MAGNETIC ANISOTROPY OF 3*d*- AND 4*f*-METALS IN THE MODEL OF CRYSTAL FIELD WITH CALCULATION OF COVALENT BONDS AND THEIR FLUCTUATIONS. 2. MAGNETIC PROPERTIES OF HEAVY RARE-EARTH METALS

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The theory, developed in part I [1], is applied to explain the magnetic properties of rare-earth metals (REM). The anomalous temperature dependences of magnetization $M_s(T)$ and magnetic anisotropy (MA) constant $K_1(T)$ are explained. The covalent theory of REM giant magnetic anisotropy allows one to explain a change of the $K_1(0)$ sign in the series of heavy REM.

1. Angular Momenta and Magnetic Anisotropy of Pure Rare-earth Metals

The magnetic order in REM is formed by local 4*f*-electrons. A good localization of the unfilled 4*f*-shell in a heavy part of series of 4*f*-elements allows one to simply connect magnetization M_s with angular moment $J = L + S$, the paramagnetic Curie temperature $\theta_p(S)$ with spin S by the de Gennes formula [2 – 4], MA constant with large nonfreezing orbital moment L [3]. This concept well explains the maximum $\theta_p = 317$ K among REM (at $T_c = 293$ K) for Gd ($[Xe]4f^7 5d^1 6s^2$) and its minimum value $|K_1| \leq 10^7$ erg/cm^3 at $S = 7/2$ and $L = 0$. The maximum value of MA constants in REM $|K_1| \geq 10^8$ erg/cm^3.

The concept explains qualitatively also a decrease in θ_p as the number of 4*f*-electrons increases from Tb($4f^9$) up to Tm($4f^{13}$), though deviations from the de Gennes formula become larger during this increase. The constants $K_{1,2}$ do not display the simple dependence on L, both on value and on sign: the K_1 sign changes with increase of the number of 4*f*-electrons in a series between Ho and Er. Much worse does this concept explain data for an easy part of REM series.

REM refractoriness and their mechanical and rather active (in contrast to goop *d*-metals) chemical properties [2] indicate a dominant role of covalent bonds. Therefore, the use of the simple $s - f$-model [2, 4] for explanation of REM properties (as for the criticism of the one-electronic band model in application to REM, see [3]) is not more than a palliative. The necessity of a direct account of covalent bonds and electrons becomes ripe. In REM, it is possible to consider 5*d*-electrons, both nominal (in Gd) and passing into covalent bonds from 4*f*- or 6*s*-shells. For them, we introduce spin and orbital ($\vec{s}_{\vec{r}}$, $\vec{l}_{\vec{r}}$) induced moments. A spin moment $\vec{\pi}_{\vec{r}}$ of band electrons is similarly introduced, and their orbital moment is considered to be frozen (= 0).

It is possible to consider that the Hamiltonian of crystal field (CF)

$$H^{\mathrm{CF}} = A_{20}^{dd}(l_{\vec{r}}^z)^2 + A_{20}^{df}(l_{\vec{r}}^z L_{\vec{r}}^z) + \ldots,$$

$$\vec{L}_{\vec{r}} = (2 - g)\vec{J}_{\vec{r}}, \quad \vec{S}_{\vec{r}} = (g - 1)\vec{J}_{\vec{r}} \tag{1.1}$$

is a solution of the CF problem, assuming that invariants as $(L_{\vec{r}}^z)^{2n}$ $(n \geq 1)$ have negligible coefficients $A^{ff} \to 0$ because of intraionic localization of magnetic 4*f*-electrons. On the variational calculation, we consider Hamiltonians – functionals $(\vec{s}_{\vec{r}}, \vec{l}_{\vec{r}}, \vec{\pi}_{\vec{r}})$. According to [2 – 4], the values (S, L, J) and g-factor are set constant, corresponding to 3-valent 4*f*-ions. The intraionic Hamiltonians are

$$H_{\vec{r}}^{\mathrm{Coul}} = U_d(1 + \vec{s}_{\vec{r}}^{\,2} + \vec{l}_{\vec{r}}^{\,2})/2 + U_{df}(\vec{l}_{\vec{r}}\vec{L}_{\vec{r}}), \quad U_{df} = U_L, \tag{1.2}$$

