QUANTUM THEORY OF MAGNETIC DIELECTRICS WITH WEAK SINGLE-ION ANISOTROPY

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We developed a microscopic quantum theory of spin configurations, spin-orientation phase transitions, and spin excitations in tetragonal antiferromagnetic dielectrics with the Dzyaloshinskii interaction of the single-ion origin. It is shown that the AFMR frequencies do not cross in the oblique non-symmetric phase and repulse one another just to the extent of a value of the Dzyaloshinskii constant. Experimental data available for antiferromagnetic iron fluoride are discussed.

1. Introduction

As is known, the magnetization in ferromagnetic crystals or the magnetic moment of a sublattice in antiferromagnetic or ferrimagnetic crystals are formed due to a spontaneous symmetry breakdown via a phase transformation. In this case, the system passes to a state, whose symmetry is lower than that of the Hamiltonian. As a rule, the broken symmetry in magnets is discrete due to the presence of finite-order anisotropy magnetic axes in them. But even such an anisotropy does not give a possibility to establish the exact direction of the magnetic vector on the whole, as two (or more) of its directions in space are always equivalent, which results in the appearance of a domain structure. In order to describe theoretically the homogeneous (single-domain) samples and to fix a certain direction of the magnetic order parameter in them, Bogolyubov proposed the so-called *method of quasiaverages* [1]. It consists in the *a priori* assumption about the existence of a weak speculative magnetic field that directly breaks the symmetry of the Hamiltonian of the system (including the anisotropic one). This Bogolyubov's assumption actually coincides with that about a finite and crystal-uniform average spin $\mathbf{s}$ at a site that is found as a self-consistent quantum-mechanical quantity. In turn, its finiteness specifies the finite value of the magnetization that forms a bare field in the Bogolyubov's approach, whose direction is determined, as a rule, by the magnetic anisotropy. If the last is of single-ion (or, to be more precise, spin-orbit (see [2])) origin, then it turns out that $|\mathbf{s}| \equiv s \leq S$, where S is the initial spin of the paramagnetic ion regardless of the dimension of a system.

This quantum approach (in contrast to the widespread phenomenological one) became especially popular for magnetic systems with a large contribution of the spin-orbit interaction or the strong single-ion anisotropy, starting from the work by Ostrovskii and the author [3] presenting the exact solution of a self-consistent (one-site) problem in the case of systems with $S = 1$ at the ion and an arbitrary relation between the magnitudes of exchange interaction, single-ion anisotropy, and external magnetic field. The subsequent studies [4–13] were devoted to the comprehensive investigation of linear and nonlinear properties of various magnetic systems for both zero and finite temperatures, the determination of the critical fields of phase transitions not only between different magnetic phases, but also between magnetic (Néel) and nonmagnetic (so-called singlet) phases, and the consideration of real compounds. At the same time, no exact self-consistent solutions for arbitrary values of S were obtained. As the majority of magnets still represent magnetic systems with relatively weak single-ion anisotropy, we will try to consider a self-consistent quantum problem for an arbitrary spin on the basis of perturbation theory.

In order to make our calculations specific, we focus on a rather representative group of crystals, namely tetragonal antiferromagnetic dielectrics. Among them, there

are two-sublattice MeF_2 crystals (Me=Mn, Fe, Co, Ni) with odd (according to Turov [14]) antiferromagnetic structure rather well investigated by means of static, resonance, optical, and magnetooptical methods. In spite of the presence of an axis of rather high order, C_4, the local symmetry of magnetic ions in these compounds is relatively low – D_{2h}, which results in a number of specific peculiarities which distinguish these crystals from purely uniaxial or biaxial ones. The space symmetry D_{4h}^{14} of these antiferrodielectrics admits the presence of the invariant $m_X l_X - m_Y l_Y$ in their thermodynamic potential which is called the Dzyaloshinskii interaction. In this case, the axes X and Y are chosen in the basal plane, the axis $Z \parallel C_4$, and the vectors $\mathbf{m}$ and $\mathbf{l}$ are the phenomenological vectors of ferro- and antiferromagnetism of the magnetic structure. It is important that the Dzyaloshinskii interaction presented in terms of ion spin operators assumes the form of the operator of single-ion anisotropy that requires a special attention as will be shown in what follows. It is also worth noting that the constant of single-ion anisotropy in NiF_2, MnF_2, and FeF_2 crystals can be considered small as compared with that of exchange interaction, which makes the use of perturbation theory justified.

