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EFFECT OF Mn$^{3+}$ ION ORBIT LATTICE COUPLING ON MAGNETIC ANISOTROPY OF Mn$_x$Fe$_{3-x}$O$_4$ SYSTEM

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Résumé. — L'anisotropie magnétique des cristaux Mn$_x$Fe$_{3-x}$O$_4$ ($x = 0.99, 1.24, 1.6$) a été mesurée jusqu'à 4.2 K par mesure de couple. L'analyse de Fourier de ces courbes de couple dans les plans (100), (110) et (111) indique que, dans ces ferrites, il est impossible de décrire la partie anisotrope de l'énergie libre seulement par les deux premières constantes d'anisotropie cubique. L'explication de ce comportement anormal est donnée par les interactions fortes entre les électrons de l'ion Mn$^{3+}$ et le réseau cristallin (effet Jahn-Teller fort).

Abstract. — Magnetic anisotropy of the Mn$_x$Fe$_{3-x}$O$_4$ ($x = 0.99, 1.24, 1.6$) single crystals was measured down to liquid helium temperatures using the torque method. Fourier analysis of the torque curves in the (100), (110) and (111) crystallographic planes showed that in these ferrites the anisotropic part of the free energy cannot be properly described by the first and the second cubic anisotropy constants only.

The explanation of this anomalous behaviour is given taking into account that there is a strong coupling between the electrons of the Mn$^{3+}$ ion and the crystal lattice (strong Jahn-Teller-effect).

1. Introduction. — Recently, the experimental found temperature dependences of the first anisotropy constant in the Mn$_x$Fe$_{3-x}$O$_4$ system [1] for $x > 1$ were explained by the Jahn-Teller effect of the octahedral Mn$^{3+}$-ions [2]. To check this hypothesis we have studied the temperature dependences of the higher anisotropy constants, which were not treated in these materials up to now neither experimentally, nor theoretically.

The free energy of a cubic ferromagnetic crystal is expressed in a form

$$F = F_0 + K_1 (a_1^2 + a_2^2 + a_3^2) + K_2 (a_1^4 + a_2^4 + a_3^4) + \cdots$$

where $a_i$ represent the direction cosines of the magnetization referred to the cubic axes. Experimental torque can be developed in a Fourier series

$$L = -\frac{\partial F}{\partial \phi} = a_0 + \sum_n \left[ a_n \sin (n \phi) + b_n \cos (n \phi) \right].$$

In a special case of (110) plane, if $\phi$ is the angle between the direction of magnetization and [001] direction and the series (1) is well approximated by the first three terms only, the coefficients $b_n$ = 0 and the anisotropy constants can be determined by

$$K_1 = \frac{8}{5} (a_4 - 4 a_2), \quad K_2 = \frac{64}{5} (3 a_2^2 - 2 a_4),$$

$$K_2' = \frac{64}{3} a_6, \ldots$$

If $K_2 = K_2'$ the abovementioned approximation appears to be sufficient, otherwise the higher terms in (1) should be taken into account.

2. Experimental procedure and results. — Magnetic anisotropy was measured on polished spheres of about 3 mm in diameter mounted in an automatic compensated torque anisometer described elsewhere [3]. Most of the measurements have been made in magnetic field of 15 kOe in (110) plane, for comparison the measurements in (100) and (111) planes were also performed. To analyse the torque curves, the values of $L_s$ were gathered for 65 angles $\phi_s = k \pi/32$ ($k = 0, 1, \ldots, 64$). After the correction for noncolinearity of the magnetization and the external field $H$ was made, the coefficients $a_n$, $b_n$ in (2) were found by means of a computer. Afterwards the anisotropy constants $K_1$, $K_2$, $K_2'$ were calculated.

![Fig. 1. — Temperature dependence of the anisotropy constants for Mn$_{0.99}$Fe$_{2.01}$O$_4$](image-url)

In figure 1 the temperature dependences of $K_i$'s are plotted for the sample $x = 0.99$. The course of $K_1$ is in a qualitative accord with Palmer's measurements [1], the differences being attributed to a slight iron excess in our sample. The most striking result is the large difference between $K_2$ and $K_2'$. This difference is even larger for the composition $x = 1.24$ the results of which are represented in figure 2. Very good agree-
ment of Palmer's data with our determination of $K_1$ in (001) plane is seen, while the absolute values of $K_1$ as determined from (110) plane are somewhat less. This fact together with the differences between $K_1$ and $K_2$ indicate that higher terms in the series (1) are not insignificant. The same holds for the sample $x = 1.6$ the anisotropy constants of which are shown in figure 3.