$$H_{\vec{r}}^{\mathrm{ex}} = -A_d(\vec{S}_{\vec{r}}\vec{s}_{\vec{r}}) - A_s(\vec{S}_{\vec{r}}\vec{\pi}_{\vec{r}}) - A_{sd}(\vec{s}_{\vec{r}}\vec{\pi}_{\vec{r}}), \tag{1.3}$$

$$H_{\vec{r}}^{s-o} = \lambda_1(\vec{S}_{\vec{r}}\vec{l}_{\vec{r}}) + \lambda_2(\vec{s}_{\vec{r}}\vec{L}_{\vec{r}}) + \lambda_3(\vec{\pi}_{\vec{r}}\vec{L}_{\vec{r}}) + \lambda_4(\vec{s}_{\vec{r}}\vec{l}_{\vec{r}}). \tag{1.4}$$

The interionic bonds, namely, covalent bond

$$H^{\mathrm{ch}} = -\sum \Gamma(|\vec{\rho}|)d_{\vec{r}}\bar{d}_{\vec{r}}(1 + \vec{s}_{\vec{r}}\vec{s}_{\vec{r}} + \vec{l}_{\vec{r}}\vec{l}_{\vec{r}}) \tag{1.5}$$

and metal (t.d.p) one

$$\Phi^{\rm el} = p_1\varepsilon_{\rm F}^{5/3} + p\vec{\pi}^2, \quad p \sim \varepsilon_{\rm F}^{1/2}, \quad \vec{\pi}_{\vec{r}} = \pi\vec{\alpha}_{\pi r} \tag{1.6}$$

are also expressed through variation parameters. The last in the mean field approximation (without the account of magnon effects) are expressed through orts $\alpha_{j\vec{r}}$ (1.6), etc. ($j = s, l$).

Variation of sum (1.2) – (1.6) under conditions (1.1) results in the system of operator equations:

$$\begin{pmatrix} \hat{U}_d & \lambda_4 - A_{sd} \\ \lambda_4 & \hat{U}_d & 0 \\ -A_{sd} & 0 & p \end{pmatrix} \begin{pmatrix} \hat{s}_{\vec{r}} \\ \hat{l}_{\vec{r}} \\ \hat{\pi}_{\vec{r}} \end{pmatrix} = \begin{pmatrix} \tilde{A}_d \\ -\tilde{\lambda}_1 \\ \tilde{A}_s \end{pmatrix} \hat{J}_{\vec{r}}, \tag{1.7}$$

where

$$\hat{U}_d = U_d - \Sigma\,\Gamma(|\vec{\rho}|)d_{\vec{r}}\bar{d}_{\vec{r}},$$

$$\tilde{A}_d = A_d(g-1) - \lambda_2(2-g),$$

$$\tilde{\lambda}_1 = \lambda_1(g-1) + U_L(2-g),$$

$$\tilde{A}_s = A_s(g-1) - \lambda_3(2-g). \tag{1.8}$$

Solutions in the operator form,

$$\vec{s}_{\vec{r}} = \hat{\Delta}_3^{-1}\hat{\Delta}_s\vec{J}_{\vec{r}}, \quad \hat{\Delta}_s = (\tilde{A}_d\hat{U}_d + \tilde{\lambda}_1\lambda_4)p + A_{sd}\hat{U}_d\tilde{A}_s,$$

$$\vec{l}_{\vec{r}} = \hat{\Delta}_3^{-1}\hat{\Delta}_l\vec{J}_{\vec{r}}$$

$$\hat{\Delta}_l = p(\tilde{\lambda}_1\hat{U}_d - A_d\lambda_4) + A_{sd}(\tilde{A}_s\lambda_4 - \tilde{\lambda}_1 A_{sd}),$$

$$\vec{\pi}_{\vec{r}} = \hat{\Delta}_3^{-1}\hat{\Delta}_\pi\vec{J}_{\vec{r}}, \quad \hat{\Delta}_\pi = \tilde{A}_s(\hat{U}_d^2 - \lambda_4^2) + A_{sd}(\hat{U}_d\tilde{A}_d - \tilde{\lambda}_1\lambda_4), \tag{1.9}$$

depend on the operator denominator

$$\hat{\Delta}_3 = \hat{\Delta}_2 p - A_{sd}^2\hat{U}_d, \quad \hat{\Delta}_2 = \hat{U}_d^2 - \lambda_4^2. \tag{1.9′}$$

We simplify the analysis, assuming below that $A_{sd} \to 0$.

