

Electron structure of the 4f shells and magnetism of rare-earth metals

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The relationship between magnetic properties of rare-earth metals and the electron structure of the f shell is considered. Simple concepts are used to show how many-electron quantum numbers of the spin, orbital and total angular momenta of the f shell are related to the Curie temperature, magnetic moment, magnetic anisotropy, and other properties of a rare-earth metal and how modern mathematical apparatus for the addition of angular momenta and specifically the Racah algebra can be used to calculate these characteristics. The differences in respect of the nature of magnetism between rare earths and metals in the iron group with partly filled d shells are discussed. A clear interpretation is given of the periodic dependence (with a period of 1/4) on the number of the f electrons exhibited by magnetic properties (particularly in the case of the magnetic anisotropy) within the rare-earth series. A brief discussion is given of magnetic properties of alloys in relationship to the local anisotropy.

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“We shall leave the one-electron theory of magnetism to butterflies and worms.” D.C. Mattis, *The Theory of Magnetism*, Harper and Row, New York (1965)

1. CLASSIFICATION OF MAGNETIC MATERIALS IN ACCORDANCE WITH THEIR ELECTRON STRUCTURE

The history of intensive study of the magnetism of rare earths, which are elements with partly filled 4f shells, begins from the middle fifties. We now know very well and utilize extensively in practice such unique properties of rare-earth magnetics as the high atomic magnetic moments and the enormous magnetocrystalline anisotropy, which make them irreplaceable in the fabrication of high-coercivity magnetic materials.

Much work has been done also on the development of a theory of magnetic properties of rare earths at microscopic and phenomenological levels. Nevertheless, there is one significant gap in the literature which is the absence of a sufficiently clear physical account of the nature of the special magnetic properties of rare earths and their relationship to the electron structure of the 4f shell. The reason for this is the complexity of the mathematical description of the f electrons, which are the carriers of the magnetism in rare earths, leading to the absence of clear ideas needed in developing a physical picture of some specific effect. We shall try to fill at least partly this gap and demonstrate that a simple qualitative account is possible of the main features of the magnetism of rare earths, in spite of the difficulties encountered in a quantitative description. We shall concentrate our attention

on the magnetic anisotropy which is probably the effect that manifests most strikingly the special properties of the 4f electrons in crystals.

The main purpose of the present review is thus to present some of the main topics in the theory of the f-electron systems in a form accessible to a wide circle of physicists. The author will regard his task as fulfilled if this account will make it easier to understand theoretical treatments by experimentalists working on rare-earth materials and will stimulate theoreticians dealing with the complex problems in solid-state physics to provide a physical interpretation in rounding off the mathematical results of their calculations.

In contrast to the d transition periods, in which magnetically ordered crystals form only a small fraction of all the elements in these periods, rare earths represent a whole period of 12 magnetic metals, so that it is possible to study in detail the relationship between their magnetic properties and the number of electrons in the 4f shell as it gradually fills. In this respect the rare-earth series is a Mendeleev periodic table in miniature and (as we shall show later) inside this table there are also cycles with a specific periodicity of the observed properties.

First of all, it is useful to define the very existence of inner partly filled 4f shells, because there is a contradiction here when we look upon this topic from a conventional point of view. The explanation of the effect is not trivial and it essentially requires going beyond the one-electron theory framework. According to this theory, the vacant levels below that of the chemical potential should naturally be filled

by transitions of electrons with higher energies. However, these levels are vacant only from the point of view of the one-electron representation according to which the energy of a given electron is independent of the state of other particles. This assertion is clearly invalid in the case of atom-like states with a strong Coulomb interaction between electrons. If, for example, in some state f^n (where $n < 14$) the one-electron energy is $\varepsilon(f^n) = n^{-1}E(f^n)$, where $E(f^n)$ is the total energy of the f^n shell found allowing for the Coulomb interaction $n(n-1)Q/2$ (Q is the Coulomb integral), then further filling of the f shell changes the one-electron energy considerably:

$$\varepsilon(f^{n+1}) - \varepsilon(f^n) = (n+1)^{-1}E(f^{n+1}) - n^{-1}E(f^n) = \frac{1}{2}Q.$$

Since $Q \approx 5-10$ eV, clearly, if $\varepsilon(f^n) < \varepsilon_F$, then $\varepsilon(f^{n+1})$ can become higher than the Fermi energy ε_F . Therefore, the Hartree-Fock one-electron energy of the f electrons depends strongly on the f -shell configuration and the filling of the vacant positions in the shell corresponds to a transition to a different configuration with very different one-electron energies and functions. In practice, this means that the validity of one-electron concepts is very limited in the case of the f shells.

If there is some interaction comparable with the difference between the energies of two configurations, we cannot confine our treatment to the Hartree-Fock one-configuration approximation and it is necessary to adopt a many-electron description of the f shell allowing for several configurations.

