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ANISOTROPY AND MAGNETOSTRICTION OF 4d AND 5d TRANSITION-METAL IONS IN GARNETS AND SPINEL FERRITES

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Résumé. — Grâce à leur couplage spin-orbite très fort, les ions des séries 4d et 5d apportent une contribution importante aux propriétés anisotropes des ferrites et grenats. En particulier les ions d^5 en état de spin bas, tels que Ru^{3+} , Os^{3+} , Rh^{4+} et Ir^{4+} , présentent un intérêt particulier car leurs niveaux d'énergie les plus bas, qui déterminent leurs propriétés magnétiques, ont une structure simple.

Les contributions à l'anisotropie et à la magnétostriction peuvent être explicitement calculées dans le cadre de la théorie à un ion et dans la gamme de températures $0 \leq T \leq T_c$, ce qui n'est plus possible pour d'autres ions anisotropes.

La comparaison entre théorie et résultats expérimentaux fournit un excellent accord dans les cas choisis, ce qui étaye l'hypothèse simple du modèle à un ion dans le cas d'un système magnétique ordonné.

Abstract. — Some 4d and 5d transition-metal ions are expected to contribute significantly to the anisotropic properties of ferrites and garnets owing to their strong spin-orbit coupling. In particular the low-spin d^5 ions such as Ru^{3+} , Os^{3+} , Rh^{4+} and Ir^{4+} are of special interest since they exhibit a very simple level structure of their lowest energy levels which determine the magnetic behaviour. For these ions the contributions to anisotropy and magnetostriction can be calculated explicitly within the single-ion theory for the complete temperature range ($0 \leq T \leq T_c$) in contrast to other strongly anisotropic ions. The comparison of the theory with experimental results yields excellent agreement for selected cases supporting the simple conception of the single-ion model in magnetically ordered systems in correspondence to paramagnetic materials.

1. Introduction. — The presence of magnetic anisotropy and magnetostriction in each magnetic material assigns to these properties a central role in the basic research and the device applications of magnetic materials. The magnetic oxides of garnet and spinel structure are mostly pure insulators which makes them very attractive for studying the anisotropic phenomena, since in contrast to the metals simpler models can be used to explain the basic effects. In ferrites and garnets attention has been drawn so far to the anisotropic behaviour of the 3d transition-metal ions and rare earth ions except for some studies in the recent past concerning some ions of the second and third transition series. This situation certainly is due to the fact that ferrimagnetism of magnetic oxides essentially is based on 3d transition-metal ions and rare earth ions. However, in the discussion of anisotropic properties the ions of the second and third transition series are of special interest. In particular the ruthenium and iridium ions were characterized by a strong anisotropic behaviour as it was expected from their energy level structure [1]. For a certain valence state ($Ru^{3+}(4d^5)$, $Ir^{4+}(5d^5)$) and at a certain crystallographic site they exhibit the most simple level structure of all anisotropic ions and thus the theory of anisotropy and magnetostriction of these ions can be

simply derived in an explicit form for the complete temperature range which is not yet possible for any other anisotropic ion. In this sense these ions represent an exceptional case and can be regarded as an important proof for the validity of the single-ion theory in the field of magnetic oxides.

Phenomenologically the anisotropy and magnetostriction can be expressed uniformly for all magnetic materials of corresponding crystal symmetry independently of the microscopic origin of these effects. Garnets and spinel ferrites are cubic and therefore the anisotropic part of the free energy can be described for both by the same expression. The free energy depending on the direction α of the magnetization and the strain tensor $\vec{\epsilon}$ generally is of the form

$$F(\alpha, \vec{\epsilon}) = F_0 + F_e(\vec{\epsilon}) + F_K(\alpha) + F_{me}(\alpha, \vec{\epsilon}) \quad (1)$$

where F_0 is a constant with respect to α and $\vec{\epsilon}$, $F_e(\vec{\epsilon})$ represents the pure elastic energy, $F_K(\alpha)$ is the magnetocrystalline anisotropy and the last term denotes the magnetoelastic energy. For cubic symmetry $F_K(\alpha)$ is given by :

$$F_K(\alpha) = K_1 s + K_2 p + K_3 s^2 + K_4 sp + \dots \quad (2)$$

$$s = \alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_1^2 \alpha_3^2, \quad p = \alpha_1^2 \alpha_2^2 \alpha_3^2.$$