The CF Hamiltonian (1.1) is reduced to the MA Hamiltonian

$$H^{\rm CF} = \hat{k}_1^i(J_{\vec{r}}^z)^2,$$

$$\hat{k}_1^i \approx A_{20}^{dd}(\hat{\Delta}_2^{-1}\hat{\Delta}_l)^2 + A_{20}^{df}(2-g)\hat{\Delta}_3^{-1}\hat{\Delta}_l, \tag{1.10}$$

or

$$\hat{k}_1^i(g) \approx A_{20}^{df}(2-g)(\hat{U}_d^2 - \lambda_4^2)^{-1}\{(g-1)\times$$

$$\times\,(\lambda_1\hat{U}_d - \lambda_4 A_d) + \lambda_2\lambda_4(2-g)\} +$$

$$+ A_{20}^{dd}(\hat{U}_d^2 - \lambda_4^2)^{-2}\{(g-1)(\lambda_1\hat{U}_d -$$

$$-\lambda_4 A_d) + \lambda_2\lambda_4(2-g)\}^2. \tag{1.10′}$$

Special case of Gd for which the second term in (1.10) goes to zero, shows that $|A^{dd}| << |A^{df}|$. As the first term in (1.10) does not change its sign, for the MA description in polymorphic (under pressure) Gd, it is necessary to calculate it similarly to Co and to take into account anisotropic exchange, similarly to Section 3 of part I [1] for MnBi. Therefore, the analysis of heavy REM with 'giant" MA is performed below only on the basis of the second term in (1.10) (A^{df}).

The values $3 \le L \le 6$ and $6 \le J \le 8$ vary in small limits. It is necessary to seek the reason for a large dispersion of MA constants, along with change of their signs, in distinction of REM parameters, which are contained in braces. The experimental dependences of MA constants $K_{1,2}(T)$ for the FM phases of REM on temperature agree with the theory of ideal ferromagnons [4], i.e., are defined by the correlator $\langle(J_{\vec{r}}^z)^{2n}\rangle$. Therefore, we suppose in this case that

$$\hat{U}_d \approx U_d - \Gamma(0), \quad \langle(J_{\vec{r}}^z)^2\rangle \sim J_T^3(T), \quad T < T_c/2 \tag{1.11}$$

and, with regard for signs of $K_1(0)$, receive the inequalities

$$\{\lambda_1[U_d - \Gamma(0)] - \lambda_4 A_d\}/\lambda_2\lambda_4 \lesssim -(2-g)/(g-1) =$$

$$= -Q_K(g) < 0 \tag{1.12}$$

for Tb, Dy, Ho (sign >) or for Er, Tm (sign <). All REM parameters are assembled in the left part (the right part is a number) and characterize covalent electrons. Their values are defined by probabilities of $4f$ – $5d$-transitions and $5d$ – $6s$-hybridization. The solution of these problems requires the account of multielectronic wave functions, which functionally define the model parameters.

Numbers in the right part of (1.12) are

RE^{3+}	Tb	Dy	Ho	Er	Tm
Q_K	1	2	3	4	5

. (1.13)

The change of a sign of $K_1(0)$, i.e., k_1^i (or anisotropy of paramagnetic temperature $\theta_{p||} \ne \theta_{p\perp}$ [2, 4]), occurs at $Q_K \ge 3$. The left part of (1.12) is a negative combination of spin-orbital parameters λ_j with

$$U_d - \Gamma(0) > 0, \quad A_d > 0, \quad (\lambda_1/\lambda_4) > 0. \tag{1.14}$$

It allows us to make conclusions about a correlation between the exchange parameter A_d (determining the covalent contribution to spontaneous magnetization), covalent bond energy $\Gamma(0)$, and Hubbard parameter U_d.

