than the phonons' role, especially for alloys of transition metals, where CBF define the phase diagrams of both atomic and spin lattices [5]. So the calculation of covalent bonds and CBF, proposed here, allows one to take into account the dependence not only of hyperfine fields but also of $\rho(0)$ (line chemical shift) on phase diagrams (on temperature T , admixture concentration, etc.).

The theory of covalent bonds and their fluctuations, developed by us earlier [5], allows one to create a self-consistent theory of phase diagrams of atomic and spin lattices. The theory gives the crossing of CBF branches with dispersion curves of band electrons. This leads to DOS(E) singularities which appear near the Fermi surfaces as an indicator of lattice instability. The singularities, which are formed on CBF branches, give visible contributions to the thermodynamical potential (t. d. p.). These contributions depend on T strongly. The concrete MEOS correlators strongly depend on T as well. They are contained in the expressions for different physical quantities, in particular in the expressions for the amplitudes of atomic wave functions.

Such is the calculated Fe diagram. Destabilization of the α -Fe lattice appear, when the density of the CBF singular part increases [5].

Hybridization of ns - and $3d$ -states on a Fe^{57} ion results in the dependence of $\rho(0)$ on the phase diagram. Amplitudes of $3d$ -contributions into ns -electrons wave functions are expressed through MEOS correlators as a result of variation calculations. So the theory interprets the observed linear temperature dependence (above some temperature $T_m \sim 10^2 \text{K}$) of chemical shift as the influence of the CBF singular part. Naturally, the quantization axis of ns -electrons in a magnetic field \mathbf{B} (or in a hyperfine field B_{HF}) also appears. The theory expresses the contributions into B_{HF} not only through spin $\mathbf{S}_{\mathbf{r}}$ (angular $\mathbf{J}_{\mathbf{r}}$ for lanthanides or actinoids) moments, but also through

MEOS correlators. So the proposed many-electron theory allows one to solve all problems of γ -resonance interpretation in magnetics.

In a magnetic field \mathbf{B} , the decompensation of electronic spins $\vec{\sigma}_{+,-}$ arises for each ns -shell, see Fig.1 for $1s$ -shell. The Hund exchange with magnetic ($3d^-$ t_{2g} in Fe^{57}) electrons acts similarly. Two quantization axes are introduced by analogy with the quantum theory of antiferromagnetism [1, 4]. Along a longitudinal axis, spins are compensated (for example, at $B = 0$). The transverse axis (along $B \neq 0$) is necessary for the quantization of the observable spin polarization

$$\mathbf{s} = \vec{\sigma}_{\perp+} + \vec{\sigma}_{\perp-}, \quad \mathbf{s} \rightarrow \mathbf{s}_{n\mathbf{r}} \quad (1.1)$$

for each ns -shell. The one-electronic theory does not allow one to consider adequately this situation. On the contrary, the local model (Heisenberg and others) of two-sublattice antiferromagnet introduces naturally the operator $\mathbf{s}_{n\mathbf{r}}$ [4] in the form (1.1). For it, the representation of multielectronic operator spinors (MEOS) [5] is used as

$$\begin{aligned} \hat{D}_{\mathbf{r}}^{ns} &= \{d_{n\mathbf{r}\sigma}, c_{n\mathbf{r}\sigma}\}, c_{n\mathbf{r}\sigma}^2 = \\ &= (1 + \vec{\sigma}_{n\mathbf{r}}^2)/2, \quad d_{n\mathbf{r}\sigma} = \prod_{\sigma=\pm} a_{n\mathbf{r}\sigma}^+ \end{aligned} \quad (1.2)$$

where σ^- operators of spin 1/2, a^+ - the Fermi-operators for localized ns - and other electrons. The condition of localization

$$d_{\mathbf{r}} \bar{d}_{\mathbf{r}} = 1, \quad \bar{d} = d^+, \quad [d_{n\mathbf{r}}, \bar{d}_{n'\mathbf{r}}]_- = \delta_{nn'} \delta_{\mathbf{r}\mathbf{r}} \quad (1.3)$$

defines the MEOC coordinate factor (1.2) in the symmetric Fock spaces.

