Magnetic anisotropy of rare earth alloys

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Magnetic anisotropy of alloys involving rare earth elements is considered. Anisotropic exchange between collectivized d-electrons and electrons of the f-shell of rare earth ions is calculated on the basis of a microscopic theory. The expression obtained describes the contribution to anisotropy in the case of alloys containing rare earth metals and metals of the iron group. Various types of concentration dependences of the anisotropy constants are discussed and their dependence on atomic number of the rare earth metal is considered.

1. The magnetic properties of alloys are much more varied than those of pure metals, a fact of great practical interest. Recently there have been particularly intensive investigations of alloys and compounds of rare-earth elements with one another (ff alloys) and with elements of the iron group (df alloys). Since the main magnetic characteristics (the magnetic moments, the Curie points, and the magnetic anisotropy constants) of pure rare-earth metals are well explained within the framework of a theory based on the concept of the atomic character of f-electrons in a crystal, it is now timely to extend this theory to include alloys.

When it comes to the magnetic moments μ (per atom of the alloy), the situation is trivial to a considerable extent, at least for the case of ff alloys, where the additivity rule $\mu_{f_1f_2} = c_1\mu_{f_1} + c_2\mu_{f_2}$ holds (c_1 and c_2 are the relative concentrations of the components). This additivity may not hold for df alloys, owing to the change in the electronic structure of the d-bands of the collectivized magnetic electrons of the d-components in the alloy. The construction of an appropriate theory is presently hindered by the lack of information on this electronic structure, even for pure d-metals.

Less trivial is the question of the Curie points. A generalization of the deGennes results[1] to the case of two-component ff alloys (assuming independence of the effective exchange integral of the concentration) is possible on the basis of the theory of disordered alloys. There are, however, two essentially different variants with linear[2] and quadratic[3] dependence of the Curie point on the alloy-component concentration, respectively. The reason why the results of[2] and[3] differ lies in the difference in the methods of introducing an effective molecular field, and in the former case the expression coincides with the result obtained for fixed sublattices (see, for example,[4] for the case of ferrites). In addition, in the experiments, starting with the work of Bozorth et al.[5], one uses for ff alloys the empirical formula $T_N \sim (c_1G_1 + c_2G_2)^{2/3}$, where $G_i = (g_i - 1)^2 J_i(J_i + 1)$ is the deGennes factor. The possibility of proving this formula is not indicated in any way in the theory.

We consider in the present paper certain questions of the theory of magnetic anisotropy of alloys. The main purpose of our analysis is to classify the possible types of concentration dependence of the magnetic anisotropy of alloys with allowance for concrete microscopic mechanisms. For the case of ff alloys, these mechanisms are the crystal field[6] and the anisotropic exchange[7,11], whereas for df alloys there can appear also an additional mechanism connected with the anisotropic df exchange, the microscopic theory of which will also be considered here. As to the contribution made to the anisotropy of the the d-component itself, it will be introduced via a constant k_d, regarded as a parameter, in view of the lack of an analytic theory of magnetic anisotropy for d-metals.

2. We consider a system of collectivized d-electrons interacting with rare-earth ions. In the **k**-representation, the d-electrons form bands[8], and if these bands are wide enough, the orbital moments are "quenched." The onset of anisotropic df exchange is possible only if the orbital momenta are partially "unquenched," by taking the spin-orbit interaction into account. We assume a weak spin-orbit interaction[10], much weaker than the electron energy in the quasiperiodic field of the lattice1). Allowance for the symmetry of the lattice, which we shall assume to be hexagonal, will be made already in the wave functions of the d-electrons. The degenerate levels of the d-states will then be split into two double levels and one single level, corresponding respectively to three possible irreducible representations of the hexagonal-symmetry group. Assuming that the splitting is larger than the width of the bands subsequently obtained by taking into account the quasiperiodic potential, it suffices to consider the lower level, which is the only filled one.

The term of greatest interest to us in the Hamiltonian of the df-exchange interaction is

$$\mathcal{H}_{df}^{\text{exch}}(\lambda) = \frac{\lambda}{2\Delta\varepsilon} I_{df}^{\text{exch}}(g-2)(s_+J_- + s_-J_+) = \frac{\lambda}{\Delta\varepsilon} I_{df}^{\text{exch}}(g-2)\{(\mathbf{sJ}) - s_zJ_z\}, \tag{1}$$

where λ is the spin-orbit interaction constant in the approximation of strongly bound electrons ($\lambda \sim 10^{-13}$—10^{-14} erg in the ions of the transition elements of the iron group), $\Delta\epsilon$ is an energy parameter[10] proportional to the splitting, and I_{df}^{exch} is a combination of the radial integrals $G_{l_1 l}^{(p)}$ previously cited in[11].

The physical meaning of (1) is that the orbital angular momenta l_z which are "unquenched" as a result of the spin-orbit interaction and have eigenvalues in the site representation, undergo exchange interaction with the orbital component $(g-2)\mathbf{J}$ of the f-electron angular momentum. It is typical that I_{df}^{exch} in formula (1) contains only quadratic components of l_z (one l_z comes from $\mathcal{H}^{\text{SO}}$, and the second comes from the Coulomb-interaction operator $(\langle|e^2/r|\rangle \sim (g-2)\mathbf{l}\cdot\mathbf{J}$, see[12]). The effect does not appear if spin-orbit interaction is not taken into account.