The Dzyaloshinskii interaction fundamentally influences the behavior of a spin subsystem in the external magnetic field – for example, makes possible a continuous spin-flop transition and changes the field dependence of the resonance frequencies [15–19]. The observed effects were investigated in the framework of the phenomenological (or quasiclassical) theory [14,20] that, strictly speaking, is valid only under the condition of the inter-ion character of the magnetic anisotropy (it can be caused by both spin-orbit and dipole-dipole interaction). If the anisotropy is induced by spin-orbit coupling and thus has a local (or single-ion) character, then the criteria of application of the phenomenological approach require additional verification.

The present work was carried out on account of the hundredth anniversary of the birthday of the outstanding mathematician and physicist-theorist M.M. Bogolyubov, whose contribution into a number of fields of theoretical physics, in particular, the physics of magnetic phenomena (let us also recall the Bogolyubov–Tyablikov transformations in the theory of antiferromagnetism) is impossible to overestimate.

2. Hamiltonian and Single-Ion Problem

Fluorides of transition metals are thought of as uniaxial antiferrodielectrics [14], whose paramagnetic ions are located in the crystal field with rhombic local symmetry. That is why the model spin-Hamiltonian of such crystals can be presented in the form

$$H = \sum_{\mathbf{n}\alpha} \left(H_{\mathbf{n}\alpha}^{(an)} + H_{\mathbf{n}\alpha}^{(Z)} \right) +$$

$$+ \frac{1}{2} \sum_{\mathbf{n}\alpha,\mathbf{m}\beta} \Big[J_{\mathbf{n}\alpha\mathbf{m}\beta} \mathbf{S}_{\mathbf{n}\alpha} \mathbf{S}_{\mathbf{m}\beta} + \Delta J_{\mathbf{n}\alpha\mathbf{m}\beta} S_{\mathbf{n}\alpha}^Z S_{\mathbf{m}\alpha}^Z +$$

$$+ J_{\mathbf{n}\alpha\mathbf{m}\beta}^D \delta_{\alpha\beta} (S_{\mathbf{n}\alpha}^X S_{\mathbf{m}\beta}^X - S_{\mathbf{n}\alpha}^Y S_{\mathbf{m}\beta}^Y) \Big], \quad (1)$$

where

$$H_{\mathbf{n}\alpha}^{(Z)} = -\mu_B g H S_{\mathbf{n}\alpha}^Z$$

is the operator of Zeeman energy, in which $\mathbf{H}$ denotes the external field, $\mathbf{S}_{\mathbf{n}\alpha}$ is the operator of the spin in the $\mathbf{n}$-th cell of the α-th (α =1, 2) magnetic sublattice, μ_B is the Bohr magneton, g is the g-factor of the ion; and

$$H_{\mathbf{n}\alpha}^{(an)} = D(S_{\mathbf{n}\alpha}^Z)^2 + E_\alpha [(S_{\mathbf{n}\alpha}^X)^2 - (S_{\mathbf{n}\alpha}^Y)^2], \quad (2)$$

stands for the operator of single-ion anisotropy, where $E_\alpha \equiv (-1)^\alpha E$, which explicitly allows for a specific point group of the tetragonal lattice of fluorides. It does not include the terms proportional to higher degrees of spin operators, as the corresponding parameters are too small in the case of weakly anisotropic systems; in addition, such terms are absent at all in operators (2) at S =1 or 3/2. It is also worth noting that almost all the results presented below (for example, solution of the self-consistent problem, longitudinal magnetic susceptibility, *etc.*) are also valid for purely biaxial crystals, where $E_\alpha = E$. Hamiltonian (1) also allows for the anisotropy of the exchange interaction $\Delta J_{\mathbf{n}\alpha\mathbf{m}\beta}$. For the sake of comparison with the conclusions of the quasiclassical theory, it also takes into account the intra-sublattice exchange anisotropy with the constant $J_{\mathbf{n}\alpha\mathbf{m}\alpha}^D = (-1)^\alpha J_{\mathbf{nm}}^D$ that formally plays the same role as the Dzyaloshinskii interaction constant E but is of interion nature.