K_i are the anisotropy constants. The magnetoelastic energy can be expressed in terms of the components of α and $\vec{\epsilon}$ by

$$F_{me}(\alpha, \vec{\epsilon}) = b_1(\epsilon_{11} \alpha_1^2 + \epsilon_{22} \alpha_2^2 + \epsilon_{33} \alpha_3^2) + b_2(\epsilon_{12} \alpha_1 \alpha_2 + \epsilon_{23} \alpha_2 \alpha_3 + \epsilon_{13} \alpha_1 \alpha_3) + \dots \quad (3)$$

where the b_i are the magnetoelastic constants. They are related to the magnetostriction constants λ_{100} and λ_{111} via the relations

$$\lambda_{100} = -\frac{2}{3} \frac{b_1}{C_{11} - C_{12}}, \quad \lambda_{111} = -\frac{1}{3} \frac{b_2}{C_{44}}. \quad (4)$$

The C_{ik} are the elastic constants. For most spinel ferrites and garnets the first two constants of eqs. (2) and (3) are sufficient to describe the observed effects.

The influence of anisotropic transition-metal ions on the K_i and λ_{hkl} is displayed in figure 1a, b and 2a, b at room temperature. Very strong changes of the

FIG. 1. — Room temperature anisotropy constants versus concentration a) K_1 and b) K_2 of yttrium iron garnet substituted with the 3d ions Mn^{3+} [2], Fe^{2+} [3, 4], Co^{2+} [5] and the 4d/5d ions Ru^{3+} [6-9], $Ir^{3+} + Ir^{4+}$ [7, 12].

FIG. 2. — Room temperature magnetostriction constants versus concentration a) λ_{100} and b) λ_{111} of yttrium iron garnet substituted with the 3d ions Mn^{3+} [2], Fe^{2+} [3, 4], Co^{2+} [5] and the 4d/5d ions Ru^{3+} [10, 11, 23] $Ir^{3+} + Ir^{4+}$ [12, 13]

anisotropy and the magnetostriction constants already occur for both the 3d ions $Mn^{3+}(3d^4)$ [2], $Fe^{2+}(3d^6)$ [3, 4], $Co^{2+}(3d^7)$ [5] and the 4d/5d ions $Ru^{3+}(4d^3)$ [6-11] and $Ir^{4+}(5d^5)$ [7, 12-13] at very small concentrations. For other ions like Fe^{3+} [14], Cr^{3+} [15] or Cu^{2+} [16] no variation would be seen in this representation (see table II). Their contribution is very small owing to their orbitally nondegenerate cubic ground state which in first order gives no contribution to anisotropy and magnetostriction. The ions presented in figures 1 and 2, however, are characterized by an orbitally degenerate cubic ground state and in addition by a strong spin-orbit coupling which fixes the spin system to certain crystallographic directions. Since the spin-orbit coupling of the 4d and 5d ions is much larger as compared to that of the 3d ions they are expected to be candidates for strong anisotropic effects which is supported by the changes of K_i and

λ_{hkl} induced by the ruthenium and iridium ions. Most attention was drawn to these ions because on one hand their level structure predicts the most prominent effects and on the other hand the chemical properties of the corresponding oxides are appropriate for their incorporation in the crystal lattice of garnets and spinel ferrites.

The ions presented in figures 1 and 2 occupy preferentially octahedral sites and this is important for the sign and magnitude of their anisotropic contribution. The local symmetry is one of the most important factors together with the spin-orbit coupling which are responsible for the observed effects. Spinel ferrites are of the composition (A) $[B_2]O_4$ and the magnetic ions occupy the two sites. The A and B sites are tetrahedrally and octahedrally surrounded by oxygen ions, respectively. Garnets are of the composition $\{C_3\} [B_2] (A_3)O_{12}$ where in addition to the above two sites the C-site with a eight-fold oxygen coordination is present. In iron garnets these sites are occupied by large ions as the rare earth ions and their occupation by transition-metal ions is unlikely. Therefore we will restrict our considerations to the octahedral and tetrahedral sites in both types of ferrimagnetic compounds and thus for both general considerations are valid.

The aim of this paper is the presentation of a simple explanation of the observed effects of these 4d and 5d transition-metal ions in terms of the single-ion theory which already has been successfully applied to 3d ions and to discuss their effects with respect to the site occupation and valence state.

