

## SPECIFIC FEATURES OF THE MAGNETIC PROPERTIES OF MONOCLINIC FERRO- AND ANTIFERROMAGNETS

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It is a study of the temperature behaviour of the easy axes of monoclinic ferro- and antiferromagnets in a wide temperature range. The monoclinic character of the magnetic interactions is due to the presence of two uniaxial anisotropies differing in nature and arranged at an arbitrary angle to one another. This is shown to be the cause of dependence of the magnetization easy axis orientation on temperature.

Experimental study of magnetic materials with symmetry below rhombic has resulted in discovery of some features of their properties that are associated with low symmetry. In particular, these include the temperature dependences of the arrangement of the susceptibility tensor principal axes and the magnetic moment direction. Temperature-dependent rotation of the susceptibility ellipsoid and the magnetic moment was observed experimentally in magnetically concentrated crystals of  $\text{NaFe}(\text{WO}_4)_2$  [1] and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  [2]. Note that the temperature-dependent rotation of the susceptibility tensor principal axes was by about  $45^\circ$  within a temperature range of about 10 K, and the antiferromagnetism vector in the ordered phase of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  changed its vector direction by some  $5^\circ$  within a range of 1.5 to 5 K.

We have considered a model of ferro- and antiferromagnets with monoclinic magnetic interactions. This model accounts for the observations. The monoclinic anisotropy is represented by two types of axial anisotropy introduced in the below Hamiltonian with different directions. One of them is determined by the interaction of each individual ion mainly with the lattice (we call it here single-site) and the other by the interaction between ions (intersite), characterized by unit vectors  $\mathbf{n}$  and  $\mathbf{n}'$ , respectively. The angle between these is  $\varphi$  ( $0 \leq \varphi \leq \pi/2$ ).

The Hamiltonian of the ferro- and antiferromagnet is

$$\mathcal{H} = -\frac{1}{2} \sum_{l,l'} J_{ll'} \mathbf{S}_l \mathbf{S}_{l'} - \frac{\beta}{2} \sum_l (\mathbf{S}_l \mathbf{n})^2 - \frac{1}{2} \sum_{l,l'} \rho_{ll'} (\mathbf{S}_l \mathbf{n}') (\mathbf{S}_{l'} \mathbf{n}') - \mu \mathbf{H} \sum_l \mathbf{S}_l, \quad (1)$$

where  $J_{ll'}$  is the exchange integral;  $\mathbf{S}_l$ ,  $\mathbf{S}_{l'}$  spin operators for sites  $l, l'$ ;  $\beta$ ,  $\rho$  constants of the single-site and intersite anisotropies, respectively;  $\mu$  the doubled Bohr magneton; and  $\mathbf{H}$  the magnetic field applied parallel to the plane  $(\mathbf{n}, \mathbf{n}')$ . Denote the angle between  $\mathbf{H}$  and  $\mathbf{n}$  by  $\psi$ . The constants  $\beta$  and  $\rho$  in eq. (1) are chosen so that the magnetization easy axis should lie in the plane  $(\mathbf{n}, \mathbf{n}')$ .

Take first the magnetically ordered ferromagnet phase. Use the coordinate system with the unit vectors  $\mathbf{l}_x, \mathbf{l}_y, \mathbf{l}_z$  such that  $\mathbf{l}_y$  and  $\mathbf{l}_z$  lie in the plane  $(\mathbf{n}, \mathbf{n}')$ . The angle between  $\mathbf{n}$  and  $\mathbf{l}_z$  will be denoted by  $\theta$ . In this coordinate system we have

$$\mathbf{S}_l = S_l^x \mathbf{l}_x + S_l^y \mathbf{l}_y + S_l^z \mathbf{l}_z$$

and hence

$$\begin{aligned} \mathcal{H} = & -\frac{1}{2} \sum_{l,l'} J_{ll'} \mathbf{S}_l \mathbf{S}_{l'} - \frac{\beta}{2} \sum_l (S_l^z \cos \theta - S_l^y \sin \theta)^2 \\ & - \frac{1}{2} \sum_{l,l'} \rho_{ll'} [S_l^z \cos(\theta - \varphi) - S_l^y \sin(\theta - \varphi)] \\ & \times [S_l^z \cos(\theta - \varphi) - S_l^y \sin(\theta - \varphi)] \\ & - \mu \mathbf{H} \sum_l [S_l^z \cos(\theta - \psi) - S_l^y \sin(\theta - \psi)]. \quad (2) \end{aligned}$$