It is convenient to perform the further calculations in proper coordinate systems introduced according to the transformation

$$\begin{pmatrix} S_{\mathbf{n}\alpha}^X \\ S_{\mathbf{n}\alpha}^Y \\ S_{\mathbf{n}\alpha}^Z \end{pmatrix} = \hat{R}_{\mathbf{n}\alpha} \begin{pmatrix} S_{\mathbf{n}\alpha}^\xi \\ S_{\mathbf{n}\alpha}^\eta \\ S_{\mathbf{n}\alpha}^\zeta \end{pmatrix},$$

where the matrix of local rotation $\hat{R}_{\mathbf{n}\alpha}$ has the form

$$\hat{R}_{\mathbf{n}\alpha} = \begin{pmatrix} \frac{\sqrt{2}}{2}(\cos\varphi_\alpha - \sin\varphi_\alpha)\cos\vartheta_\alpha & -\frac{\sqrt{2}}{2}(\cos\varphi_\alpha + \sin\varphi_\alpha) & \frac{\sqrt{2}}{2}(\cos\varphi_\alpha - \sin\varphi_\alpha)\sin\vartheta_\alpha \\ \frac{\sqrt{2}}{2}(\cos\varphi_\alpha + \sin\varphi_\alpha)\cos\vartheta_\alpha & \frac{\sqrt{2}}{2}(\cos\varphi_\alpha - \sin\varphi_\alpha) & \frac{\sqrt{2}}{2}(\cos\varphi_\alpha + \sin\varphi_\alpha)\sin\vartheta_\alpha \\ -\sin\vartheta_\alpha & 0 & \cos\vartheta_\alpha \end{pmatrix},$$

where the angle φ_α is counted off from the [110] axis, while ϑ_α – from the [001] one. The independence of rotations on the site leaves the system translation-invariant and gives a possibility to represent the spin Hamiltonian (1) in the form

$$H = \sum_{\mathbf{n}\alpha} H_{\mathbf{n}\alpha} + V + \text{const}, \tag{3}$$

where we separated the single-ion

$$H_{\mathbf{n}\alpha} = H^{(0)}_{\mathbf{n}\alpha} + v_{\mathbf{n}\alpha}, \quad H^{(0)}_{\mathbf{n}\alpha} = -H^\zeta_\alpha S^\zeta_{\mathbf{n}\alpha} \tag{4}$$

and inter-ion V parts (the operator V will be given below). In these expressions, we introduced the following notations for the term

$$v_{\mathbf{n}\alpha} =$$

$$= -D(\varphi_\alpha;\vartheta_\alpha)(S^\zeta_{\mathbf{n}\alpha})^2 - E(\varphi_\alpha;\vartheta_\alpha)[(S^\xi_{\mathbf{n}\alpha})^2 - (S^\eta_{\mathbf{n}\alpha})^2] -$$

$$-\Big[F_{\xi\eta}(\varphi_\alpha;\vartheta_\alpha)S^\xi_{\mathbf{n}\alpha}S^\eta_{\mathbf{n}\alpha} + F_{\xi\zeta}(\varphi_\alpha;\vartheta_\alpha)S^\xi_{\mathbf{n}\alpha}S^\zeta_{\mathbf{n}\alpha} +$$

$$+F_{\eta\zeta}(\varphi_\alpha;\vartheta_\alpha)S^\eta_{\mathbf{n}\alpha}S^\zeta_{\mathbf{n}\alpha} + \text{h.c.}\Big] - H^\xi_\alpha S^\xi_{\mathbf{n}\alpha} - H^\eta_\alpha S^\eta_{\mathbf{n}\alpha}, \tag{5}$$

that will be considered as a perturbation in what follows, as well as

$$H^\zeta_\alpha = \mu_B g H\cos\vartheta_\alpha - Js_\alpha - \Delta J s_\alpha\cos^2\vartheta_\alpha -$$

$$-Is_\beta\cos(\varphi_\alpha - \varphi_\beta)\sin\vartheta_\alpha\sin\vartheta_\beta -$$

$$-(I+\Delta I)s_\beta\cos\vartheta_\alpha\cos\vartheta_\beta + J^D_\alpha s_\alpha\sin 2\varphi_\alpha\sin^2\vartheta_\alpha;$$

$$H^\xi_\alpha = \Delta J s_\alpha\sin\vartheta_\alpha\cos\vartheta_\alpha + (I+\Delta I)s_\beta\sin\vartheta_\alpha\cos\vartheta_\beta -$$

