ANISOTROPIC EXCHANGE AND ANISOTROPY OF THE MAGNETIC PROPERTIES OF RARE-EARTH METALS

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An anisotropic Hamiltonian of indirect interaction via the conduction electrons is obtained in the second approximation. The Hamiltonian can serve as a basis for calculation of magnetic anisotropy in rare earths. The anisotropy $\Delta\Theta$ of the paramagnetic Curie point is calculated for the yttrium subgroup of the rare-earth metals. The theoretical dependence of $\Delta\Theta$ on the number of the element agrees qualitatively with experiment; in particular, $\Delta\Theta$ changes sign on transition from f^{10}(Ho) to f^{11}(Er).

1. In the microscopic theory of the magnetic properties of rare-earth ferromagnets (despite the comparatively short period of its development), more significant results have now been obtained than for magnetic substances with unfilled d-shells. The reason for this is the possibility of describing the magnetic f-electrons well by means of states of atomic type with complete quantum numbers **S**, **L**, and **J**; this apparently is not the case for d-metals, where the coupling between d-electrons is broken by a strong crystalline field. One of the most important achievements of the theory for rare-earth metals (REM) is the establishment of a theoretical dependence of the magnitude of the Curie point on the number of the element (de Gennes' formula), agreeing qualitatively with experiment. This is a good argument in favor of the correctness of the indirect-exchange model and of our general ideas about the origins of magnetic order in REM. A further step in the development of the theory is, in our view, to obtain similar dependences for other magnetic properties of REM, and primarily for the magnetic anisotropy.

Of course this problem is more complicated, since it is connected with anisotropic interactions that are much more diverse than the usual isotropic exchange responsible for the magnitude of the Curie point. Nevertheless, the present state of the theory of REM allows us to start on its solution. In[1,2] we presented a convenient method for deriving spin Hamiltonians of magnetic crystals in the general case of an arbitrary electron configuration; it was based on the theory of addition of angular momenta. This method was used to obtain a Hamiltonian of interaction between conduction electrons and localized electrons of the 4f-shell of REM, containing also anisotropic exchange terms. In quite analogous fashion one can, within the framework of this method, consider also the second approximation of perturbation theory, which leads, as is known, to a Hamiltonian of interaction between the localized moments of 4f-ions. The anisotropic part of this interaction can serve as a basis for calculating various effects, in REM, connected with magnetic anisotropy. In the present paper, we shall consider the anisotropy of the paramagnetic susceptibility and its dependence on the number of the element, for the second half of the REM series.

2. The second-approximation Hamiltonian can be obtained from the usual theory of second-order perturbations. We start with the form of the exchange Hamiltonian of conduction electrons with 4f-electrons (see formula (11) of[2]),

$$H_{ex} = N^{-1} \sum_{\nu\Gamma_1\Gamma_2 k k' \sigma\sigma' b_1 b_2} T^{b_1 b_2}_{\alpha_1\alpha_2} \hat{u}^{b_2}_{-\alpha_2} \hat{v}^{b_1}_{\alpha_1} A^{+}_{\nu\Gamma_1} A_{\nu\Gamma_2} a^{+}_{k\sigma} a_{k'\sigma'}, \tag{1}$$

where $A_{\nu\Gamma}$ and $a_{k\sigma}$ are, respectively, the second-quantization operators of the f electrons (ν = number of the site, Γ = SLJM) and of the conduction electrons, and the form of the tensors T, $\hat{u}$, and $\hat{v}$ was given in[2]. On treating (1) as a perturbation to the energy of the system of conduction electrons, we get, after transformations with the tensor operators that enter in (1) and after averaging with respect to the operators of the conduction electrons,

$$\begin{aligned} H^{(2)} = {} & \frac{16e^4 m}{3\pi^2\hbar^2} \sum_{\nu_1\nu_2} \sum_{ll'pl''l'''p'} \sum_{b_1 b_2 b_1' b_2' tt' l_1} (-1)^{p-p'+t'} i^{l-l'+l''+l'''+t+t'} \\ & \cdot B^{tll'p}_{t'l''l'''p'}(\nu_{12}) [b_1][b_2][b_2'][J]^2 (l\|C^p\|l_1)(l_1\|C^p\|l') \\ & \times (l_1\|C^{p'}\|l''')(l'''\|C^{p'}\|l_1)[l]^{1/2}[l']^{1/2}(t\|C^l\|l''')(t'\|C^{l'}\|l'') \\ & \times \sum_{aa'} (-1)^{a+a'} \begin{Bmatrix} L & J & S \\ L & J & S \\ a & b_2 & b_1 \end{Bmatrix} \begin{Bmatrix} L & J & S \\ L & J & S \\ a' & b_2' & b_1 \end{Bmatrix} \begin{Bmatrix} l_1 & l_1 & a \\ l & l' & p \end{Bmatrix} \begin{Bmatrix} l_1 & l_1 & a' \\ l'' & l''' & p' \end{Bmatrix} v^{(b,a)} v^{(b_1 a')} [t]^{1/2} [t']^{1/2} \\ & \times \sum_{rs} (-1)^{r-s+b_2+b_2'} \begin{Bmatrix} a & a' & r \\ b_2' & b_2 & b_1 \end{Bmatrix} \begin{Bmatrix} all' \\ rtt' \\ a'l'''l'' \end{Bmatrix} \hat{v}^{tt'r}_{-s} \hat{\delta}^{b_1 b_2' r}_{s}. \end{aligned} \tag{2}$$