Already during the first stages of the development of studies of the magnetism of rare earths it has been found that their properties differ considerably from magnetics belonging to the iron group and that the rare earths form a separate class. It has been found that many rare-earth magnetics exhibit a much stronger spontaneous magnetization (or, which is equivalent, a larger atomic magnetic moment) than any of the magnetic materials known before. The observed atomic magnetic moment agrees well with the theoretical value for the corresponding f^n configuration in a free atom (or, more exactly, in the configuration of its trivalent ion R^{3+} , where R both here and later denotes a rare-earth element). This simple relationship was the starting point of the rapid and successful development of a theory of the magnetism of rare earths because this relationship means that the magnetic $4f$ electrons in crystals retain largely their atomic properties.¹⁾ It is this circumstance that separates the rare-earth magnetics into a separate class from the point of view of the electron structure, in contrast to the $3d$ magnetics for which a simple atomic description of the d electrons is not possible because they form a collective state in crystals and this leads to serious difficulties in the theory of magnetism of the $3d$ metals. Therefore, there are two main types of magnetics: $3d$ and $4f$ (we shall ignore here diamagnetic crystals). The actinide group (i.e., the $5f$ magnetics) are currently regarded as intermediate between the other two groups.

An even more characteristic property of the rare earths is their large orbital magnetic moment, whereas the magnetism of the d magnetics is almost of pure spin nature. The quenching of the orbital moments in the latter case is related to the delocalized nature of the d electrons.

2. DESCRIPTION OF THE f ELECTRONS

The validity of the atomic description of the f electrons in a crystal removes the main difficulties associated with delocalization. Nevertheless, the problem is still quite difficult from the theoretical point of view if we bear in mind that the f shell is the most complex in the Mendeleev periodic table. The main difficulty in the description relates to a strong degeneracy of the f states ($2l+1=7$). It is appropriate to recall here that the development of a theory of atomic spectra of rare earths was completed much later than other chapters in atomic spectroscopy. For example, the well-known monograph of Condon and Shortley [The Theory of Atomic Spectra, Cambridge University Press and the MacMillan Co., New York (1935)], translated into Russian in 1949, deals only with the simplest f^n configurations ($n < 3$). Realistic calculations of the f shells had become possible only after the remarkable work of Racah carried out in 1942-1949 (an account of this work and bibliography can be found in Ref. 2). The Racah method soon found wide acceptance in the atomic theory and in the theory of nuclei, but in the early sixties it had not yet penetrated solid-state theory.²⁾

We can understand and appreciate the importance of the new methods proposed by Racah simply by examining the expression for the matrix elements of the electrostatic interaction of electrons in the f states ($l=3, -3 \leq m \leq 3, \sigma = \pm 1/2$):

$$\begin{aligned} & \hat{J}(m_1\sigma_1, m_2\sigma_2; m'_1\sigma'_1, m'_2\sigma'_2) \\ &= \int \Psi_{m_1\sigma_1}^*(r_1) \Psi_{m_2\sigma_2}^*(r_2) \frac{e^2}{r_{12}} \Psi_{m'_1\sigma'_1}(r_1) \\ & \Psi_{m'_2\sigma'_2}(r_2) dr_1 dr_2. \end{aligned} \quad (1)$$

In the calculations it is necessary to deal with all the projections of the orbital angular momentum m and of the spin σ forming a given many-electron state with the total angular momenta SL , which makes the calculations extremely time-consuming.

Nevertheless, some progress has been made even in the case of this direct method. A very simple formula for the description of the exchange interaction of the f electrons in crystals was proposed by de Gennes in 1958 (Ref. 3): it involves the replacement of the spin angular momentum S by the total angular momentum J in the Heisenberg Hamiltonian using the expression

$$S = (g-1)J. \quad (2)$$

Then, the exchange Hamiltonian \mathcal{H}_{ex} becomes (here, I_{12}^{eff} is the effective exchange integral and g denotes the Landé g factor)

$$\mathcal{H}_{ex} = \sum_{1,2} I_{12}^{eff} (g-1)^2 J_1 J_2. \quad (3)$$

This expression was used directly to describe the dependence of the paramagnetic Curie temperature θ_p on the total angular momentum J , i.e., on the number of the f electrons or on the atomic number of the rare-earth elements:

$$\theta_p \sim (g-1)^2 J(J+1). \quad (4)$$

In spite of its simplicity, Eq. (4) describes the experimental results surprisingly well.

The de Gennes expression was proved later by Liu⁴ using the method of Young schemes.

These very first investigations made it clear that the many-electron quantum numbers S , L , and J of the whole f^n shell are important in the description of the f electrons. Although in the case of such simple quantities as the magnetic moment or the Landé g factor this is a fairly trivial conclusion, the situation in the case of the other physical properties is much more complex.

For example, Eqs. (2) and (3) are sufficient to see that the magnitude of the exchange interaction is proportional only to the total spin S , in spite of the fact that the total magnetic moment is

$$\mathbf{M} = g\mu_B \mathbf{J} = g\mu_B (\mathbf{L} + \mathbf{S}), \quad (5)$$

i.e., that it contains both the spin and orbital components. It is thus found that the orbital angular momentum does not affect the Curie temperature. However, we shall later see that Eq. (4) represents only the first term of the expansion in terms of the orbital angular momenta of conduction electrons. It is the largest in the model of the indirect exchange of the f electrons via the conduction electrons on condition that the latter have basically the s -type symmetry ($l=0$). The classification of the wave functions of the conduction electrons in accordance with the orbital angular momentum should be regarded as their representation in the form of an expansion in terms of spherical or Legendre polynomials. For example, in the case of a plane wave, we have

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l j_l(\mathbf{k}\mathbf{r}) Y_{lm}(\vartheta_r, \varphi_r) Y_{lm}^*(\vartheta_k, \varphi_k).$$

In the case of exchange via the conduction electrons characterized by $l \neq 0$ the orbital components of the f shell begin to play a role. Therefore, a consistent theory not only accounts for the meaning of the de Gennes approximation, but also predicts the existence of the orbital exchange. The large magnitude of the latter should give rise to a dependence on the atomic number of the rare-earth element, which differs considerably from Eq. (4). The good agreement of Eq. (4) with the experimental results shows that the main components of the wave functions of the conduction electrons correspond to $l=0$. Nevertheless, the orbital contributions characterized by $l \neq 0$ should play an important role in various anisotropic effects.

