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CONDENSED MATTER

Single-Ion Mechanism of Weak Ferromagnetism and a Spin-Flop Transition in One- and Two-Position Antiferromagnets

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A system of equations describing the ground state in an external magnetic field has been obtained for a two-position antiferromagnet with noncollinear axes of single-ion anisotropy of moments of different sublattices. It has been shown that the antiferromagnetism vector changes sign at a spin-flop transition. This leads to a first-order magnetic phase transition with hysteresis in the field dependence of the magnetization. Explicit relations have been obtained between the parameters of a microscopic Hamiltonian and the experimentally observed spontaneous moment and spin-flop transition field. It has been shown that the field dependence of the total magnetic moment of the antiferromagnet with magnetic ions at two crystallographically nonequivalent positions (two-position antiferromagnet) obtained within the two-sublattice model is nonlinear above the transition field at any orientation of the crystal with respect to the magnetic field.

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Antiferromagnets with a weak ferromagnetic moment have been studied for more than half a century primarily because of their wide abundance and variety of their magnetic properties [1, 2]. The variety of the magnetic properties is largely explained by the existence of different mechanisms of noncollinearity of the magnetic moments of antiferromagnetic sublattices. The studies of such magnetic materials in the last decade were additionally stimulated by the existence of multiferroic properties in many of them. The manifestation of these properties is usually most pronounced near magnetic phase transitions when the magnitude or orientation of magnetic moments changes significantly. For antiferromagnets, this primarily refers to a spin-flop transition, i.e., the reversal of the moments of sublattices at the application of an external magnetic field along the easy axis of the uniaxial anisotropy of the antiferromagnet. The field strength at which the transition occurs and its form are determined primarily by the antiferromagnetic exchange interaction and magnetic anisotropy and, consequently, carry important information on the form of anisotropy and strengths of these interactions. In the absence of a weak ferromagnetic moment, the spin-flop transition occurs as a first-order phase transition, i.e., magnetic moments change their orientations stepwise. The type of transition in weak ferromagnets significantly depends on the mechanism of noncollinearity of antiferromagnetic sublattices. In particular, in the presence of the relativistic two-ion Dzyaloshinskii–Moriya interaction, which is usually treated as the main reason for noncollinearity, moments are reoriented through two second-order phase transitions; i.e., the orientation of magnetic moments changes continuously [2]. The single-ion mechanism of the noncollinearity of magnetic moments appears in the absence of the translational invariance of magnetic ions in a crystal, which results in the noncollinearity of the axes of local single-ion anisotropy at different sites of the magnetic lattice. This is a fundamental difference of this mechanism from the two-ion one. The latter is usually described in terms of the vector product of the magnetic moments of the sublattices

$$H_{\mathrm{DM}} = \mathbf{D}[\mathbf{M}_1 \times \mathbf{M}_2]$$

and leads to a weak moment isotropic in a plane orthogonal to the vector $\mathbf{D}$. On the contrary, the single-ion mechanism is strictly related to the orientation of the magnetic anisotropy axes in the crystal and the weak moment changes under rotation even to the change in its sign [2]. If the single-ion mechanism dominates, the reorientation of the moments of antiferromagnetic sublattices $\mathbf{M}_1 \longleftrightarrow \mathbf{M}_2$ should occur at the point of change in the sign of the weak moment, which will result in the recovery of the collinearity of the weak moment and external field. The aim of this work is to determine the type and conditions of exis-

tence of such reorientation, which accompanies the spin-flop transition, as well as explicit relations of the observed weak moment and the spin-flop transition field to the parameters of the microscopic Hamiltonian describing magnetic anisotropy.