This coordinate system will be specified so as to have

$$\langle S_l^z \rangle_{t \rightarrow \infty} \rightarrow \sigma, \quad \langle S_l^x \rangle_{t \rightarrow \infty} = \langle S_l^y \rangle_{t \rightarrow \infty} \rightarrow 0, \quad (3)$$

where  $\langle S_l^z \rangle = \text{Sp}(\hat{\rho} S_l^z)$ ,  $\hat{\rho}$  is the density matrix,  $\sigma$  the average value of the site spin,  $t = \text{time}$ . It follows from eq. (3) that

$$\left( \frac{d}{dt} \langle \sum_l S_l^x \rangle \right)_{t \rightarrow \infty} \rightarrow -i \text{Sp} \hat{\rho}_0 \left[ \mathcal{H}, \sum_l S_l^x \right] = 0, \quad (4)$$

where  $\hat{\rho}_0$  is the equilibrium density matrix with the Hamiltonian of eq. (2). Upon commutation of eq. (4) we have

$$\begin{aligned} & \frac{\beta}{2} \sum_l \langle (S_l^z S_l^y + S_l^y S_l^z) \cos 2\theta \\ & + [(S_l^z)^2 - (S_l^y)^2] \sin 2\theta \rangle \\ & + \sum_{l,l'} \rho_{ll'} \langle S_l^y S_{l'}^z \cos 2(\theta - \varphi) \\ & + \frac{1}{2} (S_l^z S_{l'}^z - S_l^y S_{l'}^y) \sin 2(\theta - \varphi) \rangle \\ & + \mu \mathbf{H} \sin(\theta - \psi) \sum_l \langle S_l^z \rangle = 0. \quad (5) \end{aligned}$$

From this general expression it follows in particular that in a uniaxial ferromagnet ( $\varphi = 0$ ) in a field  $\mathbf{H} \perp \mathbf{n}$  the

position of the magnetization vector in the angular phase is given by the following relation in the exchange approximation:

$$\sin \theta = \mu H \sum_i \langle S_i^z \rangle / \left[ \beta \sum_i \langle (S_i^z)^2 \rangle - \langle (S_i^y)^2 \rangle + \sum_{i,i'} \rho_{ii'} \langle S_i^z S_{i'}^z - S_i^y S_{i'}^y \rangle \right]. \quad (6)$$

Here we are interested in the temperature behaviour of the magnetization vector orientation, due to monoclinic magnetic interactions, under no magnetic field. In this case eq. (5) leads to the following:

$$\begin{aligned} \operatorname{tg} 2\theta = & \left\{ \sum_{i,i'} \rho_{ii'} [\langle S_i^z S_{i'}^z - S_i^y S_{i'}^y \rangle \sin 2\varphi - 2\langle S_i^y S_{i'}^z \rangle \right. \\ & \times \cos 2\varphi] - \beta \sum_i \langle S_i^z S_i^y + S_i^y S_i^z \rangle \left. \right\} \\ & \times \left\{ \sum_{i,i'} \rho_{ii'} [\langle S_i^z S_{i'}^z - S_i^y S_{i'}^y \rangle \cos 2\varphi + 2\langle S_i^y S_{i'}^z \rangle \right. \\ & \times \sin 2\varphi] + \beta \sum_i \langle (S_i^z)^2 \rangle - \langle (S_i^y)^2 \rangle \left. \right\}^{-1}. \quad (7) \end{aligned}$$

This equation implied that the temperature-dependent rotation of magnetization is the case when  $\varphi \neq 0, \pi/2$  (i.e. the magnetic interaction symmetry is monoclinic).

The above relation permits, upon calculation by a certain technique of the correlators of eq. (7), the temperature dependence of  $\theta$  to be found in a wide temperature range. The most consistent way to do this is by finding the Green's functions. Here we shall show a simpler variant.