The hybridized wave function of ns -shell is

$$\Psi_{\mathbf{r}}^{ns} = \xi_s \hat{D}_{\mathbf{r}}^{ns} + \xi_d \hat{D}_{d\mathbf{r}} + \xi_f \hat{D}_{f\mathbf{r}}, \quad \sum_j \xi_j^2 = 1. \quad (1.4)$$

The expressions for MEOS of covalent electrons $\hat{D}_{j\mathbf{r}}$ are similar to (1.2). We assume three covalent $3d^-$ t_{2g} magnetic electrons, one electron of $5d$ -state, and one electron of $6s$ -state. Here ξ_d - amplitude of $3d^-$ (for $3d$ -ions) or $5d$ -electrons (for $4f$ -ions). ξ_f - amplitude of (partially magnetic) $4f$ -electrons of rare earth (RE) Mossbauer ions. We remain within the hydrogen-like model of atom [6-8]. The calculation [9] is carried out within the Thomas-Fermi model.

We assume at first that ns - $3(5)$ d -hybridization (as well as with $4f$ -electrons) does not influence covalent (magnetic) and band electrons. Then the interaction

of ns -electrons with md - and $4f$ -electrons is described by the intraionic Hamiltonian

$$\begin{aligned} H_{\mathbf{r}}^i &= U_s \xi_s^4 (1 + b\mathbf{s}_{\mathbf{r}}^2)/2 - A_{sd(f)} \mathbf{s}_{\mathbf{r}} \mathbf{S}_{\mathbf{r}} - \lambda_{sf} \mathbf{s}_{\mathbf{r}} \mathbf{L}_{\mathbf{r}} + \\ &+ g_{sd} \xi_s \xi_d \hat{D}_{\mathbf{r}}^{nsf} (f_{\mathbf{r}}^+) \hat{D}_{d\mathbf{r}} + g_{sf} \hat{D}_{\mathbf{r}}^{nsf} \hat{D}_{f\mathbf{r}} \xi_s \xi_f + \text{h.c.}, \end{aligned} \quad (1.5)$$

where index n of a concrete shell is omitted. The pure metal with the own Mossbauer ion, for example Fe^{57} in α -Fe, is considered here. To (1.5), we add the covalent interaction (for example, Fe^{57}) with neighbours

$$\begin{aligned} H_{\mathbf{r}}^c &= - \sum_{\mathbf{R}} \Gamma(|\mathbf{r} - \mathbf{R}|) \hat{D}_{d\mathbf{r}} \hat{D}_{d\mathbf{R}} \xi_d - \\ &- \xi_f \sum_{\mathbf{R}} \Theta(|\mathbf{r} - \mathbf{R}|) \hat{D}_{d\mathbf{r}} \hat{D}_{f\mathbf{R}} \xi_f + \text{h.c.} \end{aligned} \quad (1.6)$$

The second term in (1.6) is necessary for RE ions. Only $4f$ - 5 d -excitations are taken into account [6, 7]. Direct $4f$ - 4 f -covalent bond is neglected. The heavy $4f$ -metals are considered and the effects of "intermediate valency" (see [8]) are not taken into account. The sum of (1.5) and (1.6) is quantized and the t.d.p. $\Phi(\xi_j)$ is received. We vary $\Phi(\xi_j)$ and receive

$$\rho(0, T) = \rho_0 \xi_s^2(T), \quad R_s \sim \rho_0 \Delta \xi_s^2, \quad (1.7)$$

i. e. the change of the density of states (DOS) on a nucleus and the chemical shift $R_s(T)$. The change at increasing T is equal to

$$\Delta R_s \sim \rho_0 [\xi_s^2(0) - \xi_s^2(T)]. \quad (1.8)$$

The similar formula is received at other changes in a ferrometal lattice.

We vary (1.5) in $\mathbf{s}_{\mathbf{r}}$ and determine the spin polarization of ns -shell (Section 2). Accounts of the chemical shifts of a γ -resonance line for α -Fe (Section 3) and REM (Section 4) differ. The stability of the hcp lattice of REM is discussed in Section 5 on the basis of the CBF account. Comparison with experiment and conclusions are given in Section 6.