The magnetic state of the weak ferromagnet is usually described using either the phenomenological Hamiltonian [1] or the expansion of the thermodynamic potential in powers of the order parameters (components of the antiferromagnetism vector $\mathbf{l} = (\mathbf{M}_1 - \mathbf{M}_2)/2M_0$ and weak moment $\mathbf{m} = (\mathbf{M}_1 + \mathbf{M}_2)/2M_0$) [2] in the Landau thermodynamic theory [3]. In the ground state ($T = 0$), the potential coincides with the magnetic energy density and both approaches are equivalent. The products of the components $\mathbf{l}$ and $\mathbf{m}$ of each term of the expansion should be invariant under transformations of the corresponding symmetry group of the crystal. For the richest class of rhombic crystals and the centrosymmetric exchange structure with the even second-order axis along the b axis of the crystal, the potential has the form

$$F = A\mathbf{m}^2 + a_1 m_a^2 + a_2 m_c^2 + b_1 l_a^2 + b_2 l_c^2 + d_1 m_a l_c + d_2 m_c l_a + h_a m_a + h_c m_c.$$

The coefficients a_1, a_2, b_1, b_2, and $d = d_1 = d_2$ (for the single-ion mechanism) are not independent parameters of the model. They can be expressed in terms of the coefficients of the single-ion anisotropy of the spins of the sublattices of the microscopic Hamiltonian and the angles of their orientations in the crystal. To determine an explicit dependence of the observed weak moment and the spin-flop transition field on these parameters, the ground state is described by the Hamiltonian

$$H = J\sum_{ij}\mathbf{S}_i\mathbf{S}_j + K_1\sum_i S_i^{\varphi 1\,2} + K_2\sum_j S_j^{\varphi 2\,2} + H_0\left(\sum_i S_i^z + \sum_j S_j^z\right), \quad (1)$$

where $J > 0$. Further, we consider the equimodular model of classical moments with isotropic g-factors and uniaxial local easy axis anisotropy $K_1, K_2 < 0$ in the external magnetic field applied in the plane formed by these axes of anisotropy. This maximally simplified model can be used to describe in the first approximation the system of S ions in both positions. In this case, the region of variation of the direction of the moments of sublattices is limited by the plane formed by the axes of anisotropy. Let the z axis be directed along the external magnetic field. The magnetic moments of the antiferromagnetic sublattices are oriented at the angles θ_1 and θ_2 with respect to the external magnetic field and the axes of anisotropy are oriented at the angles φ_1 and φ_2. The magnetic energy of two moments in the ground state has the form

$$E_2 = h_e\cos(\theta_1 - \theta_2) + (K + \Delta)\cos(\theta_1 - \varphi - \delta)^2 + (K - \Delta)\cos(\theta_2 - \varphi + \delta)^2 - h(\cos\theta_1 + \cos\theta_2), \quad (2)$$

where $K = (K_1 + K_2)S^2/2$ is the average uniaxial anisotropy, $\varphi = (\varphi_1 + \varphi_2)/2$ is the average angle, $\Delta = (K_1 - K_2)S^2/2$ and $\delta = (\varphi_1 - \varphi_2)/2$ are the deviations from the average values, and $h_e = Jz\mathcal{S}^2$ and $h = g\mu_B H_0 S$ are the reduced exchange and external fields, respectively.

The equilibrium orientation of the magnetic moments can be determined both by minimizing the magnetic energy given by Eq. (2) and by satisfying a necessary condition of collinearity of the moments to the total effective field [4, 5]. The second approach means the vanishing of the transverse components of the total local fields at each moment [6–8]. This approach provides the clearest representation of the effect of each component of the magnetic interactions given by Eq. (2) on the orientation of an individual moment. Transverse fields on the moments of the antiferromagnetic sublattices have the form

$$h_1^\theta = \frac{h_e}{2}S(\theta_1 - \theta_2) + \frac{K + \Delta}{2}S(2(\theta_1 - \varphi - \delta)) - \frac{h}{2}S(\theta_1) = 0,$$
$$h_2^\theta = \frac{h_e}{2}S(\theta_2 - \theta_1) + \frac{K - \Delta}{2}S(2(\theta_2 - \varphi + \delta)) - \frac{h}{2}S(\theta_2) = 0, \quad (3)$$

where $S(x) = \sin x$ and $C(x) = \cos x$. The sum and difference of Eqs. (3) give two equations for new variables of the problem—the relative weak moment $m = C((\theta_1 - \theta_2)/2)$ and its angle with respect to the external field $\theta = (\theta_1 + \theta_2)/2$. Retaining the first-order terms of the variable $m \ll 1$ in the expansion of trigonometric functions in transverse fields (corresponding to the m^2 terms in the expansions of the functions in Eq. (2) for the energy), we obtain different expressions for two possible orientations of the antiferromagnetic moments in the external magnetic field (Fig. 1). For state A,

$$m = \frac{-KC(2\delta)S(2(\theta - \varphi)) + \Delta S(2\delta)C(2(\theta - \varphi))}{hS(\theta) + 2h_a}, \quad (4)$$
$$m = \frac{hC(\theta) + KS(2\delta)C(2(\theta - \varphi)) - \Delta C(2\delta)S(2(\theta - \varphi))}{2\tilde{h}_e};$$