2. Theory. — **2.1 FREE ENERGY.** — From the linear concentration dependence of the anisotropy and magnetostriction constants it can be concluded that the probability to form pairs or clusters of the substituted ions is quite low for these small concentrations and thus only the effect of single ions in the garnet or spinel host have to be considered. If one percent of the octahedral iron ions is replaced by anisotropic ions which will be assumed to be statistically incorporated in the lattice, then, roughly in every fifth unit cell one of these ions is present. Therefore, the interaction between these ions will be very small and can be neglected in good approximation. These conditions, however, are just those which have to be met if the framework of the single-ion theory can be used to explain these anisotropic effects. This theory has been successfully applied to explain the anisotropic behaviour of 3d transition-metal ions even for high concentrations [7-9].

The contribution of the substituted anisotropic ions to the free energy $\Delta F(\alpha, \vec{\epsilon})$ then can be expressed in terms of the single-ion contribution $f^{(i)}(\alpha, \vec{\epsilon})$ times the number of ions N per cm^3 :

$$\Delta F(\alpha, \vec{\epsilon}) = \frac{N}{n} \sum_{i=1}^n f^{(i)}(\alpha, \vec{\epsilon}). \quad (5)$$

The summation extends over the magnetically inequivalent sites (dodecahedral : $n = 6$, octahedral : $n = 4$, tetrahedral : $n = 3$). $f^{(i)}(\alpha, \vec{\epsilon})$ is given by the expression :

$$f^{(i)}(\alpha, \vec{\epsilon}) = -kT \ln \left[\sum_j \exp \left(-\frac{E_{ij}(\alpha, \vec{\epsilon})}{kT} \right) \right] \quad (6)$$

where $E_{ij}(\alpha, \vec{\epsilon})$ are the energy levels of the ion on site i . Thus, the main task has to be focussed on the problem of calculating the energy levels of such ions as a function of the direction of magnetization and the strain. An explicit solution of this problem can be expected only for very simple configurations where the relative magnitude of the present interactions provides marked simplifications in the mathematics.

The interactions which determine the ground state of these ions in a given host and the coupling between the spin system and the lattice may be quite different in magnitude for different anisotropic ions. But all anisotropic ions roughly can be divided into three groups arranged with respect to the relative magnitude of the interactions [21]. As shown in table I the 3d ions form a group, then the 4d and 5d ions and the rare earth ions where the latter may only serve for comparison. The cubic ground state is determined by the interaction of the electrons of the unfilled d-shell E_{el}^d and the cubic crystalline field energy E_c^{cub} . The main difference in the cubic ground state between the 3d and the 4d/5d ions is their spin state. Since $E_{el}^d > E_c^{cub}$ for the 3d ions, they exhibit a high-spin state ($\text{Fe}^{3+}(3d^5) : S = 5/2$) while for 4d/5d ions $E_{el}^{cub} > E_{el}^d$ and thus these ions are in the low-spin state ($\text{Ru}^{3+}(4d^5) : S = 1/2$). In addition their spin-orbit coupling energy is much larger as compared to the 3d ions which consequently implies a much stronger coupling of the spin system to the lattice. Since the orbital momentum L tends to align along the axis of distortion of the noncubic crystalline field represented in table I by E^{loc} , the direction of the spin S depends on the relative magnitude of E_{so} and E_{exch} . For the 3d ions $E_{exch} > E_{so}$ and the spin S is approximately parallel to the exchange field and for the 4d/5d ions $E_{so} > E_{exch}$ and S is approximately parallel to L . Since the magnetic behaviour is essentially governed by the smallest perturbation, the magnitude of the anisotropy is determined by the splitting of the lowest energy levels which is proportional to E_{so} for 3d ions and to E_{exch} for 4d/5d ions. This difference in magnitude of E_{so} and E_{exch} is of significant importance for the calculation of anisotropy and magnetostriction, since E_{exch} is a strong function of temperature in contrast to E_{so} . While for 4d and 5d ions the condition $E_{so} > E_{exch}$ remains valid for all temperatures, the condition $E_{exch} > E_{so}$ for 3d ions holds only for lower temperatures which implies a different temperature dependence. However, for all configurations the central role of magnetically anisotropic effects has to be attributed to the low-symmetry crystalline fields which fixes the orbital momentum to a certain crystallogra-

TABLE I

Relative magnitude of the interactions determining the magnetic behaviour of the transition-metal ions and the rare earth ions.