2. Spin Polarization of ns -Shells and Hyperfine Field

We proceed from the contact interaction of the nucleus spin $\mathbf{I}_{\mathbf{r}}$ with the spins of ns -electrons in the form proposed by Fermi (see [1-3]):

$$H_{\mathbf{r}}^F = - \sum_n A_F(n) \mathbf{I}_{\mathbf{r}} \mathbf{s}_{n\mathbf{r}} \rho_n(0) = - \mu_N \mathbf{B}_{\text{HF}} \mathbf{I}_{\mathbf{r}}. \quad (2.1)$$

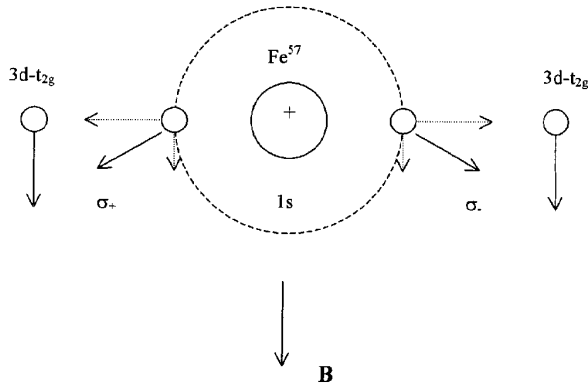


Fig. 1. The model of two quantization axes for the calculation of spin polarization of ns -shell (by the example $n=1$) in magnetic field \mathbf{B} . Magnetic (covalent) $3d-t_{2g}$ -electrons responsible for a hyperfine field B_{HF} are also noted

The large value of 'internal' hyperfine field $B_{\text{HF}} \sim 10^2 \div 10^3$ T in FM metals is caused by a small value of nuclear magneton $\mu_N \sim 10^{-23}$ CGSM. Hybridization of ns -shells with valent electrons is small ($\xi_s^2 \rightarrow 1$). Therefore, $\rho(0) \approx \rho_0$ is supposed in (2.1). Then all dependences $\mathbf{B}_{\text{HF}}(T)$ on structure are defined by \mathbf{s}_r polarization, i.e. by the spin lattice.

We vary (1.5) omitting index n :

$$\mathbf{s}_r = (A_{sd(f)}\mathbf{S}_r + \lambda_{sf}\mathbf{L}_r)/\tilde{U}_s, \quad \tilde{U}_s = bU_s, \quad 0 < b < 1. \quad (2.2)$$

The orbital moment \mathbf{L}_r of a FM $3d$ -metal is frozen, and only the first term in the parentheses in (2.2) plays a role. For $4f$ -metal [6], we have

$$\mathbf{L}_r = (2 - g)\mathbf{J}_r, \quad \mathbf{S}_r = (g - 1)\mathbf{J}_r. \quad (2.3)$$

It follows from experimental data that

$$|\lambda_{sf}| \gg |A_{sd}|, \quad (2.4)$$

which defines, apparently, a large $B_{\text{HF}} \sim 10^3$ T [1, 2].

From (2.1)-(2.3) for a FM $3d$ -metal, we get

$$\mathbf{B}_{\text{HF}}(3d) \approx \sum_n [A_F(n) A_{sd}(n)/\tilde{U}_s(n)] (\rho_0/\mu_N) \mathbf{S}_r. \quad (2.5)$$

In the FM phase, the hyperfine field

$$\mathbf{B}_{\text{HF}}^d(T) = \mathbf{B}_{\text{HF}}^d(0) \mathbf{S}_T/S, \quad \mathbf{S}_T = \langle \mathbf{S}_r \rangle \quad (2.6)$$

is defined by the mean spin \mathbf{S}_T .

Like this, for a $4f$ -ion in the FM phase of REM, we obtain

$$\mathbf{B}_{\text{HF}}(4f) = \sum_n \{ [A_{sf}(n)(g-1) + \lambda_{sf}(n)(2-g)] A_F(n)/\tilde{U}_s(n) \} (\rho_0/\mu_N) \mathbf{J}_r. \quad (2.7)$$

The temperature dependence (2.7) is

$$\mathbf{B}_{\text{HF}}^f(T) = \mathbf{B}_{\text{HF}}^f(0) J_T/J, \quad J_T = \langle J_r \rangle. \quad (2.8)$$

The change of a REM phase changes a set $A_{sf}(n)$ owing to $5d-4f$ -hybridization, and also owing to the delocalization of these electrons. The latter is displayed as the effect of variable ('intermediate') valency [8].