Here

$$b^{tll'p}_{t'l''l'''p'}(\nu_{12}) = \int_0^\infty dk n_k k^2 \int_{-\infty}^{\infty} \frac{k'^2 dk' j_l(k\nu_{12}) j_{l'}(k'\nu_{12}) G^{p}_{ll'}(kk') G^{p'}_{l''l'''}(kk')}{k^2 - k'^2} \tag{3}$$

$$\hat{v}^{tt'r}_{-s} = [r]^{1/2} \sum_{\mu\mu'} (-1)^{t-\mu+t'-\mu'} C^{t}_{\mu}(\nu_{12}) C^{t'}_{\mu'}(\nu_{12}) \begin{pmatrix} t & r & t' \\ -\mu & s & -\mu' \end{pmatrix}, \tag{4}$$

$$\hat{\delta}^{b_1 b_2' r}_{s} = [r]^{1/2} (-1)^{b_2+b_2'} \sum_{\alpha_2\alpha_2'} (-1)^{\alpha_2+\alpha_2'} \hat{u}_{\alpha_2}{}^{b_2} \hat{u}^{b_2'}_{\alpha_2'} \begin{pmatrix} b_2 & r & b_2' \\ -\alpha_2 & s & -\alpha_2' \end{pmatrix} \tag{5}$$

and $C^{t}_{\mu}(k) = (4\pi/[k])^{1/2} Y_{t\mu}(k)$, whereas $(l \| C^t \| l')$ is a reduced matrix element of $C^{t}_{\mu}(k)$ in spherical functions (n_k in (3) is the Fermi distribution function).

Formula (2) is a general expression for the Hamiltonian of indirect exchange in REM and can be used to calculate very diverse properties and effects in these metals. An estimate of the radial integrals $B^{tll'p}_{t'l''l'''p'}(\nu_{12})$ can be made, for example, in the plane-wave approximation for the conduction electrons and

in the approximation of the asymptotic expressions for the wave functions of the f-electrons. It turns out that they are functions of the two parameters $x = k_F\bar{r}_f$ and $y = 2k_F\nu_{12}$ (k_F is the Fermi quasimomentum, $\bar{r}_f$ the mean value of the radius of the f-shell), so that

$$B^{ll'l''p}_{t'l'l''p'}(\nu_{12}) = b^{ll'l''p}_{t'l'l''p'}(x)\, f_\alpha(tt', y), \quad \alpha = l + l' + l'' + l''. \tag{6}$$

Estimates of the quantities $b(x)$ and expressions for $f_\alpha(y)$ are given by Kasuya and Lyons[3].

We shall further use the Hamiltonian (2) to calculate the anisotropy of the paramagnetic susceptibility χ in REM. We remark first that, as is shown by experiment, the constant Θ in the Curie-Weiss law $\chi = c/(T - \Theta)$ possesses a marked anisotropy for all elements of the second half of the REM series, and that the anisotropy changes sign on transition from Ho to Er. For this reason, the greatest interest attaches to terms in (2) that change sign on transition from the configuration $f^{10}(f^4)$ to $f^{11}(f^3)$ (the metals are considered trivalent). We take into account also that, according to the estimates of the quantities (6) given in[3], the integral b^{0003}_{0003} is the largest, while the integrals b^{1003}_{1112}, b^{1003}_{1114}, and b^{0003}_{0023} are about an order of magnitude smaller than b^{2003}_{0003}, yet larger than all the other integrals, which we do not write down. We can then write the main part of $H^{(2)}$ in the form

$$H^{(2)} = \frac{2ne^4}{\pi\hbar^2}\sum_{\nu_1\nu_2}\{[I_1(g-1)^2 + I_2D_1(g-1) + I_3nD_2](\mathbf{J}_{\nu_1}\mathbf{J}_{\nu_2}) - 3I_2(g-1)D_1\nu_{12}^{-2}(\boldsymbol{\nu}_{12}\mathbf{J}_{\nu_1})(\boldsymbol{\nu}_{12}\mathbf{J}_{\nu_2}) - 3I_3nD_2\nu_{12}^{-2}(\boldsymbol{\nu}_{12}\mathbf{J}_{\nu_2})\},$$

$$I_1 = \frac{8}{49}\left(B^{0003}_{0003} + \frac{54}{5}B^{1003}_{1112} + 8B^{1003}_{1114}\right), \tag{7}$$

$$I_2 = -16\sqrt{\frac{2}{7}}\left(\frac{27}{175}B^{1003}_{1112} + \frac{1}{15}B^{1003}_{1114} - \frac{2}{7}B^{2003}_{0023}\right),$$

$$I_3 = -\frac{144}{35\sqrt{15}}\left(B^{1001}_{1112} + \frac{50}{9\sqrt{7}}B^{2003}_{0023}\right). \tag{8}$$