Transition-metal ions 3d(Fe ^{II} , Co ^{II})	$E_{el}^d > E_c^{cub} \gg E_c^{loc} > E_{exch} > \dots \gg E_{so} \gg E_{c,\epsilon}$
4d/5d(Ru ^{III} , Ir ^{IV})	$E_c^{cub} > E_{el}^d \gg E_{so} \simeq E_c^{loc} > \dots \gg E_{exch} \gg E_{c,\epsilon}$
Rare earth ions (Tb ^{III} , Nd ^{III})	$E_{el}^f > E_{so} \gg E_c^{cub} > E_c^{loc} > \dots \gg E_{exch} \gg E_{c,\epsilon}$
Magnitude of energy level splitting (cm ⁻¹)	$2 - 4 \times 10^4 \quad \leq 3 \times 10^3 \quad \leq 3 \times 10^2 < 10$

phic direction and, thus, the spin via the spin-orbit coupling. The smallest interaction is the strain dependent crystalline field energy $E_{c,\epsilon}$. The order of magnitude of the energies is given in table I expressed in cm⁻¹. The spin-orbit coupling becomes only effective for those ions which exhibit an orbitally degenerate cubic ground state where the three-fold degenerate T-states are most effective. From the 4d and 5d transition-metal ions only very few ions show such a degenerate ground level like the ions Rh⁴⁺(4d⁵), Ru³⁺(4d⁵), Ru⁴⁺(4d⁴), Pd⁴⁺(4d⁶), Re³⁺(5d⁴), Os³⁺(5d⁵), Os⁴⁺(5d⁴), Ir³⁺(5d⁶) and Ir⁴⁺(5d⁵) where the considered valence states have been restricted to those which have been mainly observed in other oxides. The most simple configuration is the low-spin d⁵ configuration which should be considered in some more detail.

The cubic ground state of a low-spin d⁵ configuration corresponds to that of a d¹ configuration except for the sign of the spin-orbit coupling constant. This state is sixfold degenerate and the degeneracy is removed by the local noncubic crystalline field, the spin-orbit coupling, the exchange interaction and the increment of crystal field depending on strain. The corresponding Hamiltonian with the energy terms arranged in this sequence is of the form

$$\mathcal{H} = V_c^{loc}(\mathbf{r}) + \lambda \mathbf{L} \cdot \mathbf{S} + g\mu_B \mathbf{H}_{exch} \cdot \mathbf{S} + \delta V_c(\mathbf{r}, \vec{\epsilon}). \quad (7)$$

The exchange interaction is presented in the molecular field approximation and λ represents the spin-orbit coupling constant. Applying this Hamiltonian to a suitable set of wave functions of the cubic ground state its splitting can be calculated. The lowest energy levels can be described by the relation :

$$E_{i1/2}(\alpha, \vec{\epsilon}) = E_0 \pm A[\sqrt{B + C \cos^2 \gamma_i(\alpha)} + \delta_i(\vec{\epsilon})]. \quad (8)$$

A is proportional to the exchange field and E_0 , B , and C are only functions of λ and the matrix element v of the local crystalline field. $\delta_i(\vec{\epsilon})$ describes the strain dependence and $\gamma_i(\alpha)$ denotes the angle between the local axis of distortion and the direction of the magnetization.

2.2 ANISOTROPY. — To derive the temperature dependence of the anisotropy contributions ΔK_i they have to be correlated to the free energy at certain

crystallographic directions since a direct expansion of eq. (6) in powers of the direction cosines gives rise to divergencies at low temperatures. Neglecting higher order anisotropy constants ΔK_1 and ΔK_2 can be correlated to the free energy according to the relations

$$\begin{aligned} \Delta K_1 &= 4(\Delta F[110] - \Delta F[001]) \\ \Delta K_2 &= 9(3 \Delta F[111] + \Delta F[001] - 4 \Delta F[110]). \end{aligned} \quad (9)$$

For the anisotropy case we can neglect the strain dependence and for low-spin d⁵ ions the energy separation of the two lowest levels are relatively small as compared with the separation to the next higher levels. Thus, the effect of the higher levels can be neglected in good approximation. Introducing the splitting ΔE_{001} of the two lowest levels for $\mathbf{M} \parallel [001]$ and the quantity

$$\eta = -\frac{C}{3} \left(\frac{A}{2 \Delta E_{001}} \right)^2$$

the free energy contribution of eq. (6) can be rewritten as

$$f^{(i)}(\alpha) = -kT \ln \cosh \left(\frac{\Delta E_{001} \sqrt{1 - \eta g_i(\alpha_k)}}{2kT} \right). \quad (10)$$

For octahedral sites the functions $g_i(\alpha_k)$ are given by :

$$\begin{aligned} g_{1/2} &= \alpha_1 \alpha_2 \pm (\alpha_2 \alpha_3 + \alpha_1 \alpha_3) \\ g_{3/4} &= -\alpha_1 \alpha_2 \mp (\alpha_2 \alpha_3 - \alpha_1 \alpha_3). \end{aligned} \quad (11)$$