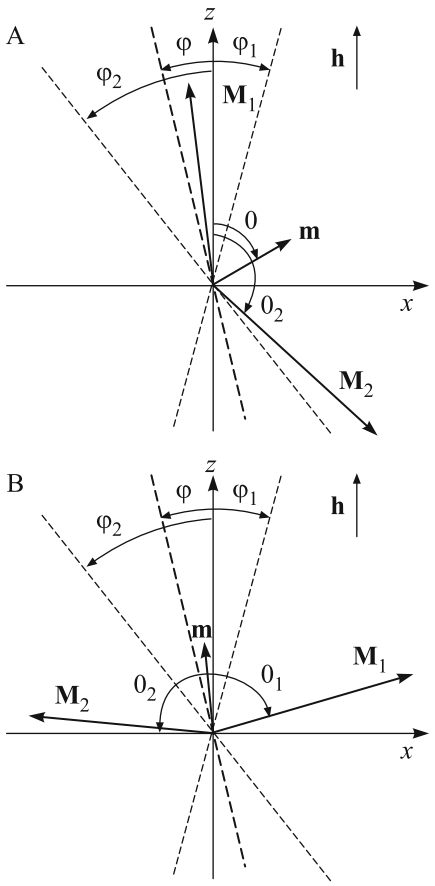

Fig. 1. Orientations of the moments of antiferromagnetic sublattices and the total magnetic moment in two different states. At the angle between the easy axes of the sublattices $\delta < \pi/4$, states A and B dominate at $h < h_{sf}$ and $h > h_{sf}$, respectively.

for state B,

$$m = \frac{-KC(2\delta)S(2(\theta-\varphi)) + \Delta S(2\delta)C(2(\theta-\varphi))}{hS(\theta) - 2h_a}, \quad (5)$$
$$m = \frac{hC(\theta) - KS(2\delta)C(2(\theta-\varphi)) + \Delta C(2\delta)S(2(\theta-\varphi))}{2\tilde{h}_e}.$$

Here, $\tilde{h}_e = h_e + KC(2\delta)C(2(\theta-\varphi)) + \Delta S(2\delta)S(2(\theta-\varphi))$ is the exchange field modulated by the anisotropy field and $h_a = KS(2\delta)S(2(\theta-\varphi)) + \Delta C(2\delta)C(2(\theta-\varphi))$ is the anisotropy field component transverse to the weak moment.

First, it is noteworthy that the single-ion contribution

$$m_I = \pm\frac{-KS(2\delta)C(2(\theta-\varphi)) + \Delta C(2\delta)S(2(\theta-\varphi))}{2\tilde{h}_e} \quad (6)$$

to the total relative magnetization is a periodic function of both the angle 2θ and the noncollinearity parameter of the axes of anisotropy 2δ. Consequently, this contribution periodically changes sign, which is characteristic of not only the tetragonal crystal [1] but also other weak ferromagnets with the noncollinear axes of anisotropy [2] and/or different magnitudes of anisotropy at different positions. In Eq. (6), the upper and lower signs correspond to states A and B, respectively. The dependence of the total moment angle θ on the external field h in the general case of arbitrary values K, Δ, δ, and the crystal orientation angle φ can be obtained from the equality of the right-hand sides of Eqs. (4) and (5) for states A and B, respectively.