$$-Is_\beta\cos(\varphi_\alpha - \varphi_\beta)\cos\vartheta_\alpha\sin\vartheta_\beta +$$

$$+J^D_\alpha s_\alpha\sin 2\varphi_\alpha\sin\vartheta_\alpha\cos\vartheta_\alpha - \mu_B g H\sin\vartheta_\alpha; \tag{6}$$

$$H^\eta_\alpha = Is_\beta\sin(\varphi_\alpha - \varphi_\beta)\sin\vartheta_\beta + J^D_\alpha s_\alpha\cos 2\varphi_\alpha\sin\vartheta_\alpha,$$

where $\alpha \neq \beta$, and

$$D(\varphi_\alpha;\vartheta_\alpha) =$$

$$= \frac{1}{2}\left[(D - 3E_\alpha\sin 2\varphi_\alpha) - 3(D - E_\alpha\sin 2\varphi_\alpha)\cos^2\vartheta_\alpha\right];$$

$$E(\varphi_\alpha;\vartheta_\alpha) =$$

$$= \frac{1}{2}\left[(D + E_\alpha\sin 2\varphi_\alpha) - (D - E_\alpha\sin 2\varphi_\alpha)\cos^2\vartheta_\alpha\right]; \tag{7}$$

$$F_{\xi\eta}(\varphi_\alpha;\vartheta_\alpha) = E_\alpha\cos 2\varphi_\alpha\cos\vartheta_\alpha;$$

$$F_{\eta\zeta}(\varphi_\alpha;\vartheta_\alpha) = E_\alpha\cos 2\varphi_\alpha\sin\vartheta_\alpha;$$

$$F_{\xi\zeta}(\varphi_\alpha;\vartheta_\alpha) = -\frac{1}{2}(D - E_\alpha\sin 2\varphi_\alpha)\sin 2\vartheta_\alpha;$$

and finally,

$$\text{const} = -\frac{1}{2}\sum_{\mathbf{n}\alpha,\mathbf{m}\beta}\Big[J_{\mathbf{n}\alpha\mathbf{m}\beta}s_\alpha s_\beta\cos(\varphi_\alpha - \varphi_\beta)\times$$

$$\times\sin\vartheta_\alpha\sin\vartheta_\beta + (J_{\mathbf{n}\alpha\mathbf{m}\beta} + \Delta J_{\mathbf{n}\alpha\mathbf{m}\beta})\times$$

$$\times s_\alpha s_\beta\cos\vartheta_\alpha\cos\vartheta_\beta\Big] + \frac{1}{2}\sum_{\mathbf{n}\alpha,\mathbf{m}} J^D_{\mathbf{n}\alpha\mathbf{m}\alpha}s^2_\alpha\sin 2\varphi_\alpha\times$$

$$\times\sin^2\vartheta_\alpha - \frac{1}{2}S(S+1)\sum_{\mathbf{n}\alpha}(D - E_\alpha\sin 2\varphi_\alpha)\sin^2\vartheta_\alpha; \tag{8}$$

$$\left\{ \begin{array}{c} I \\ \Delta I \end{array} \right\} = \frac{1}{2} \sum_{\mathbf{m}\beta,\alpha} (1-\delta_{\alpha\beta}) \left\{ \begin{array}{c} J_{\mathbf{0}\alpha\mathbf{m}\beta} \\ \Delta J_{\mathbf{0}\alpha\mathbf{m}\beta} \end{array} \right\};$$

$$\left\{ \begin{array}{c} J \\ \Delta J \end{array} \right\} \equiv \frac{1}{2} \sum_{\mathbf{m}\beta,\alpha} \delta_{\alpha\beta} \left\{ \begin{array}{c} J_{\mathbf{0}\alpha\mathbf{m}\beta} \\ \Delta J_{\mathbf{0}\alpha\mathbf{m}\beta} \end{array} \right\};$$

$$J^D_\alpha = (-1)^\alpha J_D; \quad J_D = \sum_{\mathbf{m}} J_{0\alpha\mathbf{m}\alpha}.$$