Here D_1 and D_2 are the same as in paper[2], and n is the number of electrons in the f-shell. The first term in (7) is isotropic, but the two others are anisotropic and can serve to explain the anisotropy of various effects in REM. We can determine the anisotropy of the paramagnetic Curie point by calculating the energy given by (7) when the vector J is directed along the hexagonal axis z and when it is in the basal plane (κ is Boltzmann's constant):

$$\Delta\Theta = \Theta_{xx} - \Theta_{zz} = {}^2/_3\varkappa^{-1}(E_{xx} - E_{zz}). \tag{9}$$

From (7) we have

$$\Delta\Theta = \frac{4e^4m}{3\pi^2\hbar^2\varkappa}[pD_1(g-1) + qnD_2]J(J+1), \tag{10}$$

where

$$p = -\sum_{\nu_1\nu_2}\frac{A_1}{\nu_{12}^2}[I_2(\nu_{12}^x)\nu_{12}^{x^2} - I_2(\nu_{12}^z)\nu_{12}^{z^2}],$$

$$q = -\sum_{\nu_1\nu_2}\frac{A_2}{\nu_{12}^2}[I_3(\nu_{12}^x)\nu_{12}^{x^2} - I_3(\nu_{12}^z)\nu_{12}^{z^2}]. \tag{11}$$

The appearance of the anisotropy $\Delta\Theta$ is due to the dependence of the integrals B on the distance ν_{12} between ions, and also on the symmetry of the distribution of neighbors. With limitation to the first sphere of anisotropy in a face-centered close-packed lattice, it appears solely on account of the different numbers of neighbors in the basal plane and in the direction of the z axis, because the distance to all of these are equal.

	Gd	Tb	Dy	Ho	Er	Tu
$\Delta\Theta_{exp}$	~0	44	43	15	−29	
$\Delta\Theta_{theor}$	0	48	40	21	−25	−24

If we regard p and q as two parameters, we can choose their values by the method of least squares from the condition of best agreement of the anisotropy $\Delta\Theta$ with experiment. The results of the calculations are given in the table for $p = -6.01 \times 10^{-3}$ and $q = 2.65 \times 10^{-4}$. The experimental data in the table are taken from the book of Belov et al.[4][1)].

These values of p and q give satisfactory agreement for the dependence of $\Delta\Theta$ on the number of the element. We shall now estimate the ratio of the absolute values of the anisotropic and isotropic contributions; or, what amounts to the same thing, the magnitude of $\Delta\Theta/\Theta$. By use of (6), we have

$$\frac{\Delta\Theta}{\Theta} = \sim 10\frac{D_1}{(g-1)}\frac{b^{1003}_{1112}}{b^{0003}_{0003}}\frac{f_2(11,y)}{f_0(00,y)}, \tag{12}$$

where, according to[3],

$$f_0 = \frac{\cos y}{y^3} - \frac{\sin y}{y^4}, \quad f_2 \sim -\left(\frac{\cos y}{y^3} - \frac{7\sin y}{y^4}\right). \tag{13}$$

With $f_0/f_2 \sim 1$, and supposing that $b^{1003}_{1112}/b^{0003}_{0003} \sim 10^{-1}$, we get $\Delta\Theta/\Theta \sim 1\%$, instead of the 10% actually observed. There are several factors that can improve the agreement of theory with experiment.

First, the value of the parameter $y = 2k_FR$ may be such that f_2/f_0 will be ~ 10. Thus, for example, for $y = 10.85$[2)] we have $f_0 \approx -4 \times 10^{-5}$ but $f_2 \approx 4 \times 10^{-4}$, and consequently we get the right order of magnitude for $\Delta\Theta/\Theta$. It must be expected, however, that when we decrease the values of the quantity f_0, which determines the absolute value of Θ, we should correspondingly increase the values of the radial integrals b^{0003}_{0003}, b^{1003}_{1112}, etc.; that is, consider them about an order of magnitude larger than usual.

Second, it is possible that the ratio $b^{1003}_{1112}/b^{0003}_{0003}$ in (12) is nevertheless ~1. The fact is that the estimate 10^{-1} of the order of magnitude of this ratio is essentially dependent on the assumption that the conduction electrons can be described by plane waves. In actuality this may be incorrect (for example, in the presence of an appreciable p-component).

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[1)] In recently conducted experiments [5], somewhat different values were obtained for $\Delta\Theta$ in Er.

[2)] In the free-electron model, $y = 10.06$ [3].