Earlier we found the  $\theta(T)$  relation for  $T \ll T_c$  ( $T_c$  being the Curie temperature) in ref. [3] in the spin-wave approximation from an expression for  $\theta$  less general than eq. (7). In this range, the  $\Delta\theta(T)$  relation ( $\theta = \theta_0 - \Delta\theta$ ,  $\theta_0$  is the angle value at  $T=0$ ) is found for a ferromagnet from the relation

$$\Delta\theta \sim \sum_k (\rho_0 - \rho_k) N_k, \quad (8)$$

where  $\rho_k$  is the intersite anisotropy Fourier component and  $N_k$  the magnon distribution function.

In the high temperature range we shall use the molecular field method. Since the part due to anisotropy has been revealed in eq. (7), we shall make averaging of eq. (7) with the use of the molecular field Hamiltonian:

$$\mathcal{H}_{\text{mol}} = J_0 \sigma \sum_i S_i^z, \quad (9)$$

where  $J_0 = \sum_i J_{ii}$ . In this approximation,

$$\operatorname{tg} 2\theta = 2\rho_0 \sin 2\varphi \langle S_z \rangle_{\text{mol}}^2 / \left\{ 2\rho_0 \langle S_z \rangle_{\text{mol}}^2 \cos 2\varphi + \beta \left[ \langle S_z^2 \rangle_{\text{mol}} - \langle S_y^2 \rangle_{\text{mol}} \right] \right\}. \quad (10)$$

The averages of eq. (10) have the simple form for  $S = 1$ . In this case,

$$\operatorname{tg} 2\theta = 2\rho_0 \sin 2\varphi / [2\rho_0 \cos 2\varphi + \beta f(x)], \quad (11)$$

where

$$f(x) = (\operatorname{ch} x - 1)(1 + 2\operatorname{ch} x) / 2\operatorname{sh}^2 x, \quad x = J_0 \sigma / T.$$

The function  $f(x)$  determines the temperature behaviour of the easy magnetization axis orientation in a monoclinic ferromagnet. Clearly, for  $T = 0$ ,

$$\operatorname{tg} 2\theta_0 = 2\rho_0 \sin 2\varphi / (2\rho_0 \cos 2\varphi + \beta), \quad (12)$$

in agreement with the result of ref. [3].

For  $T \rightarrow T_c$ , the angle  $\theta \rightarrow \theta_c$ , where

$$\operatorname{tg} 2\theta_c = 8\rho_0 \sin 2\varphi / (8\rho_0 \cos 2\varphi + 3\beta). \quad (13)$$

These are the limiting angle values between which the magnetization vector rotates with temperature. The rotation angle will be the largest, when the denominator of eq. (11) goes to zero in the particular temperature range\*, which may be the case when the constants  $\beta$  and  $\rho$  have opposite sign.

It is evident that eq. (11) is a qualitatively adequate representation of the temperature dependence of the angle  $\theta$ , except when  $T \approx 0$  (see ref. [3]) and in the vicinity of  $T_c$  (where fluctuations must be allowed for).

As regards the paramagnetic phase, note the following. In this case, in the absence of a magnetic field,  $\langle S_i \rangle = 0$ ; therefore, the directions of the susceptibility ellipsoid principal axes in the plane ( $\mathbf{n}, \mathbf{n}'$ ) are found from eq. (5) in a field at  $\psi = \theta$  which finally tends to zero. By this method we find from eq. (7) for  $T \gg T_c$  that  $\theta = \theta_c$ , being specified by eq. (13).

The above approach applied to a monoclinic antiferromagnet enables the determination of the general expression for the angle specifying the antiferromagnetism vector orientation as dictated by temperature. Here we note only that in the molecular field approximation the expression for  $\theta$  has the form of eq. (10), with substitution  $\rho_0 \rightarrow \rho_0 - \rho'_0$  where  $\rho_0$  and  $\rho'_0$  are characteristics of the intra- and intersublattice anisotropies, respectively.

\* In more symmetric cases ( $\varphi = 0, \pi/2$ ), the going to zero of the denominator of eq. (11) may let one determine the orientation transition temperature.

## References

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