The quantum calculations of $3d$ -metals [9] can be used for the estimation of the parameters $A_{sd}(n)$ in (2.5). However, unclear initial assumptions [9] complicate the separation of specific energy parameters. It is connected, in particular, with insufficient development of the theory of hydrogen-like atomic shells in a magnetic field.

The somewhat more complex situation for heavy ions ($4f$ - and others) does not allow even such calculations as those in [9]. The behaviour of $4f$ -electrons requires a more careful research of the problem of their delocalization. It complicates the calculation of $\rho(0)$. Probably, a specification of the contact Fermi interaction is required.

3. Chemical Shift of the γ -Resonance Line of $3d$ -Ions by the Example of Fe^{57}

A wide use of iron alloys (and Fe^{57} in them) allows us to compare details of the theory with experiment. The shell model of atoms allows the finite density of ns -electrons on a nucleus. Their wave function in the MEOS representation simply connects $\rho(0)$ with atomic structure. We suppose $\xi_f = 0$. For α -Fe, only the interaction with $3d-t_{2g}$ -electrons is taken into account. Their local (covalent) bonds with neighbours add

$$H^{\text{cov}} = - \sum_{\mathbf{rR}} \Gamma(|\mathbf{r}-\mathbf{R}|) \hat{D}_{d\mathbf{r}} \hat{D}_{d\mathbf{R}} \quad (3.1)$$

into (1.6). The interaction with band electrons of the $4s$ - and $3d^- e_g$ -types is partially taken into account by $ns^- d$ -hybridization (1.5) and by the correlator

$$K_{nsd} = \langle \hat{D}_{\mathbf{r}}^{ns} f_{\mathbf{r}}^+ \hat{D}_{d\mathbf{r}} \rangle. \quad (3.2)$$

Other interactions with collective electrons are considered as the effects of higher orders.

The account of each ns -shell is carried out separately. Then the received expressions (1.7) are summarized. Index is omitted as before. (The additivity of the shell model allows it.) The influence of spin polarization on $\rho(0)$ is usually (and here too) neglected. Averaging the sum (1.5) and (3.1) gives the t. d. p.

$$\Phi(\xi_j) = U_s \xi_s^4 / 2 + gK_{sd} \xi_s \xi_d - \Gamma(0) K_{dd}(T) \xi_d,$$

$$y = \xi_d^2 \ll 1. \quad (3.3)$$

The t. d. p. is varied taking into account the inequality in (3.3), and the sum is received:

$$y = y_0 + y_1(T), \quad y_0 = (g/2U_s)^2, \quad (3.4)$$

when $\langle K_{sd} K_{sd}^+ \rangle \approx 1$.

The constant term y_0 is derived from intraionic correlations. Its dependence on changes in the lattice of a given crystal phase is neglected. Thermal excitation (CBF, phonons, etc.) are taken into account by the second term (3.4):

$$y_1 = (g\Gamma/2U_s^2) K_{dd}(T) = \langle d_{rs} \bar{d}_{RS} \rangle \approx 1 - Q_d \exp(-\beta E_0) T. \quad (3.5)$$

The correlator $K_{dd}(T)$ was calculated in [10] for the singular CBF part. Function (3.5) gives the dependence of chemical shift (1.8) on T , see Fig. 2,

$$\Delta R_s(T) \sim \rho_0 y_1(T), \quad \beta = 1/k_B T, \quad Q_d < 1. \quad (3.6)$$

Result (3.5) interprets experimental data [3, 11-14] (points in Fig. 2). Weak (almost a horizontal line) dependence on T for $T \leq 10^2$ K is caused by a gap E_0 in the CBF spectrum in α -Fe (see [10]). The linearity of $\Delta R_s(T)$ at $T > E_0/k_B$ is universal. It is observed in α -Fe [3], in stainless steel (and does not change under solving hydrogen in it) [11], and in chemical compound R_2Fe_{17} [12]. Function (3.5) is universal for all positions of Fe atoms in a lattice. Its form is not changed under solving deuterium ($Ho_2Fe_{17}D_{3,8}$) [12].

