DIPOLE INTERACTION IN THE ANTIFERROMAGNETS $MnCO_3$ *AND* $CsMnF_3$

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We calculate the dipole interaction in the antiferromagnets $MnCO_3$ and $CsMnF_3$. Numerical values are obtained for the second-order anisotropy constants in the expansion of the thermodynamic potential in the dipole approximation. Comparison with the experimental data shows that the main contribution to the anisotropy energy of the investigated antiferromagnets is made by the dipole interaction.

1. Experiments on antiferromagnetic resonance have shown that the temperature dependences of the energy gap in the high-frequency branch of the AFMR spectra of certain antiferromagnets[1-3] are close to the square of the reduced Brillouin function. This gives grounds for assuming that the anisotropy energy is proportional to the square of the magnetization of the sublattices, and consequently the main component in the anisotropy energy of such substances is the dipole interaction.

In this paper we calculate the anisotropy constants for the "easy-plane" antiferromagnets $MnCO_3$ and $CsMnF_3$ in the dipole approximation. The results are in good agreement with the experimental data.

2. The crystal symmetry of $MnCO_3$ is described by the space group D_{3d}^6 (Fig. 1). The atomic coordinates of the Mn^{++} ions are ¼, ¼, ¼ and ¾, ¾, ¾; the lattice parameters are a = 5.84 Å and α = 47°20′ [4]. According to[1], the anisotropy terms in the expansion of the thermodynamic potential up to second order are given by

$$\Phi = \frac{a}{2} l_z^2 + \frac{b}{2} m_z^2 = \frac{a+b}{2}(s_{1z}^2 + s_{2z}^2) + (b-a) s_{1z} s_{2z},$$

where $\mathbf{s}_1$ and $\mathbf{s}_2$ are the magnetic moments of the sublattices, $\mathbf{l} = \mathbf{s}_1 - \mathbf{s}_2$, and $\mathbf{m} = \mathbf{s}_1 + \mathbf{s}_2$ (the z axis is directed along the principal axis of the crystal).

Let us consider two states of the spin system with $s_{1z} = s_{2z} = 0$ and $|s_{1z}| = |s_{2z}| = M_0$, where the magnetization of each sublattice is $M_0 = (1/2) N g \mu_B S = 13.95 \times 10^3$ cgs emu/mole, N is Avogadro's number, μ_B is the Bohr magneton, S is the spin of the Mn^{++} ion and equals 5/2, and the g-factor is g = 2.00[1]. We denote the proper dipole energies of each sublattice and the interaction energy of the two sublattices $E_{1\rightarrow}$ and $E_{2\rightarrow}$ respectively in the first state and by $E_{1\uparrow}$ and $E_{2\uparrow}$ in the second state. Equating the corresponding terms in the increments of the energy and of the thermodynamic potential, we obtain

$$\frac{a+b}{2} = \frac{1}{M_0^2}(E_{1\uparrow} - E_{1\rightarrow}), \quad a - b = \frac{1}{M_0^2}(E_{2\uparrow} - E_{2\rightarrow}).$$

The dipole energies were calculated by the Kornfeld-Ewald method[5] with a computer and two different values of the auxiliary parameter were specified to monitor the calculation. We obtained the following results:

$$E_{1\uparrow} - E_{1\rightarrow} = 1{,}12 \cdot 10^7 \text{ erg/mole}, \quad E_{2\uparrow} - E_{2\rightarrow} = 1{,}80 \cdot 10^7 \text{ erg/mole},$$

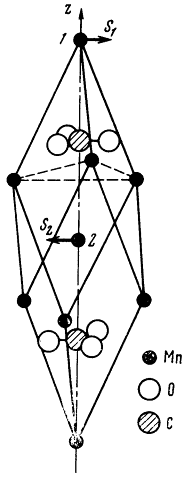

FIG. 1. Unit cell of $MnCO_3$.