Similar relations hold for the tetrahedral case [9]. Combining eqs. (5), (9), (10), and (11) the temperature dependence of low-spin d⁵ ions on octahedral sites with the axis of distortion along a [111] direction can be expressed by the relations

$$\begin{aligned} \Delta K_1 &= 2kTN \ln \left[\frac{\cosh^2(t)}{\cosh(t\sqrt{1+\eta}) \cosh(t\sqrt{1-\eta})} \right] \\ \Delta K_2 &= \frac{9}{4}kTN \times \\ &\times \ln \left[\frac{\cosh^8(t\sqrt{1+\eta}) \cosh^8(t\sqrt{1-\eta})}{\cosh^4(t) \cosh^3(t\sqrt{1-2\eta}) \cosh^9(t\sqrt{1+2/3\eta})} \right] \end{aligned} \quad (12)$$

where $t = \Delta E_{001}/2kT$. These expressions generally hold for all ions where the two lowest levels can be described by eq. (8) and the higher levels do not

contribute significantly and this applies approximately also to the 3d ions Fe^{2+} and Co^{2+} . However, the functional dependence of the constants A, B and C on the atomic parameters then is different.

Similar relation can be derived for tetrahedral sites [9]. The general features of the ΔK_i can be discussed most easily for low temperatures where these relations reduces considerably. Generally ΔK_1 turns out to be positive for octahedral sites and negative for tetrahedral sites while ΔK_2 is negative for both sites. For $T = 0\text{K}$ the ratio $\Delta K_2/\Delta K_1$ only depend on the parameter B/C . Thereby, in the first case a distortion along the [111] directions and in the second along the [100] directions is assumed. If other axis of distortion are present sign and magnitude of the ΔK_i will change. It should be pointed out that for low-spin d^5 ions ΔE_{001} is proportional to E_{exch} which itself depends on temperature.

2.3 MAGNETOSTRICTION. — In correspondence to the anisotropy the magnetoelastic constants can be related to the free energy. If higher order terms are neglected in eq. (2) the magnetoelastic constants are simply related to the functions

$$f_{pq}(\alpha) = \frac{\partial \Delta F(\alpha, \epsilon)}{\partial \epsilon_{pq}} \quad (13)$$

by the relations

$$\begin{aligned} \Delta b_1 &= f_{33}[010] - f_{33}[001] \\ \Delta b_2 &= f_{12}[110]. \end{aligned} \quad (14)$$

The magnetostriction constants are obtained using eq. (3). With the assumptions made for the anisotropy the functions $f_{pq}(\alpha)$ are obtained from eqs. (5), (8), (10), and (13) yielding

$$f_{pq}(\alpha) = -\frac{N}{2n} \sum_{i=1}^n \frac{\partial \Delta E_i}{\partial \epsilon_{pq}} \tanh \left(\frac{\Delta E_i}{2kt} \right) \quad (15)$$

where $\Delta E_i = E_{2i} - E_{1i}$. From eqs. (4), (14), and (15) we can calculate the temperature dependence of the magnetostriction constants. For octahedral sites the result can be expressed by

$$\begin{aligned} \Delta \lambda_{100}(T) &= \Delta \lambda_{100}(0) q(T) \tanh(t) \\ \Delta \lambda_{111}(T) &= \frac{\Delta \lambda_{111}(0) q(T)}{1+C} \times \\ &\times \{ \tanh(t\sqrt{1+\eta}) + C \cdot \tanh(t\sqrt{1-\eta}) \} \end{aligned} \quad (16)$$

where all constants have been absorbed by $\Delta \lambda_{100}(0)$ and $\Delta \lambda_{111}(0)$. In particular, these are proportional to the concentration and the matrix element over the strain dependent increment of the crystal field where the magnitude of the latter in general is unknown and, thus $\Delta \lambda_{100}(0)$ and $\Delta \lambda_{111}(0)$ have to be regarded as adjustable parameters. C is essentially only a function of η and $q(T)$ represents the relative temperature dependence of the exchange field since ΔE_i is proportional to H_{exch} according to eq. (8). For octahedral

sites $q(T)$ can be well approximated by the specific temperature dependence of the tetrahedral sublattice magnetization. It should be pointed out, that ΔE_{001} also is proportional to H_{exch} and thus to $q(T)$. A slightly different theoretical approach is presented in ref. [11].