In the last notations, we used the spin moment s_α at each site of the α-th magnetic sublattice determined by calculating the quantum-mechanical averages on the functions of the ground state of the single-ion operator $H_{\mathbf{n}\alpha}$ (see (4)). They will be searched for with the help of perturbation theory by operator (5). In the standard way, we obtain that the solution of the Schrödinger equation to within the second order has the form [21]

$$\Psi^{(S-M_S)}_{\mathbf{n}\alpha}(S;M_S) = \left[1 - \frac{1}{2}\sum_{M'_S} \frac{|v_{\mathbf{n}\alpha}(M'_S;M_S)|^2}{[\varepsilon_\alpha(M_S)-\varepsilon_\alpha(M'_S)]^2}\right] \times$$

$$\times |M_S\rangle_{\mathbf{n}\alpha} + \sum_{M'_S} \frac{v_{\mathbf{n}\alpha}(M'_S,M_S);}{\varepsilon_\alpha(M_S)-\varepsilon_\alpha(M'_S)} |M'_S\rangle_{\mathbf{n}\alpha} +$$

$$+ \sum_{M'_S,M''_S} \frac{v_{\mathbf{n}\alpha}(M'_S,M''_S)v_{\mathbf{n}\alpha}(M''_S;M_S);}{[\varepsilon_\alpha(M_S)-\varepsilon_\alpha(M'_S)][\varepsilon_\alpha(M_S)-\varepsilon_\alpha(M''_S)]} \times$$

$$\times |M'_S\rangle_{\mathbf{n}\alpha} - \sum_{M'_S} \frac{v_{\mathbf{n}\alpha}(M_S;M_S)v_{\mathbf{n}\alpha}(M'_S;M_S)}{[\varepsilon_\alpha(M_S)-\varepsilon_\alpha(M'_S)]^2} |M'_S\rangle_{\mathbf{n}\alpha}, \quad (9)$$

where $v_{\mathbf{n}\alpha}(M'_S;M_S)$ denote the matrix elements of operator (5) on the eigenfunctions $|M_S\rangle_{\mathbf{n}\alpha}$ of the operator $S^\zeta_{\mathbf{n}\alpha}$. Moreover, $|M_S| < S$, whereas $\varepsilon_\alpha(M_S)$ stand for the corresponding energies of the zero-order operator $H^{(0)}_{\mathbf{n}\alpha}$ (see (4)). In this case, function (9) for $M_S = S$ corresponds to the ground single-ion state. In order to determine the angles φ_α and ϑ_α, it is necessary to impose the conditions of the absence of transverse spin projections in proper (local) coordinate systems in the ground state, namely:

$$\langle \Psi^{*(0)}_{\mathbf{n}\alpha}(S;S)|S^{\xi,\eta}_{\mathbf{n}\alpha}|\Psi^{(0)}_{\mathbf{n}\alpha}(S;S)\rangle = 0. \quad (10)$$

On the other hand, these conditions actually represent the definitions of the proper coordinate system for each of the magnetic ions. In the case of the explicit use of functions (9), equalities (10) yield the equations

$$v_{\mathbf{n}\alpha}(S-1;S)\left[1 - \frac{v_{\mathbf{n}\alpha}(S-1;S-1)}{H^\zeta_\alpha}\right] =$$

$$= \frac{v_{\mathbf{n}\alpha}(S-2;S)}{2H^\zeta_\alpha}\Big[v_{\mathbf{n}\alpha}(S-1;S-2) +$$

$$+ \sqrt{\frac{2S-1}{S}} v^*_{\mathbf{n}\alpha}(S-1;S)\Big], \quad (11)$$

which determines the spin configurations to within the second order in operator (5). From Eq. (11), one can also see that the diagonal matrix elements $v_{\mathbf{n}\alpha}(M_S;M_S)$ actually determine the third-order corrections and should be omitted in order to maintain the specified accuracy.

The analysis demonstrates that the first-approximation equations

$$v_{\mathbf{n}\alpha}(S-1;S) = 0 \quad (12)$$

completely coincide with the quasiclassical ones usually obtained from the minimization of the energy of an antiferrodielectric as a function of the classic magnetization vectors of sublattices [14,20] in the case where the single-ion anisotropy can be replaced by the anisotropy field. The second-order equation is obtained from (11), by using the first-order expression for $v_{\mathbf{n}\alpha}(S-1;S)$, and has the form

$$2H^\zeta_\alpha v_{\mathbf{n}\alpha}(S-1;S) = v_{\mathbf{n}\alpha}(S-2;S)v_{\mathbf{n}\alpha}(S-1;S-2). \quad (13)$$