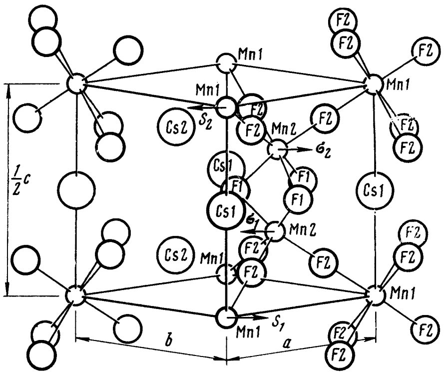

FIG. 2. Half of the unit cell of $CsMnF_3$.

whence

$$a = 0{,}104 \text{ erg/mole} / (\text{cgs emu})^2,$$
$$b = 0{,}117 \cdot 10^{-1} \text{ erg/mole} / (\text{cgs emu})^2.$$

The accuracy of the obtained values is determined by the accuracy with which the lattice parameter and the g-factor are specified, and if calculation error is taken into account it amounts to ~2%.

3. The crystal symmetry of $CsMnF_3$ is described by the space group D_{6h}^4 (Fig. 2). The Mn^{++} ions in $CsMnF_3$ are in two crystallographically nonequivalent positions. The unit cell contains two ions, denoted MnI, in positions with point symmetry D_{3d}, and four ions MnII in positions with point symmetry C_{3v}. We see therefore that to describe the magnetic properties of $CsMnF_3$ it is necessary to consider six magnetic sublattices. The crystal lattice parameter are: a = 6.213 Å, c = 15.074 Å, u = 0.849[6]. The atomic coordinates of the Mn^{++} ions are (0, 0, 0) and (0, 0, ½) for Mn I and (⅓, ⅔, u), (⅓, ⅔, ½ − u), (⅔, ½, ½ + u), (⅔, ⅓, − u) for Mn II[6].

We denote the magnetic moments of the sublattices of MnI by $\mathbf{s}_1$ and $\mathbf{s}_2$, and those of MnII by $\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \boldsymbol{\sigma}_3$, and $\boldsymbol{\sigma}_4$. Taking into consideration the alternation of the sublattices along the z axis: $\mathbf{s}_1, \boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \mathbf{s}_2, \boldsymbol{\sigma}_3, \boldsymbol{\sigma}_4$, we denote by E_1 the proper energy of each sublattice, and by E_2, E_3, E_4, E_5, E_6, and E_7 the interaction energies of the sublattices 1 and 4, 2 and 3, 2 and 5, 2 and 6, 1 and 3, and 1 and 2, respectively (1–6 are the numbers of the sublattices along the z axis, starting with s_1).

The general formula for the anisotropy terms in the expansion of the thermodynamic potential for crystals of the type $CsMnF_3$[2] is

$$\Phi = \frac{a_1}{2} l_{1z}^2 + \frac{a_2}{2} l_{2z}^2 + c l_{1z} l_{2z} + \frac{a_3}{2} l_{3z}^2 + \frac{a_4}{2} l_{4z}^2$$

$$+ \frac{b_1}{2} m_{1z}^2 + \frac{b_2}{2} m_{2z}^2 + d m_{1z} m_{2z} = \frac{a_1 + b_1}{2} (s_{1z}^2 + s_{2z}^2)$$

$$+ (b_1 - a_1) s_{1z} s_{2z} + \frac{a_2 + a_3 + a_4 + b_2}{2} (\sigma_{1z}^2 + \sigma_{2z}^2 + \sigma_{3z}^2$$

$$+ \sigma_{4z}^2) + (- a_2 + a_3 - a_4 + b_2)(\sigma_{1z}\sigma_{2z} + \sigma_{3z}\sigma_{4z})$$

$$+ (- a_2 - a_3 + a_4 + b_2)(\sigma_{1z}\sigma_{3z} + \sigma_{2z}\sigma_{4z}) + (a_2 - a_3 - a_4$$

$$+ b_2)(\sigma_{1z}\sigma_{4z} + \sigma_{2z}\sigma_{3z}) + (c + d)(s_{1z}\sigma_{2z} + s_{1z}\sigma_{3z} + s_{2z}\sigma_{1z} + s_{2z}\sigma_{4z})$$

$$+ (d - c)(s_{1z}\sigma_{1z} + s_{1z}\sigma_{4z} + s_{2z}\sigma_{2z} + s_{2z}\sigma_{3z}),$$

where

$$\mathbf{l}_1 = \mathbf{s}_1 - \mathbf{s}_2,\ \mathbf{m}_1 = \mathbf{s}_1 + \mathbf{s}_2,\ \mathbf{l}_2 = -\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_3 - \boldsymbol{\sigma}_4,\ \mathbf{l}_3 = -\boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2$$
$$+ \boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_4,\ \mathbf{l}_4 = -\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2 - \boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_4,\ \mathbf{m}_2 = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_4.$$