Our theory also allows one to indicate a nature of deviations of the values θ_p of REM series from the de Gennes formula [2, 4]. Assuming that the covalent contribution to the exchange parameter $A_j(g)$ of the local Heisenberg model is main, and considering that the $s-f$-exchange contribution is smaller, we receive the exchange Hamiltonian from the covalent one (1.5) by using (1.1):

$$H^{\mathrm{ex}} = -\Sigma\Gamma(|\vec{r}-\vec{r}'|)\,[\hat{\Delta}_3(\vec{r})\hat{\Delta}_3(\vec{r}')]^{-1}\times$$

$$\times\ \{\Delta_s(\vec{r})\Delta_s(\vec{r}') + \Delta_l(\vec{r})\Delta_l(\vec{r}')\}(\vec{J}_{\vec{r}}\vec{J}_{\vec{r}'}). \qquad (1.15)$$

In approximation (1.10), we write down the exchange parameter A_J (coefficient before the binary form of angular moments $\vec{J}_{\vec{r}}$ in (1.15)), separating the de Gennes contribution $\sim (g-1)^2$:

$$A_J(|\vec{r}-\vec{r}'|) \approx \Gamma(|\vec{r}-\vec{r}'|)\langle\Delta_2^{-2}(\vec{r})\rangle Q_{\mathrm{ex}}(g)\,,$$

$$\hat{U}_d \approx U_d - \langle\hat{\Gamma}_{\vec{r}}\rangle = \tilde{U}_d, \qquad (1.16)$$

where the covalent parameter is

$$\hat{\Gamma}_{\vec{r}} = \Sigma\Gamma(|\vec{r}-\vec{r}'|)d_{\vec{r}}\bar{d}_{\vec{r}'} \approx \Gamma(0). \qquad (1.16')$$

We receive

$$Q_{\mathrm{ex}}(g) = (g-1)^2[(A_d\tilde{U}_d - \lambda_1\lambda_4)^2 + (\lambda_1\tilde{U}_d - \lambda_4 A_d)^2] +$$

$$+ (2-g)^2(\lambda_2^2\tilde{U}_d^2 + \lambda_2^2\lambda_4^2) +$$

$$+ 2(g-1)(2-g)[-\lambda_2\tilde{U}_d(A_d\tilde{U}_d - \lambda_1\lambda_4) +$$

$$+ \lambda_2\lambda_4(\lambda_1\tilde{U}_d - \lambda_4 A_d)].$$

The de Gennes term (the first in (1.17)) depends on the intraionic (U_d and A_d) and interionic ($\Gamma(0)$) parameters, even if to neglect spin-orbital parameters λ_j. A quite good agreement of a number of experimental values θ_p for heavy REM with the de Gennes formula shows, that the parameters (U_d, A_d, Γ) vary weakly in this series. A deviation of the experimental θ_p from the de Gennes formula to smaller values [4] can be connected with the last term in (1.17), linear in λ_j. This implies the inequality $\lambda_2 > 0$. The given conclusion is caused by smaller values $|\lambda_j| << (U_d, A_d)$ for covalent electrons, in contrast to magnetic $4f$-electrons.

2. Comparison of the Theory with Experiment and Conclusions

MA of magnetics, as the even effect by Akulov, is well described by expansion of magnetic t.d.p. in even invariants, composed from projections of magnetic moments' vectors. It simplifies the MA identification, gives a mathematical basis of such experimental methods as a method of rotational moments, angular dependence of FMR frequencies, magnetic susceptibility tensor in weak magnetic fields, etc.. Primary MA theories, see [5], assumed the t.d.p. expansion in harmonic invariants. However, the treatment of experiment (by Fourier expansion) has resulted in a simplified expansion in trigonometric functions of M_s angular components of equal degrees, see [4, 6]. The quantum-statistical theory of ferromagnons [7] has shown that simplified experimental expansions result in crossing of temperature dependences of MA constants of different orders. The pure result of Akulov – Zener for MA constants of the n-th order,

$$K_n(T) = K_n(0)(J_T/J_0)^{n(2n+1)}\,,\quad \vec{J}_T = |\langle\vec{J}_{\vec{r}}\rangle|\,,\quad n \geq 1. \qquad (2.1)$$

is received only for the harmonic expansion of MA t.d.p. [7]. It is especially important in the case of Gd, for which $|K_2(0)| > K_1(0)|$, and also for FM alloys, especially cubic ones.