The unsufficiency of popular interpretations [3] of $\Delta R_s(T)$ on the basis of the Debye theory was noted in [11]. Result (3.6) proposed by the given theory reflects the strong dependence of $\rho(0)$ on covalent bonds and CBF.

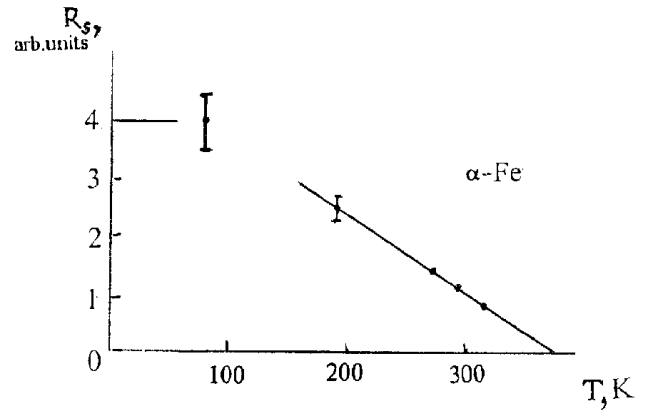


Fig. 2. The dependence of the chemical shift of the γ -resonance line of Fe^{57} ions in α -Fe on temperature T : the theory (solid line (3.5)) and experiment (points [14])

4. Calculation of Chemical Shift of the γ -Resonance Line of 4f-ions

The participation of 5d- and 4f-electrons in covalent bonds of RE ions complicates the calculation. The additional detailed elaboration is required for such REE as Ce, Pr, Yb. Their 'intermediate' valency means the instability of atomic shells. Highly active participation of a variable number of 4f-electrons in covalent bonds [6-8] is typical of them. The state of band electrons DOS (E) is also unstable, see Section 5. So (1.4) is used in the complete form ($\xi_f \neq 0$). Similarly to (3.1), the covalent Hamiltonian is introduced ($\Theta \approx \Gamma_f$) as

$$H^{\text{cov}} = - \xi_d \sum_{\mathbf{rR}} \Gamma_d(|\mathbf{r} - \mathbf{R}|) \hat{D}_{d\mathbf{r}} \hat{D}_{d\mathbf{R}} - \xi_f \sum_{\mathbf{rR}} \Gamma_f(|\mathbf{r} - \mathbf{R}|) \hat{D}_{f\mathbf{r}} \hat{D}_{f\mathbf{R}} + \text{h. c.} \quad (4.1)$$

For heavy REE, the f - f -interaction is neglected. It is possible at $J \approx \text{const}$. Formula (4.1) is averaged, and the t. d. p. of Mossbauer ions is obtained as

$$\Phi[4f] = U \xi_s^4 / 2 + g_{sd} \xi_s \xi_d + g_{sf} \xi_s \xi_f - \tilde{\Gamma}_d \xi_d - \tilde{\Gamma}_f \xi_f, \quad (4.2)$$

where the shell index n is omitted, i. e.

$$U_{ns} = U, \dots, \tilde{\Gamma}_d = \Gamma_d K_{dd}(T), \tilde{\Gamma}_f(T) = K_{df} \Gamma_f, \quad |\xi_{d,f}| \ll 1. \quad (4.3)$$

Correlators

$$K_{dd} = \langle \hat{D}_{d\mathbf{r}} \hat{D}_{d\mathbf{R}} \rangle, \quad K_{df} = \langle \hat{D}_{f\mathbf{r}} \hat{D}_{d\mathbf{R}} \rangle \quad (4.4)$$

as CBF functionals are estimated in Section 5.