In the single-position antiferromagnet ($\Delta = 0$), the average orientation angle of the anisotropy axes φ and the orthogonal direction become odd second-order axes, which corresponds to a rhombic crystal. In the absence of the external magnetic field, each of the systems (4) and (5) has two solutions

$$S(2(\theta-\varphi)) = 0: \quad \theta = \varphi, \quad \theta = \varphi + \pi/2,$$

whose stability depends on the sign of $C(2\delta)$. At $\delta < \pi/4$, the average easy axis is the φ axis along which the vector **l** is oriented. Correspondingly, the ground state is state A with $\theta = \varphi + \pi/2$ and the positive single-ion weak moment

$$m_I^{A}(h=0) = -\frac{KS(2\delta)}{2(h_e - KC(2\delta))}. \quad (7)$$

At $\delta > \pi/4$, the average easy axis becomes the $\varphi + \pi/2$ axis and state B with $\theta = \varphi$ becomes the ground state. The single-ion moment remains positive:

$$m_I^{B}(h=0) = -\frac{KS(2\delta)}{2(h_e + KC(2\delta))}. \quad (8)$$

In both cases, single-ion anisotropy increases the exchange field because the direction of the average anisotropy field coincides with the antiferromagnetism vector.

In a low magnetic field for $\delta < \pi/4$, the moment **m** in state A is rotated toward the direction of the magnetic field. In this case, both the angle θ and the spontaneous moment m_I given by Eq. (6). The spontaneous moment vanishes at the angle $\theta = \varphi + \pi/4$. The same behavior occurs at a decrease in the field from high values, where the ground state is state B. However, the spontaneous moment in different states vanishes at different magnetic fields $h_c^{A,B}$

$$h_c^{A,B} = \mp\frac{2KS(2\delta)C(\varphi+\pi/4)}{C(2\varphi)} + \sqrt{\left(\frac{2KS(2\delta)C(\varphi+\pi/4)}{C(2\varphi)}\right)^2 - \frac{4h_eKC(2\delta)}{C(2\varphi)}}. \quad (9)$$

Here, the upper and lower signs of the first term correspond to the critical field in states A and B, respectively. Thus, the field at which the spontaneous moment in state A vanishes exceeds the corresponding field for state B, which indicates that the field depen-

dence of m_I has hysteresis. When the anisotropy axes are collinear ($\delta = 0$) and the external field is oriented along the second-order axis ($\varphi = 0$), Eq. (9) gives the spin-flop transition field in the easy-axis two-sublattice antiferromagnet in the form

$$h_{sf} \approx \sqrt{-4h_e KC(2\delta) + 2K^2S^2(2\delta)}. \quad (10)$$

The analysis of the stability of states A and B at $\varphi = 0$ shows that state A is stable in the field range $0 \le h \le h_c^A$, whereas state B is stable at $h \ge h_c^B$. The energy of state A in the field h_c^A is already higher than the energy of state B with $\theta = 0$ in the same field. In turn, state A is the ground state at $h = h_c^B$. Thus, the transition between states A and B occurs near the spin-flop transition field h_{sf} (10) and is accompanied by hysteresis in the field range $\Delta h \propto h_c^A - h_c^B$ (Fig. 2). This range is determined by the region of stability of both states near a change in the relation between their energies and, therefore, is an estimate.

The application of the field orthogonal to the common easy axis (φ in Fig. 1) is equivalent to the change $\delta \to \pi/2 - \delta > \pi/4$ and state B with $\theta = \varphi = 0$ remains the ground state at any field. In this case, the field dependence of the magnetization is a straight line with the spontaneous moment m_I^B given by Eq. (8) (the dashed line in Fig. 2). If the orientation of the common easy axis does not coincide with the direction of the external magnetic field ($\varphi \ne 0$), the magnetic moment in state B above the spin-flop transition field will be oriented between the axis of anisotropy φ and the direction of the external field, asymptotically approaching the latter at $h \to \infty$. In this case, the phase transition remains a first-order transition with hysteresis, which is its characteristic difference from the spin-flop transition in an antiferromagnet without weak moment [2].