Difference of the real functions $K_n(T)$ from the simple formula (2.1) can be explained sometimes (see [7]), by distinction of harmonic and simple trigonometric (used by experimenters) expansions of MA energy. However, the analysis of MA genesis is required in substances, in which orientation magnetic phase transitions take place [6] (rare-earth $3d$ – $4f$-intermetallides, MnBi, ferrometals, showing polymorphism at rather low temperatures (Co, $T_0 \approx 600$ K) or pressure (Gd, $P \leq 40$ kbar), Ni [8], etc.) and which have anomalous (in comparison with (2.1)) dependences $K_n(T)$.

The given work is devoted to this problem. The neglect of covalent energies both in the simple local Heisenberg model (resulting in (2.1), and in the simple band [9], or $s-d$ (f)-model, does not allow one connect $K_n(T)$ anomalies with instability of an atomic lattice, leading to instability of a spin lattice. The direct account of covalent contributions to MA connects anomalies of MA t.d.p. with peculiarities (extrema) of CBF spectra.

The theory of ideal ferromagnons explains data on $K_n(T)$ on the basis of (2.1) with account [7] for

ferrometals with stable lattices. These are Fe, heavy REM, except Gd. It is necessary to note that the simple ferromagnon theory within the Heisenberg model is supposed to be applicable to ferrodielectrics, for example, to yttrium ferrite [4]. This assumption is based on a possibility to disregard the effects of $s-d$-exchange [2 – 4]. However, the results received in the given work (see also [10, 11]) indicate the necessity to take into account covalent bonds of magnetic ions which are more essential for magnetics. We note the successful application of the covalent theory for explanation of a fractional spin moment and MA anomalies of cubic Ni [8].

Specific Conclusions of the Theory

1. The MA Hamiltonian, in agreement with the Akulov symmetry theory of even effects, is expressed through even combinations of the projections of the angular moment operator $\vec{J}_{\vec{r}}$ of a magnetic ion at site $\vec{r}$. The expansion coefficients (k_n^p) are expressed through spin-orbital parameters, multiplied by operator combinations of the Coulomb, exchange, and covalent parameters $(p = i, \text{ex})$.

2. One-ionic MA (i), expressing through the CF parameters A_{nm}^{tj} of electronic subsystems $(t, j) = (p, d, f)$, has practically constant parameters k_n^p. MA constants are received in this case in the form of (2.1) with the amendments [7], under the condition of stability of the lattice and electronic system.

3. The simultaneous account of one-ionic MA (i) and anisotropic exchange (ex) results in the operator form of $\hat{k}_n(\hat{\Gamma}_{\vec{r}})$. Operator forms $\hat{\Gamma}_{\vec{r}}$ of the covalent bond, included in $\hat{k}_n^i$, after their averaging on CBF ensembles, result in the additional temperature dependence of MA constants through T-dependences of average MA parameters $k_n^p(T)$

$$K_n(T) = \sum_p k_n^p(T)\, \kappa_p(J)(J_T/J)^{n(2n+1)},$$

$$\kappa(J) = \text{const}, \quad p = i, \text{ ex}. \tag{5.2}$$

The function $k_n^p(T)$ is expressed through CBF correlators.

4. Unstable lattices, having soft CBF modes, are characterized by the strong dependence $k_n^p(T)$. Under a competition of one-ionic MA and of anisotropic exchange, it can result in a strong dependence on T and even in changes of the signs of MA constants $K_n(T)$.

5. Nonfreezing orbital moments $L \geq 1$ of a magnetic ion cause the large MA parameter $k_n^i \sim \lambda L$, linear in the spin-orbital parameter λ. In ferrometals with frozen orbital moment (Gd, 3d-magnetics), MA is the effect of the second order in λ. The smaller value $k_n^i \sim k_n^{\text{ex}} \sim (\lambda^2/U)$ agrees with predictions in [2, 3].

6. Soft CBF modes are accompanied by DOS peaks near the Fermi surfaces.