T. d. p. (4.2) is varied taking into account inequality (4.3) and

$$y(T) = 1 - \xi_s^2(T) = y_0 + y_1(T). \quad (4.5)$$

The observable chemical shift is given by $y_1(T)$. The solutions are

$$\xi_j \approx (g_{sj} - \Gamma_j)/2U, y_0 = \sum_j (g_{sj}/2U)^2, j = d, f. \quad (4.6)$$

For the observable chemical shift of the γ -resonance line of a 4f-ion in the own REM, we get

$$y_1(T) \approx \sum_j [g_{sj} \Gamma_j K_{dj}(T)]/2U^2. \quad (4.7)$$

The calculation of REE with variable ("intermediate") valency [8] requires the addition of terms describing the delocalization of 4f-electrons to (4.1). The singularities of band spectra DOS (E) and CBF appear. This distinguishes their B_{HF} and chemical shift from the stable REM.

5. CBF Spectra and REM Stability

The stability of the hcp lattices of heavy REM is broken only near the melting temperature $T_L \approx 10^3$ K [6]. It indicates the domination of a metal bond. The lower value $T_L(4f) < T_L(3d) \approx (1.5 \div 2) \times 10^3$ K also indicates the smaller energy of the covalent bond than that in 3d-metals. The small value $|\Gamma_j| \ll \epsilon_F$ is supposed. The total Hamiltonian is taken [5, 8, 10] as

$$\begin{aligned} H \approx H_0 + \sum_{\mathbf{k}} \tilde{\epsilon}_{\mathbf{k}} f_{\mathbf{k}}^+ f_{\mathbf{k}} + N \sum_{\mathbf{k}} \Gamma_{d\mathbf{k}} d_{\mathbf{k}} \bar{d}_{\mathbf{k}} \xi_d^2 + \\ + N \xi_f \xi_d \sum_{\mathbf{k}} (\Gamma_{f\mathbf{k}} d_{\mathbf{k}} \bar{d}_{f\mathbf{k}} + \text{h.c.}) - \\ - \sqrt{N} \sum_{j\mathbf{k}} \xi_j [t_j(\mathbf{k}) d_{j\mathbf{k}} f_{\mathbf{k}} + \text{h.c.}], \quad \tilde{\epsilon} = \epsilon - \epsilon_F. \end{aligned} \quad (5.1)$$

Spin index σ is omitted. The expression for 4f-MEOS [10] reads

$$\hat{D}_{f\mathbf{r}} = \{d_{f\mathbf{r}} c_{f\mathbf{r}S} v_{f\mathbf{r}L}\}, \quad c_{f\mathbf{r}S}^2 = (1 + \mathbf{S}\mathbf{S}_{\mathbf{r}})/(2S + 1),$$

$$v_{f\mathbf{r}L}^2 = (1 + \mathbf{L}\mathbf{L}_{\mathbf{r}})/(2L + 1), \quad \Gamma_{\mathbf{k}} = \Gamma(0) - \Gamma(k),$$

$$d_{\mathbf{k}} = \sum_{\mathbf{r}} d_{\mathbf{r}} e^{-i\mathbf{k}\mathbf{r}}/N, \quad \Gamma(\mathbf{k}) = \sum_{\mathbf{r}} \Gamma(|\mathbf{r}|) e^{-i\mathbf{k}\mathbf{r}}. \quad (5.2)$$

The influence of the orbital moment \mathbf{L} on CBF is also neglected.

The anticommutators of two-time Green functions are introduced [10] as

$$G_{\mathbf{k}}^{c,f,d} = \langle\langle f_{\mathbf{k}}(\bar{d}_{f\mathbf{k}}, \bar{d}_{d\mathbf{k}}) | f_{\mathbf{k}}^+ \rangle\rangle_+, \quad \xi_{ij} = \xi_i/\xi_j. \quad (5.3)$$