We can now draw the following conclusion: the differences between the simplest magnetic properties of various rare-earth metals are governed by the quantum numbers of the ground terms of these metals. For example, in the case of Tb (f^6 , 7F term), we have $S=3$, $L=3$, $J=6$, $g=3/2$, $M=g\mu_B J=9\mu_B$, and $\theta_p=(21/2)I^{\text{eff}}$; the corresponding values for Er (f^7 , 4I term), we have $S=3/2$, $L=6$, and $J=15/2$, and we find that $g=6/5$, $M=6.15/5.2=9\mu_B$, and $\theta_p=(51/20)I^{\text{eff}}$. This provides a partial answer to the question asked in a footnote: what is the difference between Tb and Er? If we now consider other more complex properties, such as the magnetic anisotropy, quadrupole effects, etc., we find that the simple representation is no longer adequate. Nevertheless, the problem (including determination of the relevant dependences on the atomic number of an element) is readily soluble if we use more general and more powerful mathematical apparatus, which is discussed below. Once again the observable physical quantities can then be expressed in terms of the quantum numbers S , L , and J .

Kondo published in 1962 a review⁵ in which he gave the Hamiltonian of the electrostatic interaction between the conduction and f electrons and found the coefficients of the various terms using equations relating the one-electron operators of the angular momenta to the operators \mathbf{S} , \mathbf{L} , and \mathbf{J} of the f^n configuration. Some of these coefficients were tabulated in Ref. 5.

In contrast to the outstanding work of Kondo published in 1964, the 1962 review remained practically ignored and was not used in the subsequent development of the theory of rare-earth metals.³⁾

Another more logical approach is to use the methods of atomic spectroscopy in dealing with crystals.

A paper of Kaplan and Lyons⁶ of 1963 and one by the author of the present review⁷ of 1966 were based on the same idea of using the Racah method to calculate the interaction between the f electrons in rare-earth metals. Kaplan and Lyons used the Racah method in its conventional form to calculate the matrix elements of the electrostatic interaction in the representation of many-electron wave functions. The present author⁷ employed the Racah method in the second quantization representation by introducing many-electron operators of groups of electrons corresponding to the f^n configurations. The latter method is particularly convenient in the derivation of the "spin" Hamiltonians usually employed in the theory of magnetism.

It was found possible to relate the second quantization operators of groups of electrons A_{JM} , the angular momenta \mathbf{J} (or \mathbf{S} and \mathbf{L}) by expressions of the type⁴⁾

$$\mathbf{J} = \sum_{M_j M'_j} (JM_J | \mathbf{J} | JM'_j) A_{JM_J}^\dagger A_{JM'_j}, \quad (6)$$

which represent generalization of the familiar one-electron expressions for $s=1/2$:

$$s^z = \frac{1}{2}(a_+^\dagger a_+ - a_-^\dagger a_-), \quad s^\pm = a_\pm^\dagger a_\mp. \quad (7)$$

It is very important to note that the matrix elements of the operators of the momenta can be expressed in terms of the Wigner $3j$ symbols

$$(JM_J | J_i | JM'_j) \sim \begin{pmatrix} J & J & 1 \\ M & -M' & M' - M \end{pmatrix} \quad (i=z, \pm), \quad (8)$$

which are precisely the main elements of the Racah algebra and obey convenient summation rules. For example,

$$\sum_{M_1 M_2} \begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J' \\ M_1 & M_2 & M' \end{pmatrix} = (2J+1)^{-1} \delta_{MM'} \delta_{JJ'}, \quad (9)$$

$$\sum_{\mu_1 \mu_2 \mu_3} (-1)^{\sum_{i=1}^3 l_i + \mu_i} \begin{pmatrix} J_1 & l_2 & l_3 \\ M_1 & \mu_2 & -\mu_3 \end{pmatrix} \begin{pmatrix} l_1 & J_2 & l_3 \\ -\mu_1 & M_2 & \mu_3 \end{pmatrix} \\ \times \begin{pmatrix} l_1 & l_2 & J_3 \\ \mu_1 & -\mu_2 & M_3 \end{pmatrix} = \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J_3 \\ l_1 & l_2 & l_3 \end{pmatrix}. \quad (10)$$

The quantity

$$\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$$

is called the Racah $6j$ symbol and it represents the Racah method in a nutshell: the time-consuming summation over

the numerous projections of the momenta is performed in this way. Both analytic expressions and tabulated values are available for the coefficients.