3. Comparison of theory and experiment. —

3.1. ANISOTROPY. — The theoretical results of the preceding chapter can be compared with experimental data of ruthenium- and iridium-substituted garnets and spinels. The most definite cases appear to be the ruthenium-substituted garnets like $\text{Y}_3\text{Fe}_{5-x}\text{Ru}_x\text{O}_{12}$ [8, 21, 22], $\text{Gd}_3\text{Fe}_{5-x}\text{Ru}_x\text{O}_{12}$ [23]. In these materials the trivalent ruthenium $\text{Ru}^{3+}(4d^5)$ on octahedral sites dominate. For very small concentrations the accurate determination of the number of substituted ions N is very difficult. This problem can be avoided by considering the ratio $\Delta K_2/\Delta K_1$ which is independent on N as obvious from eqs. (12). In figures 3a, b $\Delta K_2/\Delta K_1$ is plotted versus temperature for the ruthenium-substituted garnets for different concentrations. The independence on concentration is well fulfilled for all temperatures. The solid line represents the theory

FIG. 3. — Temperature dependence of the ratio of the anisotropy contributions $\Delta K_2/\Delta K_1$ of $\text{Ru}^{3+}(4d^5)$ on octahedral sites in a) yttrium iron garnet [8, 22, 23] and b) gadolinium iron garnet [23]. The solid line represents the single-ion theory according to eqs. (12).

assuming the temperature dependence of the exchange field to be represented by that of the specific tetrahedral sublattice magnetization ($\Delta E_{001} \sim q(t) = \sigma_d(t)$). For d^5 ions the two atomic parameters $\mu_B H_{\text{exch}} v/\xi$ ($\lambda = -\xi$, where ξ is the one-electron spin-orbit coupling parameter) determine the temperature behaviour of the anisotropic properties. For $\text{Y}_3\text{Fe}_{5-x}\text{Ru}_x\text{O}_{12}$ (Fig. 3a) the theoretical curve according to eqs. (12) is based on the values $v/\xi = -1.0$ and $g\mu_B H_{\text{exch}} = 514 \text{ cm}^{-1}$. The ratio of the local trigonal field and spin-orbit coupling v/ξ in addition has been measured for the approximately isomorphous system $\text{Y}_3\text{Ga}_{5-x}\text{Ru}_x\text{O}_{12}$ by paramagnetic resonance yielding $v/\xi = -1.06$ [24]. Since these values of v/ξ deduced from independent measurements agree well the exchange interaction between the ruthenium ions and the iron ions has to be regarded as the only adjustable parameter. With a suitable choice of this quantity obviously an excellent fit of the experimental data for $T \leq T_0$ can be achieved. In the corresponding system $\text{Gd}_3\text{Fe}_{5-x}\text{Ru}_x\text{O}_{12}$ the temperature dependence of $\Delta K_2/\Delta K_1$ also can be well described by the single-ion theory as shown in figure 3b. The scatter of the experimental data in the room temperature range originates from the presence of the compensation temperature at $T_{\text{comp}} = 286 \text{ K}$. For this case the values $v/\xi = -0.48$ and $g\mu_B H_{\text{exch}} = 626 \text{ cm}^{-1}$ have been used.

Thus, for different hosts the single-ion theory accounts well for the anisotropy of these low-spin d^5 ions. For selected temperature and contributions per ion are summarized in table II. In addition the data of the weakly anisotropic ion Fe^{3+} , Cr^{3+} and

Cu^{2+} and for the most anisotropic 3d ion Co^{2+} ($3d^7$ in yttrium iron garnet are listed for comparison [5]. It should be noted that the per ion values are not of high accuracy, since in spite of a very careful analysis the determination of N for these small substitutions is quite difficult.

3.2. MAGNETOSTRICTION. — The magnetostriction of ruthenium-substituted yttrium iron garnet has been investigated by several authors [10, 11, 25, 16]. The relative temperature dependence of $\lambda_{100}(T)/\lambda_{100}(0)$ is displayed in figure 4a for different concentrations [25]. The solid line represents the theory according to eqs. (16). In correspondence to the anisotropic behaviour the complete temperature dependence can be well described. For the second magnetostriction constant a similar result is obtained using the atomic parameters already deduced from the fit of the anisotropy data. The effects of ruthenium ions in epitaxially grown garnet films correspond to those in flux-grown crystals [27, 28].