Equations (13) remain incomplete, as they include the unknown quantities s_α. Just their determination from the self-consistence equations first given in [22] in the course of investigations of biaxial antiferrodielectrics completes the solution of the single-ion problem:

$$s_\alpha = \langle \Psi^{*(0)}_{\mathbf{n}\alpha}(S;S)|S^\zeta_{\mathbf{n}\alpha}|\Psi^{(0)}_{\mathbf{n}\alpha}(S;S)\rangle =$$

$$= S\left[1 - \frac{2S-1}{2}\frac{E^2(\varphi_\alpha;\vartheta_\alpha) + F^2_{\xi\eta}(\varphi_\alpha;\vartheta_\alpha)}{(H^\zeta_\alpha)^2}\right]. \quad (14)$$

It is worth emphasizing that the quantity $\Delta s_\alpha \equiv S - s_\alpha$ characterizing the reduction of the average spin at a site is of second order and depends only on the constants of single-ion anisotropy. In addition, it is easy to ascertain that the relative reduction $\Delta s_\alpha/S \sim 1/S$, i.e. it coincides with the increase of S, which agrees with the well-known criterion of applicability of the quasiclassical approach in the theory of magnetism $S \gg 1$ [20].

3. Spin Configurations and Lability Fields

In the first approximation (where $s_\alpha = S$), Eqs. (12) that specify the desired spin configurations have the form

$$-\frac{2S-1}{2}(D - E_\alpha \sin 2\varphi_\alpha)\sin 2\vartheta_\alpha + (I + \Delta I)\times$$

$$\times S \sin\vartheta_\varepsilon \cos\vartheta_\beta - IS\cos(\varphi_\alpha - \varphi_\beta)\cos\vartheta_\alpha \sin\vartheta_\beta +$$

$$+\frac{1}{2}(\Delta IS + J^D_\alpha S \sin 2\varphi_\alpha)\sin 2\vartheta_\alpha - \mu_B g H \sin\vartheta_\alpha = 0; \quad (15)$$

$$[(2S-1)E_\alpha - J^D_\alpha S]\cos 2\varphi_\alpha \sin\vartheta_\alpha +$$

$$+IS\sin(\varphi_\alpha - \varphi_\beta)\sin\vartheta_\beta = 0, (\alpha \neq \beta).$$

Their solutions were analyzed in [15] (see also [14]), and we do not discuss them. It is only worth noting that the quantum-mechanical approach results only in the redetermination of the values of anisotropic interactions and automatically excludes the single-ion anisotropy from the calculations, if the ion spin S =1/2. The solutions of the quasiclassical equations (15) are given by the following spin configurations: *i*) collinear – $\varphi_\alpha = 0$, $\vartheta_1 = 0$, $\vartheta_2 = \pi$; *ii*) oblique – $\varphi_\alpha = \pi/4$; $\vartheta_1 \neq \vartheta_2 \neq 0$; *iii*) spin-flop – $\sin 2\varphi_\alpha = (-1)^\alpha \sin 2\varphi_D$, $\vartheta_1 = -\vartheta_2 \equiv \vartheta \neq 0$, where

$$\sin 2\varphi_D = \frac{[(2S-1)E + J_D]}{\sqrt{(IS)^2 + [(2S-1)E + J_D]^2}};$$

and *iv*) ferromagnetic – $\vartheta_\alpha = 0$.

The lability field H_l of the collinear phase is determined by the expression

$$\mu_B g H_l = \Big\{[(\Delta I + \Delta J)S + (2S-1)D]\times$$

$$\times[(2I + \Delta I - \Delta J)S + (2S-1)D]\Big\}^{1/2}, \quad (16)$$

and the spin-flip filed $H_{\mathrm{s-f}}$ –

$$\mu_B g H_{\mathrm{s-f}} = (I + \Delta I + \Delta J)S - (2S-1)D +$$

$$+\sqrt{(IS)^2 + [(2S-1)E + J_D]^2}. \quad (17)$$

An interesting peculiarity of the solutions of system (15) consists in the fact that the turn plane of the antiferromagnetic vector **l** appears to be the [010] plane, i.e. the plane "easy" for the spins directed against the field and thus "hard" for those directed along the external field (see (2)). The kind of a magnetic phase transformation from the collinear phase to the oblique one can be found from the solution of system (15) for small angles:

$$\left(\frac{\pi - \vartheta_1 - \vartheta_2}{2}\right)^2 = \mu_B g(H - H_l)\Big\{2[(2S-1)E + J_D S] +$$

$$+2\frac{[\Delta JS + (2S-1)D][(\Delta I - \Delta J)S + (2S-1)D]}{\mu_B g H_l + (2S-1)E + J_D S}\Big\}^{-1}.$$