The application of this method to our task of calculating the spin Hamiltonian is very instructive. For example, in the lowest order [involving expansion of $\exp(i\mathbf{k}\cdot\mathbf{r})$ in terms of spherical harmonics] the exchange Hamiltonian is found to be ($[Y] = 2Y + 1$)

$$\mathcal{H}_{\text{ex}}^{\text{ex}} = \sum_{(\nu\mathbf{k}\mathbf{k}'\sigma\sigma')} (-1)^{J-S-L-1} I_{\nu}(\mathbf{k}\mathbf{k}') \left[\frac{[J][S]S(S+1)}{J(J+1)} \right]^{1/2} \times \begin{Bmatrix} L & S & J \\ 1 & J & S \end{Bmatrix} (\mathbf{s}\mathbf{J}_{\nu}) a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}'\sigma}. \quad (11)$$

Equation (11) appears more cumbersome than the expressions proposed by de Gennes, Liu, or Kondo:

$$\mathcal{H}_{\text{ex}} = \sum_{(\nu\mathbf{k}\mathbf{k}'\sigma\sigma')} I_{\nu}(\mathbf{k}\mathbf{k}') (g-1) (\mathbf{s}\mathbf{J}_{\nu}) a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}'\sigma}. \quad (12)$$

However, since

$$\begin{Bmatrix} L & S & J \\ 1 & J & S \end{Bmatrix} = (-1)^{L+S+J+1} (g-1) \left[\frac{J(J+1)}{S(S+1)[S][L]} \right]^{1/2}, \quad (13)$$

we find—as expected—that Eqs. (11) and (12) are identical and Eq. (11) does not provide any new result. Nevertheless, Eq. (11) is very important from the methodological point of view. The method behind it is readily extended to more complicated cases, whereas without Eq. (11) generalization of Eq. (12) meets with considerable difficulties.

The Hamiltonian of the sf interaction (up to the second order $l = 2$ in the case of conduction electrons) was obtained in Refs. 7, 10, and 11 on the basis of this method and its exchange part is as follows:

$$\mathcal{H}_{\text{ex}}^{22}(f^n[\text{SLJ}]) \\ c) = \sum_{\nu\mathbf{k}\mathbf{k}'\sigma\sigma'} e^{i(\mathbf{k}-\mathbf{k}')\cdot\nu} a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}'\sigma'} \left\{ A \left[\frac{n}{2} + 2(g-1) (\mathbf{s}\mathbf{J}_{\nu}) \right. \right. \\ \left. \left. + B(\mathbf{k}\mathbf{J}_{\nu})(\mathbf{k}'\mathbf{J}_{\nu}) + iC(2-g)([\mathbf{k}\mathbf{k}']\mathbf{J}_{\nu}) \right. \right. \\ \left. \left. + \dots \text{ (total of 9 invariants)} \right\}. \quad (14)$$

All the coefficients A, B, C, etc. were calculated as a function of the numbers S, L, and J for all the f^n configurations. The first term in Eq. (14) represents the isotropic part of the exchange interaction and the third corresponds to the orbital exchange of the type

$$(2-g)(\mathbf{1}\mathbf{J}) = (\mathbf{1}\mathbf{L}), \quad (15)$$

which may become anisotropic in a crystal field. The majority of the other terms (for example, the second term) can also make anisotropic contributions to the various physical properties (magnetic anisotropy, electrical resistivity, etc.).

3. MAGNETIC ANISOTROPY OF RARE EARTHS

We shall now use the method described above to tackle the problem of the magnetic anisotropy of rare earths. The following principal characteristics of the anisotropy have been established experimentally:

1) the magnetic anisotropy has the giant value $K_1 \approx 10^8$ erg/cm³ (in the case of the most strongly anisotropic d metal, which is Co, the anisotropy is an order of magnitude less);

2) there are two types of anisotropy: easy axis and easy plane. Reversal of the sign of the anisotropy occurs⁵⁾ on transition from Nd(f^3) to Sm(f^5) and in the second half of the rare-earth series on transition from Ho(f^{10}) to Er(f^{11}).

As pointed out already, the main distinctive features of the rare-earth magnetism are associated with the major contribution of the orbital components. These are the components which are responsible for the strong magnetic anisotropy. We shall illustrate this conclusion by comparing the mechanisms of the appearance of the magnetic anisotropy of the 3d and 4f magnetics.

In the case of the 3d magnetics we find that, in contrast to rare earths, a very strong crystal field destroys the atomic structure of the SL terms of the d^n configuration and particularly the multiplet structure of the total angular momentum J. We therefore have to consider the orbital angular momentum l of single electrons. The experimental results demonstrate that these angular momenta are also almost completely quenched. By quenching of l we usually understand that the average value \bar{l} vanishes in the ground state. In the case of the atomic levels this occurs when the ground state is a singlet (i.e., when it is spherically symmetric). In the case of the d electrons in a crystal the ground state can be a singlet in the presence of a crystal field of sufficiently low point symmetry which splits off, for example, a sublevel $m = 0$ from the other states. However, real ferromagnetic metals are characterized by a high symmetry and the quenching of l is clearly due to a different mechanism associated with the periodic part of the crystal potential $V(\mathbf{r})$. A very important feature of this mechanism is that the orbital angular momentum operator $\mathbf{l} = \hbar[\mathbf{r}\cdot\mathbf{k}]$ is diagonal in respect of the electron quasimomentum \mathbf{k} . Then, all the diagonal matrix elements l_{ij} expressed in terms of the crystal functions of the degenerate subbands vanish because of the symmetry (or antisymmetry) of the wave functions $\psi_{\mathbf{k}}$ relative to reversal of the sign of the projection of m , whereas the off-diagonal matrix elements l_{ij} , although not equal to zero, are associated with different energies $\varepsilon_i(\mathbf{k})$ for a fixed value of \mathbf{k} . This means that the contribution of these off-diagonal matrix elements l_{ij} to \bar{l} , in the presence of some perturbation mixing of the states $\psi_{\mathbf{k}}^i$ and $\psi_{\mathbf{k}}^j$ is given by $\approx h_{ij} l_{ij} / \Delta_{ij}(\mathbf{k})$, where h_{ij} is the off-diagonal matrix element of the perturbation and $\Delta_{ij}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) - \varepsilon_j(\mathbf{k})$ is a large quantity of the order of the band width Δ [with the exception of some special points \mathbf{k} at which degeneracy sets in and we have $\Delta_{ij}(\mathbf{k}) = 0$].