The equations of motion

$$\begin{pmatrix} E - \tilde{\epsilon}_{\mathbf{k}} & \xi_f t_f^*(\mathbf{k}) & \xi_d t_d^*(\mathbf{k}) \\ t_f(\mathbf{k})/\xi_f & E & \xi_{df} \Gamma_{f\mathbf{k}}^* \\ t_d(\mathbf{k})/\xi_d & \xi_{fd} \Gamma_{f\mathbf{k}} & E - \Gamma_{d\mathbf{k}} \end{pmatrix} \begin{pmatrix} G_{\mathbf{k}}^c \\ G_{\mathbf{k}}^f \\ G_{\mathbf{k}}^d \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (5.4)$$

are solved in the limit of the large Fermi energy ϵ_F

$$\epsilon_F \gg |t_j|, |\Gamma_j|. \quad (5.5)$$

The CBF spectrum in a crystal phase (hcp) is interesting for small $k \ll 1$. The dispersion equation is

$$(E - \Gamma_{d\mathbf{k}}) E - Q_{df}(\mathbf{k})/\epsilon_F \approx 0, \quad k \ll 1, \quad (5.6)$$

where

$$\begin{aligned} Q_{df} = 2\text{Re} \{t_f^*(\mathbf{k}) t_d(\mathbf{k}) \Gamma_{f\mathbf{k}}^*\} - |t_f(\mathbf{k})|^2 \times \\ \times (E - \Gamma_{d\mathbf{k}}) - |t_d(\mathbf{k})|^2 E \end{aligned} \quad (5.7)$$

is not reduced to zero, when $k \rightarrow 0$.

The CBF spectrum (solution of (5.6))

$$E^{\text{CBF}}(\mathbf{k}) \approx \Gamma_{d\mathbf{k}} + \sum_j |t_j(\mathbf{k})|^2/\epsilon_F, \quad j = d, f, \quad (5.8)$$

contains a gap created by the delocalization of 5d- and 4f-electrons. The gap $E^{\text{CBF}}(0) \sim 10^{-2} \div 10^{-1}$ eV is large enough. It exponentially freezes the CBF contribution into t. d. p. The first term in (5.7) is here omitted. Its account does not influence a gap. But, in the first approximation, it results in the CBF splitting into two branches. It corresponds to the interaction of two subsystems (5d- and 4f-) of covalent electrons.

In a general case, there are also two branches of band electrons,

$$E_{\mathbf{k}}^+ \approx \tilde{\epsilon}_{\mathbf{k}} + \sum_j |t_j(\mathbf{k})|^2/\tilde{\epsilon}_{\mathbf{k}}, \quad E_{\mathbf{k}}^- \approx - \sum_j |t_j(\mathbf{k})|^2/\tilde{\epsilon}_{\mathbf{k}}, \quad (5.9)$$

separated by a large enough forbidden band. Near the Fermi surface ($\tilde{\epsilon}_{\mathbf{k}} \rightarrow 0$), we get

$$E_{\mathbf{k}}^+ \approx \tilde{\epsilon}_{\mathbf{k}} + |t_f(\mathbf{k})|^2 (\Gamma_{d\mathbf{k}}/|\Gamma_{f\mathbf{k}}|^2) + 2\text{Re}(t_f^* t_d/\Gamma_{f\mathbf{k}}). \quad (5.10)$$

The singularities of DOS (E) calculated from (5.10) are fuzzy. The observable sharp peaks of photoelectronic spectra (see [7]) fairly concern to intraatomic transitions.

The inhomogeneities of covalent energies $\Gamma_j(\mathbf{r})$, and also $t_j(\mathbf{r})$ are responsible for polymorphic deformations of the hcp lattice [5, 8, 10]. The energies of these inhomogeneities are small in comparison with $E^{\text{CBF}}(0)$ for heavy REM. It causes the observable [6] stability of heavy REM lattices. However, the situation in light REM changes appreciably [6-8].

6. Comparison with Experiment and Conclusions

The theory describes the influence of atomic and spin lattices on electron density on a nucleus $\rho(0)$ by hybridization of ns -electrons with covalent (magnetic) electrons. The contact Fermi interactions created by the spin polarization of ns -electrons which is due to the Hund exchange A_{sd} with magnetic $3d-t_{2g}$ -electrons of an ion Fe^{57} in $\alpha\text{-Fe}$. The calculated hyperfine field $B_{\text{HF}}(T) \sim S_T$ and is defined by the local mean spin S_T of an ion in the FM lattice. This result describes experimental data on local B_{FH} in different sublattices of Fe compounds [1-3, 11-14]. The large B_{HF} value on nuclei of $4f$ -ions [1, 2] is explained by the addition of spin-orbital bond λ_{sf} of ns -shells' spins with the orbital moment L of an ion to the Hund exchange. Here, $B_{\text{HF}}(T) \sim J_T$ is expressed through the mean angular momentum J_T of a $4f$ -ion.