3. It is not difficult to generalize the phenomenological theory of magnetic anisotropy to include alloys. Nonetheless, we consider it useful, in view of the almost complete lack of literature on this subject, to write out the corresponding formulas and to discuss them with allowance for the concrete results of the microscopic theory.

In the study of alloys, particular importance attaches to the existence of two types of anisotropy, single-ion and two-ion, each of which leads to a different concentration dependence of the anisotropy constants. As is well known, the single-ion anisotropy is brought about by the crystal-field mechanism. All the mechanisms of the anisotropic exchange connected with pair interaction result in two-ion anisotropy.

Since the energy of the pair interaction in a disordered binary alloy, without allowance for short-range order, is determined by the formula[8]

$$E_{AB}=\frac{zN}{2}(c_A{}^2v_{AA}+c_B{}^2v_{BB}+2c_Ac_Bv_{AB}), \tag{2}$$

we obtain for the anisotropy constant of the alloy, with allowance for both mechanisms[2)]

$$\begin{aligned}K=c_Ak_A{}^{\mathrm{cr}}+c_Bk_B{}^{\mathrm{cr}}+c_A{}^2k_A^{\mathrm{exch}}\\+c_B{}^2k_B^{\mathrm{exch}}+c_Ac_Bk_{AB}^{\mathrm{exch}}.\end{aligned} \tag{3}$$

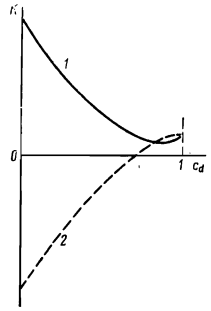
The results of[6,7,11] and of Sec. 2 of the present paper yield the following expressions for the second-order constants in crystals of hexagonal symmetry[3)]

$$\begin{aligned}k_f{}^{\mathrm{cr}}&=A_2\alpha J(2J-1),\\k_f^{\mathrm{exch}}&=I_f^{\mathrm{exch}}zn\alpha J(2J-1),\\k_{f_Af_B}^{\mathrm{exch}}&=I_{f_Af_B}^{\mathrm{exch}}z\{n_A\alpha_BJ_B(2J_B-1)\\&\quad+n_B\alpha_AJ_A(2J_A-1)\},\\k_{df}^{\mathrm{exch}}&=\frac{\lambda}{\Delta\varepsilon}I_{df}^{\mathrm{exch}}(g-2)J,\end{aligned} \tag{4}$$

where z is the number of nearest neighbors, n is the number of f electrons in the rare-earth ion, α is the Stevens coefficient, and A_2 and I^{exch} are the crystal-field and exchange-interaction parameters. The constant k_d is the only one for which we have no microscopic expressions at present, and should be regarded as a certain parameter.

Relations (3) and (4) lead to some interesting conclusions and permit a classification of the possible types of concentration dependence of the anisotropy constant in alloys. A comparison of (3) and (4) with experiment makes it possible to separate the contributions of the crystal field and of the exchange interaction in concrete alloys. Greatest interest attaches in this case to research in a wide interval of concentrations, using the entire series of rare-earth metals as one or both components of the alloy.

Let us discuss first ff alloys. By virtue of the relations in (4), all the rare-earth elements are divided into two groups, depending on the sign of α, which determines also the sign of the anisotropy. The first group includes Ce, Pr, Nd, Tb, Dy, and Ho, while the second includes Pm, Sm, Er, and Tm (Gd, for which $\alpha = 0$, stands alone). It follows then from (3) that for alloys within each group one should observe monotonic concentration dependences without a change in the sign of the anisotropy constant (provided that $k_{f_Af_B} < k_{f_A}, k_{f_B}$). To the contrary, for alloys of elements from different groups one should expect a reversal of the sign and the appearance of extrema in the function K(c). It is curious to note that the mixed constant $k_{f_Af_B}$ should be larger for alloys made up of metals of the same group than of metals from different groups.



Qualitative dependence of the magnetic-anisotropy constant of df alloys on the d-component concentration, $|k_f^{\mathrm{cr}}| \sim |k_f^{\mathrm{exch}}| \sim |k_{df}^{\mathrm{exch}}| \gg |k_d|$. Curve 1–$k_f^{\mathrm{exch}}$, k_d, and $k_f^{\mathrm{cr}} > 0$; $k_{df}^{\mathrm{exch}} < 0$; curve 2–$k_d$, k_{df}^{exch} and $k_f^{\mathrm{cr}} > 0$; $k_f^{\mathrm{exch}} < 0$.

Similar arguments hold also for df alloys. Typical curves for this case are shown in the figure.

At present there exist only isolated experimental results of the measurements of the magnetic-anisotropy constants in rare-earth alloys. Chikazumi et al.[14] investigated only low concentrations of the rare-earth component in the alloy, at which only linear concentration dependences of K could be observed. Of considerable interest is work by Levitin et al.[15], who did observe a quadratic contribution to the concentration dependence for Gd-Dy alloys, but arrived at the conclusion that this contribution is connected with the dependence of the single-ion constant k_f on the lattice parameter. To solve this problem it is necessary, above all, to perform additional experimental research in this field.

[1)] The case of strong spin-orbit interaction of the conduction electrons was considered by Levy [9].

[2)] Yang Shih [13] obtained higher degrees of the concentration dependence of K (for the case of the cubic crystals) by choosing a different Hamiltonian.

[3)] Expressions (4) represent only the hitherto considered theoretical mechanisms that do not exhaust all the possibilities. Moreover, there is no proof that they are the principal ones.

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