A good example is provided by the triple representation t_{2g} of cubic crystals. It contains three functions ψ^i which are combinations of functions φ_m with specific values of m :

$$\psi^{1,2} = \frac{1}{\sqrt{2}}(\varphi_1 \pm \varphi_{-1}), \quad \psi^3 = \frac{1}{\sqrt{2}}(\varphi_2 - \varphi_{-2}), \quad (16)$$

when (as is clear from the structure in respect of m) we have $l_{ii} = 0$ for all cases and we find that, for example, $(\psi_1 | l^z | \psi_2) = l_{12}^z = 1$.

If ψ^i had corresponded to a degenerate local level, the existence of $l_{ij}^z \neq 0$ would have meant that in fact the orbital angular momenta are not quenched since in a magnetic field H_z a regrouping of the functions would have taken place and the degeneracy would have been lifted in accordance with the values of the electron energy $g\mu_{13}mH_z$. This in turn would have given rise to a large orbital angular momentum $\approx l$.

In the case of crystal functions of the band type the degeneracy of the functions $\psi_{\mathbf{k}}^i$ is lifted for almost all values of \mathbf{k} . This means that as long as $g\mu_B mH_z \ll \Delta(\mathbf{k})$, regrouping of the functions in a field H_z is not favored by the energy considerations and the value of the angular momentum unquenched by the field is proportional to a small quantity $\approx g\mu_B mH_z / \Delta(\mathbf{k})$.

If we now consider some internal interaction dependent on the vector \mathbf{l} , we find that it can also mix the states $\psi_{\mathbf{k}}^i$ and thus unquench \mathbf{l} . This function can be performed by the spin-orbit interaction

$$\mathcal{H}_{so} = \lambda(\mathbf{l}\mathbf{s}), \quad \lambda = \frac{\hbar^2}{2m^2c^2} \int \frac{1}{r} \frac{dV}{dr} |\psi^2| r^2 dr. \quad (17)$$

This interaction is important in discussing the magnetic anisotropy because it relates the vectors \mathbf{s} and \mathbf{l} . Here, \mathcal{H}_{so} unquenches \mathbf{l} and gives rise to a small orbital angular momentum $\tilde{\mathbf{l}} \approx \lambda / \Delta$ which becomes oriented in a crystal and again because of \mathcal{H}_{so} it orients the spin \mathbf{s} .

If \mathcal{H}_{so} is small [$\mathcal{H}_{so}^i(k) \ll \Delta(\mathbf{k})$], the anisotropy energy E_a can be calculated from perturbation theory. In the case of uniaxial crystals this result appears in the second order (and for cubic crystals it appears in the fourth order) and its magnitude is governed by a simple combination of the parameters of the theory λ and Δ : $E_a \approx \lambda^2 / \Delta$ ($\Delta \approx \epsilon_F$). In fact, E_a corresponds to the spin-orbit interaction energy with an unquenched orbital momentum $\tilde{\mathbf{l}}$:

$$E_a \approx \tilde{E}_{so} \cdot \lambda(\tilde{\mathbf{l}}\mathbf{s}) \approx \frac{\lambda^2}{\Delta}. \quad (18)$$

We can readily estimate the order of magnitude of the various quantities. For example, if $\lambda \approx 10^{-14}$ erg and $\Delta \approx \epsilon_F \approx 10^{-11}$ erg, it follows that $E_a \approx 10^{-17}$ erg $\approx 10^{-1}$ K.

The magnetization process is then as follows (Fig. 1). In $H = 0$ the vectors \mathbf{l} and \mathbf{s} are oriented along the easy axis z . The application of a field H_x along the difficult axis tilts \mathbf{s} from the z axis as the ratio $\mu_B H / \tilde{E}_{so}$ is increased (the vector $\tilde{\mathbf{l}}$ hardly tilts away from the z axis, because its direction is set by the electrostatic forces of the crystal field E_{cr} , which is much stronger than \tilde{E}_{so} in the case of the d metals). If $H \approx H_a = \tilde{E}_{so} / \mu_B$, the coupling between $\tilde{\mathbf{l}}$ and \mathbf{s} is broken by the field and the magnetization reaches saturation along the difficult direction. The quantity H_a is called the anisotropy field and it is an important characteristic of the magnetic hardness of a material.

The actual calculations of the magnetic anisotropy based on the band structure were made for Ni. In one of the latest papers of Kondorskiĭ and Straube¹² it was found that

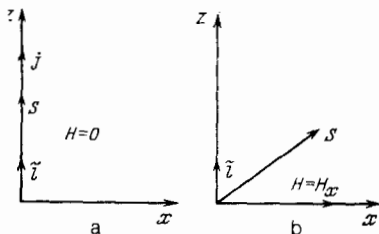


FIG. 1. Positions of the vectors representing the orbital $\tilde{\mathbf{l}}$ and spin \mathbf{s} angular momenta in 3d ferromagnets in the case of a weak spin-orbit interaction: a) in the absence of an external field; b) in the presence of an external field $H = H_x$ directed along the difficult axis.

the main contribution to the magnetic anisotropy of Ni comes from those states in a crystal which lie near the points of degeneracy where $\Delta(\mathbf{k}) = 0$. Quantitative results depend strongly on details of the energy band structure. There may also be qualitative deviations from the results given above, which are valid in the nondegenerate parts of the \mathbf{k} space.