The chemical (isomeric) shift of a γ -resonance line is expressed through the covalent parameters $\hat{\Lambda}$. The hybridization of $ns-3(5)d$ -electrons decreases $\rho(0)$. This decrease contains the interionic covalent part. It depends on CBF, i.e. on temperature T . The singular CBF part gives a linear dependence for the chemical shift in $\alpha\text{-Fe}$ and Fe compounds on T . It explains the classical experimental data on $\alpha\text{-Fe}$ [3], stainless steel [11], and intermetallide $\text{Ho}_2\text{Fe}_{17}$ [12]. The theoretical form of this dependence (3.5) is not practically changed on the addition of H [11] or D [12] (for $\text{Ho}_2\text{Fe}_{17}\text{D}_{3,8}$), though, at hydrogenation (deuteration), the value of chemical shift at $T = 0$ K changes strongly.

The interpretation of γ -resonance data in Fe alloys [11] in the Debye theory leads to a sharp contradiction with another data [13]. The introduction of $\sim 1 - 10$ at.% of hydrogen leads to a strong isomeric shift. But the observed temperature dependence of chemical shift remains in the form (3.5). Interpretation of these data in the Debye theory requires the increase of the Debye temperature by more than 50% at hydrogenation (up to 550 K). The latter contradicts

the well-known data on metal-hydrogen systems [13].

Our theory explains the data in [11] by small changes of wave function amplitudes (1.4). The change of coefficients (3.5), which interpret the temperature dependence of chemical shift, is connected with the H ions' contribution into covalent bonds. This result in the deformation of the singular part of CBF dispersion on the H introduction. So the proposed theory explains completely all observed characteristics of γ -resonance lines. This gives the quantitative basis for the γ -resonance use in the analysis of phase diagrams and properties of transition metals and their alloys.¹

The theory proves the stability of hcp lattices of heavy REM by a large gap in the CBF spectrum. This gap is created by the delocalization energy of $5d$ - and $4f$ -electrons into the conduction band. The CBF freezing stabilizes a hcp lattice practically in the whole interval of the existence of a crystal phase.

Conclusions:

1. The theory connects the dependence of electronic density on a nucleus $\rho(0)$ on a state of atomic and spin lattices with hybridization of ns -shells with covalent electrons.

2. In $\alpha\text{-Fe}$, it is $3d-t_{2g}$ -electrons. The hyperfine field $B_{\text{HF}}(T) \sim S_T$ and is created by the local spin $S_T(T)$. The CBF excitation is responsible for the chemical shift of a γ -resonance line $R_s(T)$ at changing T . The singular part of CBF is responsible for the linear $R_s(T)$ dependence in $\alpha\text{-Fe}$ and Fe alloys (compounds) [10].

3. For $4f$ -ions, it is $5d$ - and $4f$ -electrons. The spin-orbital $ns-4f$ -bond ($\sim \lambda_{sf}$) gives a large contribution into their hyperfine field $B_{\text{HF}}(T) \sim J_T$. It defines a large value of $B_{\text{HF}}(4f) \sim 10^2 \div 10^3$ T.

The chemical shift (4.7) is proportional to the parameters of covalent bonds Γ_d and Γ_f , multiplied accordingly by the correlators of $5d$ - and $4f$ -electrons.

4. The calculated CBF spectra in heavy REM have the large energy gap $E(0)$ (5.8). It is caused by delocalization of covalent electrons. The relatively weak dependence of Γ_j on deformations does not practically influence $E(0)$. These factors stabilize the hcp lattice of heavy REM.

The inhomogeneity of covalent bonds Γ_j is responsible for the destabilization of light REM (their polymorphism). It results in the strong dependence of Γ_j and $E(0)$ on lattice deformations [8].

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¹The detailed calculation of the H influence is completely analogous to that in [5, 15] and is not given here.

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