For the two-position antiferromagnet ($\Delta \ne 0$), the field dependence of the ferromagnetic moment is fundamentally different from a similar dependence for the single-position case. In the latter case, the crystal in the state after the spin-flop transition can always be oriented so that the numerator and denominator in the first equation of the system (for $\delta < \pi/4$, Eq. (5)) vanish at $\theta = 0$. Such an orientation corresponds to the field-aligned common axis of anisotropy ($\varphi = 0$). The degeneracy of the system of equations to the single second equation ensures the independence of the single external parameter h from the fixed angle θ. In the general case, such an orientation cannot be chosen for a two-position antiferromagnet because different functions in the numerator and denominator of the first equation cannot vanish simultaneously. This can

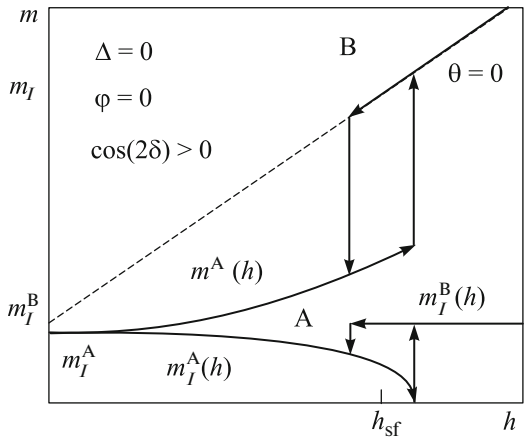

Fig. 2. Field dependence of the total magnetic moment m and the spontaneous single-ion contribution m_I at $\delta < \pi/4$ in states A and B before and after the spin-flop transition, respectively.

be easily verified if the equation is represented in the form

$$m = \frac{rS(2(\theta - \varphi) + \eta)}{hS(\theta) - 2\rho S(2(\theta - \varphi) + \gamma)}, \quad (11)$$

where

$$r = \sqrt{K^2C^2(2\delta) + \Delta^2S^2(2\delta)},$$
$$\rho = \sqrt{K^2S^2(2\delta) + \Delta^2C^2(2\delta)},$$
$$S(\eta) = \frac{\Delta S(2\delta)}{r}, \quad C(\eta) = -\frac{KC(2\delta)}{r},$$
$$S(\gamma) = \frac{\Delta C(2\delta)}{\rho}, \quad C(\gamma) = \frac{KS(2\delta)}{\rho}.$$

Since additional phase shifts at $\Delta \ne 0$ are different ($\eta \ne \gamma$), the system of equations describing the dependence of the angle θ on h includes both equations at any orientation of the crystal. This means that each field provides an individual orientation of the total ferromagnetic moment different from the direction of the field. Consequently, within the two-sublattice model of the two-position antiferromagnet, a linear dependence $m(h)$ is absent at any orientation of the crystal with respect to the external magnetic field.

Within the two-sublattice model of the two-position antiferromagnet $Pb_2Fe_2Ge_2O_9$ [9], the authors of [10] attempted to describe the field dependences of the magnetization using the expansion of the thermodynamic potential. They explained the weak ferromagnetism of the magnet by the single-ion mechanisms. According to the calculations reported above, the spin-flop transition in this case is a first-order phase transition and should be accompanied by the hysteresis of magnetization in the field dependence. However, the experimental magnetization curve near the

transition has the form of two second-order transitions, which is characteristic of the dominance of the two-ion Dzyaloshinskii–Moriya interaction [2]. Furthermore, the weak ferromagnetic moment extrapolated to $h = 0$ from the high-field part of the magnetization curve (above the spin-flop transition) is almost twice as high as the value obtained from the low-field part. The difference between weak moment values is characteristic of the situation where both mechanisms contribute [2]. In this case, at the dominant role of the Dzyaloshinskii–Moriya interaction, the moments for the orthogonal orientations of the antiferromagnetism vector will have the form

$$m_a \propto \frac{d_{12} - d_1}{A}, \quad m_c \propto \frac{d_{12} + d_1}{A}, \tag{12}$$

where d_{12} and d_1 are the parameters of the expansion of the potential corresponding to two- and single-ion mechanisms, respectively, and A is the exchange field. At $d_{12} > d_1$, the total spontaneous moment given by Eq. (12) remains positive without the reversal of the antiferromagnetism vector; i.e., the spin-flop transition becomes continuous. It is convenient to apply a more realistic four-sublattice model to the detailed analysis of the field dependences obtained in [10]. When analyzing the magnetic properties of weak ferromagnets, information necessary for estimating the contribution of the single-ion mechanism and anisotropy of the g-factors to the total spontaneous moment can be obtained by analyzing single-ion EPR spectra of magnetic ions in both crystallographically nonequivalent positions in a diamagnetic analog of a magnetic compound.

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