We shall now consider the situation in rare earths. In the case of the 4f electrons the energy of the crystal field E_{cr} is low compared with the electrostatic interaction and with the spin-orbit energy. For this reason the total atomic quantum numbers S , L , and J of the f^n configuration are retained also in the case of a crystal (at least, for the ground state). Consequently, the process of magnetization in a rare earth occurs in a different way from the corresponding process in a d magnetic.

If $H = 0$, the vector $\mathbf{J} = \mathbf{L} + \mathbf{S}$ lies along the easy z axis governed by the minimum of the crystal energy E_{cr} of the angular momentum L in a crystal. In a field H_x the coupling between \mathbf{L} and \mathbf{S} is retained (because $E_{cr} \ll E_{so}$) and they rotate as a whole, approaching the direction of H_x (Fig. 2). The angle of rotation is governed by the ratio $g\mu_B JH / E_{cr}$. Although the energy $E_{cr} \approx 10^{-2} - 10^{-3}$ eV for the 4f electrons is the smallest among the energies of other interactions [$E_{so}(4f) \approx 10^{-1}$ eV], it is considerably higher (by two or three orders of magnitude) than the effective energy $\tilde{E}_{so} \approx 10^{-5}$ eV [see Eq. (18)] responsible for the magnetic anisotropy of the 3d metals with quenched orbital angular momenta. This accounts for the giant anisotropy exhibited by rare-earth magnetics.

The existence of unquenched orbital angular momenta results in another important consequence in the theory of magnetic properties of rare earths. We can easily show that the sf exchange interaction of Eq. (14) leads, in the second order of perturbation theory, not only to an indirect ff exchange of the Heisenberg (or the de Gennes) type, but it also creates terms of the type

$$\mathcal{H}_{orb}^{ex} = \sum_{1,2} (2-g)^2 I_{12}^{eff} (\mathbf{J}_1 \mathbf{J}_2) \dots \sum_{1,2} I_{12}^{eff} (\mathbf{L}_1 \mathbf{L}_2), \quad (19)$$

i.e., it results in orbital exchange. The latter (in contrast to spin exchange) readily becomes anisotropic after allowance for the anisotropy of the crystal.

Equation (19) can be deduced directly from the third term on the right-hand side of Eq. (14). Other anisotropic contributions (for example, those of the pseudodipole exchange type) were considered in Refs. 10 and 11 and corresponding magnetic anisotropy energy was calculated. This energy is governed by the crystal field and by the anisotropic exchange (we shall write down only the largest terms):

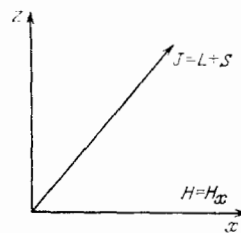


FIG. 2. Strong spin-orbit interaction (4f ferromagnets). The vectors \mathbf{L} and \mathbf{S} (related by $\mathbf{J} = \mathbf{L} + \mathbf{S}$) rotate in an external field (applied along the difficult axis) as a whole.

TABLE I

R	Gd	Tb	Dy	Ho	Er	Tm
$K_1^{cr}, 10^8 \text{ erg/cm}^3$	0	-5,5	-5,05	-1,98	1,97	5,5
$K_1^{ex}, 10^8 \text{ erg/cm}^3$	0	-5,5	-4,6	-1,43	1,1	1,85
$K_1^{exp}, 10^8 \text{ erg/cm}^3$	$\approx 0,005$	-5,5	-5	-2,2	—	—
$\Delta\theta^{cr}, \text{K}$	0	44	38	15	-16	-44
$\Delta\theta^{ex}$	0	48	40	21	-25	-24 (-66)
$\Delta\theta^{exp}$	≈ 0	44	48	15	-29	-58

$$E_R = (K_1^{cr} + K_1^{ex}) \cos^2 \vartheta,$$

$$K_1^{cr} = \alpha_J A_2 J (J-1/2), \quad K_1^{ex} = (g-1) D_1 J^{eff} J^2,$$

$$A_2 = \frac{e^2 Z^{eff}}{a} \frac{\bar{r}_f^2}{a^2} 1,035 \left(\frac{c}{a} - 1,633 \right),$$

$$D_1 = \left(\frac{2J+1}{J(J+1)} \right)^{1/2} \begin{Bmatrix} L & J & S \\ L & J & S \\ 2 & 1 & 1 \end{Bmatrix}, \quad J^{eff} \approx \frac{|J^f|^2}{e_F}. \quad (20)$$

Here, α_J is the Stevens factor (its relationship to the $6j$ coefficients can be found in, for example, Ref. 13); Z^{eff} is the effective charge of the ions; \bar{r}_f^2 is the average of the square of the radius of the f shell; the rest of the notation is standard.

The expressions in Eq. (20) readily yield estimates of the orders of magnitude of K_1^{cr} and K_1^{ex} . Since $A_2 \approx 10^{-14} \text{ erg} \approx 100 \text{ K}$ and $\alpha_J \approx 10^{-2} - 10^{-3}$ (for heavy rare earths), it follows that $K_1^{cr} \approx 10 - 100 \text{ K} \approx 10^7 - 10^8 \text{ erg/cm}^3$. We then have $D_1 \approx 10^{-2}$, $J^{eff} \approx 10^{-15} \text{ erg}$, so that $K_1^{ex} \approx 1 - 10 \text{ K} \approx 10^6 - 10^7 \text{ erg/cm}^3$.