The remaining difficulty in magnetostriction is the calculation of the constants $\lambda_{hkl}(0)$ which are proportional to the matrix elements of the increment of crystalline field depending on stress. Sign and magnitude of these quantities have not yet been studied in a satisfactory manner. Further the strain dependence of the exchange field has not been considered. For example the $\lambda_{hkl}(0)$ of the Co^{2+} ions are much smaller and in addition $\lambda_{100}(0)$ is negative as can be seen from table II. The anisotropy constants, however, correspond to those of the Ru^{3+} ions. This different behaviour in the anisotropy and magnetostriction

TABLE II

Anisotropy and magnetostriction contributions of the 3d ions Fe^{3+} , Cr^{3+} , Cu^{2+} , Co^{2+} and the 4d ion Ru^{3+} in garnets of composition $\text{Y}_3\text{Fe}_{5-x}\text{M}_x\text{O}_{12}$ and $\text{Gd}_3\text{Fe}_{5-x}\text{M}_x\text{O}_{12}$

Composition of the host	Substituted ion (configuration)	Cubic ground state	T (K)	$\Delta K_1/N$ (cm^{-1})	$\Delta K_2/N$ (cm^{-1})	Ref.	$10^4 \lambda_{100/x}$	$10^4 \lambda_{111/x}$	Ref.
$\text{Y}_3\text{Fe}_5\text{O}_{12}$	$\text{Ru}^{3+}(4d^5)$	$^2T_{2g}$	4.2	28	- 120	[8,9,23]	2.7	2.9	[10]
			77	22	- 68		2.7	2.6	
			295	2	- 3		2.5	0.8	
$\text{Gd}_3\text{Fe}_5\text{O}_{12}$			4.2	25	- 70	[23]	—	—	—
			130	8	- 14		—	—	
			330	0.4	- 0.2		—	—	
$\text{Y}_3\text{Fe}_5\text{O}_{12}$	$\text{Fe}^{3+}(3d^5)$	$^6A_{1g}$	4.2	- 0.005	0	[14]	- 0.025	0.02	[14]
	$\text{Cr}^{3+}(3d^3)$	$^4A_{2g}$	4.2	- 0.05	—	[15]	—	—	—
	$\text{Cu}^{2+}(3d^9)$	$^2T_{2g}$	4.2	- 0.2	$\sim - 0.01$	[16]	—	—	—
			77	- 0.18	0				
			295	- 0.05	0				
	$\text{Co}^{2+}(3d^7)$	$^2T_{1g}$	4.2	27	- 124	[5]	- 0.5	1.0	[5]
			77	21	- 71		- 0.6	1.2	
			292	1	- 0.5		- 0.4	0.7

FIG. 4. — The temperature dependence of the reduced magnetostriction contributions *a*) $\Delta\lambda_{100}(T)/\Delta\lambda_{100}(0)$ [25] and *b*) $\Delta\lambda_{111}(T)/\Delta\lambda_{111}(0)$ for $\text{Ru}^{3+}(4d^5)$ on octahedral sites in yttrium iron garnet. The solid line represents the single-ion theory according to eqs. (16).

contributions can also be observed for other anisotropic ions and the explanation requires further detailed investigations.

4. Complex behaviour of 4d and 5d ions. — The 4d and 5d transition-metal ions are known to be present in different valencies in many compounds. Further their ionic radius in the low-spin state is of the

same size or even smaller than that of the trivalent iron ions which implies that no site preference can be predicted from the size of these ions. Thus, in general a very complex situation can occur where a certain ion in more than one valence state is present and in addition these ions occupy both tetrahedral and octahedral sites. The condition for these various states concerning valency and site occupation is essentially determined by the growth conditions of the flux-grown crystals and the impurities present.

In table III the results for the garnet and spinel hosts are summarized where a strong evidence is present for such a complex behaviour. A very striking case is that of the yttrium iron-aluminium garnets where for small aluminium content the anisotropy contributions of the ruthenium ions is in accordance with that of yttrium iron garnet, but for higher aluminium content ΔK_1 changes sign indicating a stronger preference for tetrahedral sites [29]. The presence of different valencies is also indicated by the optical studies of garnets [30], the magnetic properties of yttrium iron garnets containing zinc and of calcium-bismuth iron-vanadium garnets [31-33]. For iridium-substituted yttrium iron garnet the tetravalent state also is a low-spin d^5 configuration and for this ion comparable effects are expected with respect to Ru^{3+} . However, ΔK_1 turns out to be very small and ΔK_2 positive indicating a compensation of the contributions from different sites. Therefore, the interpretation of the anisotropy and magnetostriction assuming a pure octahedral occupation leads to a positive value of v/ξ [12, 13] in contrast to paramagnetic resonance measurements [34-36]. Indeed optical studies indicate the presence of Ir^{4+} on tetrahedral sites [36, 37].