Using the same reasoning as for the case of $MnCO_3$, we obtain

$$\frac{a_1 + b_1}{2} = \frac{a_2 + a_3 + a_4 + b_2}{2} = \frac{1}{M_0^2}(E_{1\uparrow} - E_{1\rightarrow}),$$

$$a_1 - b_1 = \frac{1}{M_0^2}(E_{2\uparrow} - E_{2\rightarrow}),$$

$$a_2 - a_3 + a_4 - b_2 = \frac{1}{M_0^2}(E_{3\uparrow} - E_{3\rightarrow}),$$

$$a_2 + a_3 - a_4 - b_2 = \frac{1}{M_0^2}(E_{4\uparrow} - E_{4\rightarrow}),$$

$$a_2 - a_3 - a_4 + b_2 = \frac{1}{M_0^2}(E_{5\uparrow} - E_{5\rightarrow}),$$

$$c + d = \frac{1}{M_0^2}(E_{6\uparrow} - E_{6\rightarrow}), \qquad c - d = \frac{1}{M_0^2}(E_{7\uparrow} - E_{7\rightarrow}),$$

where $M_0 = (1/6) N g \mu_B S = 4.66 \times 10^3$ cgs emu/mole ($g = 2.00$[7]). Computer calculations yielded (in erg/mole)

$$E_{1\uparrow} - E_{1\rightarrow} = 0{,}476 \cdot 10^7, \quad E_{2\uparrow} - E_{2\rightarrow} = 0{,}276 \cdot 10^7,$$
$$E_{3\uparrow} - E_{3\rightarrow} = 1{,}066 \cdot 10^7, \quad E_{4\uparrow} - E_{4\rightarrow} = 0{,}268 \cdot 10^7,$$
$$E_{5\uparrow} - E_{5\rightarrow} = -0{,}238 \cdot 10^7, \quad E_{6\uparrow} - E_{6\rightarrow} = -0{,}255 \cdot 10^7,$$
$$E_{7\uparrow} - E_{7\rightarrow} = -0{,}119 \cdot 10^7.$$

From this we obtain (in erg-mole/(cgs emu)^2)

$$a_1 = 2{,}83 \cdot 10^{-1}, \quad a_2 = 2{,}36 \cdot 10^{-1}, \quad a_3 = 0{,}451\ 10^{-1}, \quad a_4 = 2{,}29 \cdot 10^{-1},$$
$$b_1 = 1{,}56 \cdot 10^{-1},\ b_2 = -0{,}714 \cdot 10^{-1},\ c = -0{,}861 \cdot 10^{-1},\ d = -0{,}313 \cdot 10^{-1}.$$

Substance	Measured quantity	Experimental value	Theoretical value
$MnCO_3$	$H_A = 2aM_0$ $2bM_0$	3.0 kOe ± 3% [8,1] 0 ± 1 kOe [9]	2.89 kOe ± 2% 0.34 kOe ± 2%
$CsMnF_3$	$H_A = {}^2/_3 M_0 (a_1 + 4a_2 + 4c)$	2.48 kOe ± 3%[2]	2.72 kOe ± 2%

4. The table lists the results of an experimental investigation of the magnetic anisotropy and the calculated data obtained on the contribution of the dipole interaction for the antiferromagnets $MnCO_3$ and $CsMnF_3$.

A comparison of the calculated and experimental results shows that the main contribution to the anisotropy energy of the antiferromagnets $MnCO_3$ and $CsMnF_3$ is made by the dipole interaction. The slight deviation from experiment is due to the presence of other types of anisotropic interactions.

We note that an estimate of the dipole interaction in $CsMnF_3$ was presented in[7], where a two-sublattice model was used. The value obtained for H_A was 6.80 kOe. Such an appreciable discrepancy between the results can be attributed to the strong simplifications used by the authors of[7] in the calculations.

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