We thus find that the magnetic anisotropy of rare earths is one or two orders of magnitude higher than of the most strongly anisotropic hexagonal d magnetics. We have seen that this difference is a consequence of the fact that in the case of rare earths the magnetic anisotropy is governed by the electrostatic interaction of the crystal field or anisotropic exchange type involving unquenched orbital angular momenta and not the weak spin-orbit interaction in the case of almost completely quenched orbital angular momenta, which is true of the d magnetics.

Table I gives the anisotropic characteristics of rare earths: K_1 and the anisotropy of the paramagnetic Curie temperature $\Delta\theta_p$. The quantity $\Delta\theta_p = \theta_{\parallel} - \theta_{\perp}$ represents the anisotropy of the paramagnetic susceptibility tensor of uniaxial crystals characterized by χ_{\parallel} and χ_{\perp} and it is found by extrapolation of the Curie-Weiss law $\chi_{\parallel,\perp}^{-1} = C^{-1}(T - \theta_{\parallel,\perp})$ up to the temperature $T = \theta_{\parallel,\perp}$ at which $\chi^{-1} = 0$. The phase transition point, i.e., the Curie point T_c , is not generally equal to θ_p and is isotropic. For clarity, a comparison with the experimental results will be made separately for the crystal field and exchange anisotropy mechanisms.¹¹

The largest difference between the theoretical values for these two mechanisms is found in the case of Tm which is therefore of the greatest interest from the point of view of the magnetic anisotropy. Although a complete comparison of the theory with experiments is difficult because of the absence of accurate data, the contribution of the crystal field is clearly dominant and the anisotropic exchange⁶⁾ contributes only 10-20% (Ref. 14). A reliable experimental determination of this exchange would be of fundamental interest in the theory of the exchange interaction. In contrast to the single-ion mechanism of the crystal field, the anisotropic exchange gives rise to a two-ion anisotropy so that it can be separated on the basis of the composition dependence. It would therefore be of interest to study experimentally the magnetic anisotropy of rare-earth alloys. One should mention also the possibility of using methods based on the hyperfine interactions and used to detect the anisotropic exchange.¹⁶

We shall now consider the sign of the magnetic anisotropy. Here the theory provides precise predictions. It is clear from Table II that the signs of both α_J and D_1 are reversed on transition from the f^3 (f^{10}) to the f^4 (f^{11}) configurations in the first (second) halves of the rare-earth series and also on transition from the first to the second half. If we bear in mind that Pm has not yet been investigated, whereas Eu and Yb have cubic lattices and, consequently are of no interest to us, the agreement with the experimental results is satisfactory. It follows from the simple discussion given below that this mathematical result has a clear physical meaning.

Since the magnetic anisotropy is related to the orbital components of the total angular momenta, we must consider the magnitude and orientation of these components in an electric crystal field. We shall consider the value of L throughout the rare-earth series (Table III). It is clear from this table that, apart from the trivial electron-hole symmetry between the first and second halves of the series, there is also a symmetry within each half associated with the occupancy of the orbital quantum states. For example, we can see that in the f^1 and f^6 states we have the same value $L = 3$ and it would seem that the anisotropy should also be the same. However,

TABLE II

R^{3+}	Gd	Tb	Dy	Ho	Er	Tm
α_J	0	-0,0101	-0,0063	-0,0022	0,0025	0,0101
D_1	0	-0,075	-0,060	-0,022	0,024	0,075

TABLE III

R ³⁺	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Con- figu- ration	f ¹	f ²	f ³	f ⁴	f ⁵	f ⁶	f ⁷	f ⁸	f ⁹	f ¹⁰	f ¹¹	f ¹²	f ¹³
	F 3	H 5	I 6	I 6	H 5	F 3	S 1	F 3	H 5	I 6	I 6	H 5	F 3
	Plane			Axis				Plane			Axis		

we must bear in mind that $L(f^1) = 3$ is the angular momentum of one electron, whereas $L(f^6) = 3$ is the angular momentum of six electrons or, which is equivalent, of a hole in the f^7 spherical configuration characterized by $L = 0$. However, in this case it is obvious that the anisotropy of the distribution of the electric charge will be opposite for the f^1 and f^6 configurations. We can assume that f^6 is equivalent (in the orbital anisotropy sense) to a hole in the f^1 configuration.⁷⁾ Figure 3 shows schematically the electron clouds for the f^1 and f^6 configurations. The shaded regions represent a hole.

It is worthwhile to point out another factor which strongly affects both the magnitude and sign of the anisotropy. This is the geometric factor of the crystal field $(1.633 - c/a)$.⁸⁾ For all the rare-earth metals we find that $c/a = 1.58-1.61 < 1.63$. However, in principle, we can alter the sign of the anisotropy by means of this factor.

To the best of the present author's knowledge, reversal of the sign of the first anisotropy constant K_1 had been observed experimentally not only for pure metals, but also for all alloys and compounds of rare earths and this happened in the configurations predicted by the theory. By way of example, Table IV gives the experimental values of K_1 for intermetallics with the formula RCo_5 .