3. Discussion. — Octahedrally coordinated Mn$^{3+}$ ion tends to remove the orbital degeneracy of the ground state by distorting its environment. We assume that the degeneracy is removed by a tetragonal distortion along one of the cubic axes. As the three cubic axes are equivalent and spin of Mn$^{3+}$ ion equals 2, there are fifteen low lying states $|x, M >, |y, M >, |z, M >$ of the system considered ($x = x, y, z ; M = -2, -1, ... 2$). The Hamiltonian appropriate to describe the splitting of this multiplet in the presence of magnetization and random strains is

$$\mathbf{H} = g_\beta \mathbf{H}_\text{m} \cdot \mathbf{S} + \begin{pmatrix} S_x^2 - 2 & 0 & 0 \\ 0 & S_y^2 - 2 & 0 \\ 0 & 0 & S_z^2 - 2 \end{pmatrix} \begin{pmatrix} \delta_x \\ \delta_y \\ \delta_z \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{4}$$

The first term in (4) represents the exchange interactions, the second the coupling between Mn$^{3+}$ ion spin and axial distortion and the third the splitting by random strains.

From the Curie temperature of Mn$_3$O$_4$ the value $\beta H_\text{m}$ is estimated to be of the order of ten cm$^{-1}$. Theoretical prediction as well as EPR data [4] give $2 \text{ cm}^{-1} < |D| < 4 \text{ cm}^{-1}$. The splitting by random strains varies from site to site; for simplicity let us consider two limiting cases only:

a) Unstabilized Jahn-Teller effect. — If there is no random strain, then the energy levels of the three lowest lying states $|x, -2 >, |y, -2 >, |z, -2 >$ mutually intersect when the magnetization is rotated. Anisotropy constants, which correspond to such a case are linearly proportional to $D$ and consequently very large at low temperatures. They are very strongly temperature dependent due to the small energy interval between the states $|x, -2 >, |y, -2 >, |z, -2 >$.

b) Strain stabilized Jahn-Teller effect. — Let in (4) $\delta_x = g_\beta H_\text{m}; \delta_y = \delta_z = 0$. The states $|z, M >$ are then separated from the states $|x, M >$ and $|y, M >$ by a large energy interval. At temperature not too high only the states having $z$ as a distortion axis are populated. Such a situation clearly corresponds to what was previously called a static Jahn-Teller effect. Corresponding anisotropy constants may then be determined by a perturbation procedure [5].

The temperature dependences of $K_1/N, K_2/N, K_3/N$ are shown in figure 4.

![Figure 2](image1.png)  
**Figure 2.** Temperature dependence of the anisotropy constants for Mn$_{1.24}$Fe$_{1.76}$O$_4$.

![Figure 3](image2.png)  
**Figure 3.** Temperature dependence of the anisotropy constants for Mn$_{1.6}$Fe$_{1.4}$O$_4$.

![Figure 4](image3.png)  
**Figure 4.** Theoretically calculated temperature dependence of the one-ion anisotropy constants of Mn$^{3+}$ ion. Parameter $D = 2.5 \text{ cm}^{-1}, \beta H = 25 \text{ cm}^{-1}$. 
for unstabilized and strain-stabilized Jahn-Teller effect are displayed in figure 4. Qualitative analysis of the experimental data shows that for most of the Mn$^{3+}$ ions the Jahn-Teller effect is strain stabilized. There are some of the Mn$^{3+}$ ions, however, for which the random strains are small. If figure 4 is confronted, it is seen that these ions are responsible for the minimum of $K_1$ and for the sudden decrease of $K_2$ at low temperature. Stoichiometric manganese ferrite has partially inverse structure, which invokes large strains. In Mn$_{1.6}$Fe$_{1.4}$O$_4$ the increase in concentration of Mn$^{3+}$ ions is also accompanied by large local strains. We expect therefore the unstabilized Jahn-Teller effect to be the most effective for the sample with $x = 1.24$. This is also supported by the experiment.

Preliminary calculations have shown that the difference between $K_2$ and $K'_2$, which appears for all three samples may be explained if the perturbation procedure for strain stabilized Mn$^{3+}$ ion is carried to higher orders and if the spin canting is also taken into account. More details will be published elsewhere.

References