In the spinel host the Ir^{4+} on octahedral sites seems to dominate [38], however, the ratio $\Delta K_2/\Delta K_1$ shows a concentration dependence which indicates the presence of an other valency or different site occupation in the crystals with different concentration. A similar uncertainty about the valence state and the site occupation is present in the ruthenium-substituted nickel and lithium ferrites [39, 40].

An accurate description of the behaviour of the ruthenium and iridium ions in these hosts requires further work. In particular independent measurements as optical studies, paramagnetic resonance on the corresponding diamagnetic hosts and nuclear spin echo measurements are necessary to obtain additional information on the atomic parameters of the electronic configurations and about the site occupation. Otherwise the number of unknown parameters is too large and a comparison of experimental magnetic data with the single-ion theory will not give reliable results. Other ions like palladium, rhodium, rhenium, osmium and platinum would be of large interest, however, no results have been reported. The incorporation of these ions in a particular valence state in garnets and spinels in some cases is very difficult owing to the chemical conditions of the growth process.

TABLE III

Anisotropy and magnetostriction contributions of the ruthenium and iridium ions in garnets and spinel ferrites. In these hosts the ions are present presumably in different valencies and occupy both tetrahedral and octahedral sites

Host	Substituted ion (configuration)	T (K)	$\Delta K_1/N$ (cm ⁻¹)	$\Delta K_2/N$ (cm ⁻¹)	$10^4 \Delta\lambda_{100/x}$	$10^4 \Delta\lambda_{111/x}$	Ref.
$Y_3Fe_{4.7}Al_{0.3}O_{12}$	$Ru^{3+}(4d^5), Ru^{4+}(4d^4)$	4.2	8.7	- 45.6	—	—	[29]
		77	6.8	- 24.5			
		295	0.4	- 0.3			
$Y_3Fe_{4.1}Al_{0.9}O_{12}$	$Ru^{3+}(4d^5), Ru^{4+}(4d^4)$	4.2	- 5.1	- 17.0	—	—	[29]
		77	- 2.2	- 10.1			
		295	- 0.1	~ 0			
$Y_3Fe_{5-y}Zn_yO_{12}$	$Ru^{3+}(4d^5), Ru^{4+}(4d^4)$	77	30	—	—	—	[31, 32]
		295	2	—			
$Ca_{2.7}Bi_{0.3}Fe_{3.65}V_{1.35}O_{12}$	$Ru^{3+}(4d^5), Ru^{4+}(4d^4)$	77	- 2.8	—	—	—	[33]
		295	- 0.8	—			
$Y_3Fe_5O_{12}$	$Ir^{3+}(5d^6), Ir^{4+}(5d^5)$	4.2	1.6	26	- 5.1	~ - 0.2	[12, 13]
		77	1.5	18	- 4.8	~ - 0.1	
		295	0.2	0.1	- 1.9	~ 0	
$NiFe_2O_4$	Ir^{4+}	4.2	2.5	- 10	—	—	[38]
		77	1.4	- 7			
		298	~ 0.1	~ - 0.5			
$NiFe_2O_4$	$Ru^{3+}(4d^5), Ru^{4+}(4d^4)$	77	- 13	- 18	~ 0	~ 0	[39]
		150	- 9.8	- 7.9			
		295	- 3.6	- 1.4			
$Li_{0.5}Fe_{2.5}O_4$	$Ru^{3+}(4d^5), Ru^{4+}(4d^4)$	77	+ 1.5	- 16	- 3.5	- 5.8	[39]
		150	+ 0.8	- 4.8	- 2.0	- 3.9	
		295	+ 0.4	- 0.4	~ 0	- 2.9	

5. Conclusion. — The 4d and 5d ions exhibit large anisotropy and magnetostriction contributions in garnets and spinel ferrites. In particular the low-spin d^5 ion Ru^{3+} on octahedral sites in garnets has been investigated in some more detail since in this case the experimental data are in excellent agreement with the predictions of the single-ion theory. For this configuration a very simple level structure is present owing to the fact that the spin-orbit coupling is much larger than the exchange field. This condition leads to ex-

cit relations for the temperature dependence of anisotropy and magnetostriction in contrast to any other strongly anisotropic ion. The good description of the experimental results by the single-ion theory attributes this configuration a special status in understanding of magnetically anisotropic effects in magnetic oxides.

For other hosts and ions more complicated configurations with respect to valence states and site occupation occur and further work is needed to obtain an accurate description of the observed effects.

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