The theory predicts the possibility of existence of orientational plane-axis transitions in RCo_5 compounds with $R = Ce, Pr, Nd, Tb, Dy, Ho$. In the case of these elements the ground state is the orientation of the angular momentum J in the basal plane of the hexagonal lattice, which is observed at low temperatures. The Co ions have an easy axis, but because of the exchange interaction with the R ions they are oriented so that their magnetic moments are aligned in a plane at low temperatures. As a sample is heated, the magnetization of the R sublattice decreases faster than that of the

Co sublattice, so that at some temperature T the plane-axis transition takes place, so that the increase in the anisotropy energy of the Co sublattice characterized by a stronger magnetization is greater than the reduction in the case of the R sublattice.¹⁷ Such transitions had indeed been observed experimentally.¹⁸

The anisotropy of the f shells plays an important role also in many other physical properties of rare earths. In most cases this role is still to be investigated. Here, we shall mention only two possible directions of study (for which some results are already available): 1) anisotropy of transport effects; 2) possible existence of a strong local magnetic anisotropy in rare-earth alloys.

1) A very strong anisotropy of many transport effects had been observed experimentally for rare earths. For example, the anisotropy of the electrical resistivity

$$\Delta\rho/\rho = (\rho_c - \rho_a)/\rho_a \quad (21)$$

(ρ_c and ρ_a are the values of the electrical resistivity along the c axis and in the basal plane) can reach 10-100%. One of the possible mechanisms is the anisotropic scattering of carriers by quadrupole moments of the f shells.^{13,19} An important role is then played by the terms of the Hamiltonian (14) of the type

$$B(\mathbf{k}J_y)(\mathbf{k}'J_y), \quad (22)$$

which after allowance for the uniaxial anisotropy of the Fermi surface (very important in this effect) become

$$B_z(k_zJ^z)(k'_zJ^z) + B_{\perp}(k^+J^- + k^-J^+)(k'^+J^- + k'^-J^+). \quad (23)$$

The contribution to $\Delta\rho/\rho$ which follows from Eq. (23) must be separated from the background of the anisotropy of the effective mass of carriers in uniaxial rare-earth crystals. An analysis reported in Refs. 13 and 19 shows that further investigations (primarily experimental) are needed to solve this problem.

2) The possibility of appearance of strong local anisotropy effects in rare-earth alloys because of lowering of the local asymmetry of the environment of a given rare-earth ion is very interesting. An effect of this kind was considered in

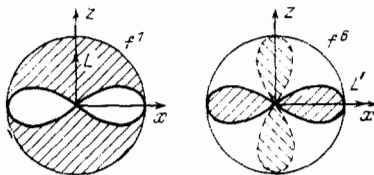


FIG. 3. Anisotropic distribution of the f-electron density (schematic representation) expected for the f^1 and f^6 configurations with $L = 3$. The continuous curve in Fig. 3b represents an orbital hole which appears when f^1 is replaced with f^6 . If an allowance is made for the magnetic anisotropy energy (proportional to $\cos^2\vartheta$ in the case of uniaxial crystals), which has opposite signs for a hole and an electron, a hole and its vector L' are rotated by 90° (dashed curve) relative to the electron.

TABLE IV

i	Ce	Pr	Nd	Sm	Gd
$K^{exp}(RCo_5), 10^4 \text{ erg/cm}^3$	—	-1.5	-5	2.2	0.5

Ref. 20. It was found that, apart from the usual anisotropy constants corresponding to the macroscopic (average) symmetry of an alloy, there are also new hitherto uninvestigated constants of lower symmetry of the local type (for example, K_{21}). After averaging over the various possible configurations of the immediate environment, these local constants contribute to the observed macroscopic anisotropy of a crystal giving rise to a specific dependence on the composition of the alloy. The $R(\text{Co}_x\text{Ni}_{1-x})_5$ alloy system was considered specifically in Ref. 20.

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¹We shall ignore some of the exceptions in the series of the 4f magnetics due to the "mixed" valence when the states of the f electrons in a crystal lose their atomic nature. This mixed valence is exhibited by Ce, Tm, and Yb and sometimes by Sm and Eu.¹

²The exception is the theory of the spectra of atoms of rare-earth impurities in solids. In this case the situation is practically the same as that of free atoms.

³This is partly due to the fact that this review was mainly concerned with galvanomagnetic effects and its title was "Anomalous Hall effect and magnetoresistance of ferromagnetic metals." Moreover, the results given without indicating the method have caused and are still causing considerable difficulties in efforts to understand and reproduce them.

⁴In the case when \mathbf{J} (or \mathbf{S} and \mathbf{L}) are not conserved, it is convenient to replace A_T with the transition operators $X_{T\Gamma}$. (see Hubbard's paper⁸ of 1965; the problem is also dealt with in Ref. 9), which can be expressed in terms of the products $A_T^+ A_T$.

⁵According to the data on the anisotropy of the paramagnetic susceptibility of rare earths and on the magnetic anisotropy of $R\text{Co}_5$ alloys (Table IV).

⁶The theory of the anisotropic exchange was tackled recently by Veltrusky and Nekvasil.¹⁵

⁷It should be pointed out that $\alpha = \alpha_{SL}$, i.e., that this quantity depends not only on L , but also on S and J . Therefore, there is no exact symmetry of the coefficient α in relation to L . The product $\alpha J(J - 1/2)$ is symmetric, but only in respect of $J = L + S$, i.e., it is symmetric in the second half of the rare-earth series.

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