It is worth noting that, in the absence of the single-ion anisotropy, the last formula is exact; it directly implies that if $(2S-1)E > \Delta JS$, then there exists a critical value of $(2S-1)E + J_D S$ that ensures the continuity (or the second order) of the transition from the collinear phase to the oblique one. Otherwise ($(2S-1)E < \Delta JS$), the transition will always be jump-like, which coincides with the result obtained in [14] for purely uniaxial antiferrodielectrics, for which one should set $(2S-1)E + J_D S = 0$ in the above-given formulas.

Now let us consider the changes induced by the allowance for quantum corrections in the equations for spin configurations. For the sake of simplicity, yet without loss of generality, we assume that $\Delta I = \Delta J = J_D = 0$ and put down the equation corresponding to a plane turn ($\varphi_\alpha = \pi/4$) as

$$\frac{2S-1}{2}(D - E_\alpha)\sin 2\vartheta_\alpha - Is_\beta \sin(\vartheta_\alpha - \vartheta_\beta) +$$

$$+\mu_B g H \sin\vartheta_\alpha = \frac{2S-1}{2H^\zeta_\alpha}(D - E_\alpha)E_\alpha \sin 2\vartheta_\alpha.$$

Its analysis demonstrates that the most pronounced variations take place in the collinear structure. Remaining antiferromagnetic, it differs from the quasiclassical structure in that $s_1 \neq s_2$ now, and

$$s_1 - s_2 = \chi_\parallel \mu_B g H; \quad \chi_\parallel = \frac{2S(S-1)}{S^3}\frac{E^2}{(I-J)^3}. \quad (18)$$

In other words, there appears a longitudinal magnetic susceptibility in the system that results in the induction of the ferrimagnetic phase; its lability field is determined by the expression

$$\mu_B g H_l = \sqrt{\Omega^2(0;0) + (2S-1)^2 E^2} - (2S-1)E;$$

$$\Omega(0;0) = \{(2S-1)D[2IS + (2S-1)D] -$$

$$-(2S-1)\frac{(2S-3)I-(2S-1)J}{I-J}E^2\Big\}^{1/2}. \qquad (19)$$

As will be seen below, the quantity $\Omega(0;0)$ specifies the frequency of uniform precession (or the AFMR frequency) in the absence of a field. The comparison of formulas (16) and (19) demonstrates that the corrections introduce the dependence on the exchange between the spins belonging to the same magnetic sublattice into the AFMR frequency and the lability field. It is not difficult to find the corrections to the field $H_{\rm s-f}$, but we shall not adduce here the corresponding formulas, as they actually duplicate the quasiclassical ones.

4. Phase Diagrams

The phase diagrams can be easily calculated from the comparison of the energies of the antiferromagnetic and weakly ferromagnetic spin configurations at $\mathbf{H}=0$. The ground state energy of the system under consideration can be presented in the form

$$E_{\rm gr} = {\rm const} + \sum_{\alpha}[e_{\alpha}^{(0)} - D(\varphi_{\alpha};\vartheta_{\alpha})S^2] \equiv E_{\rm cl} + \Delta E_{\rm quan}, \qquad (20)$$

where "const" is specified in (8), $D(\varphi_{\alpha};\vartheta_{\alpha})$ – in (7), whereas

$$e_{\alpha}^{(0)} = \langle\Psi_{\mathbf{n}\alpha}^{*(0)}(S;S)|H_{\mathbf{n}\alpha}|\Psi_{\mathbf{n}\alpha}^{(0)}(S;S)\rangle =$$

$$= H_{\alpha}^{\zeta}s_{\alpha} + \langle\Psi_{\mathbf{n}\alpha}^{*(0)}(S;S)|v_{\mathbf{n}\alpha}|\Psi_{\mathbf{n}\alpha}^{(0)}(S;S)\rangle$$

is the energy of the ground single-ion level. In such a representation, the quantity E_{cl} completely coincides with the classical energy, i.e. it does not depend on second-order corrections, while $\Delta E_{\rm quan} = -\sum\limits_{\alpha} H_{\alpha}^{\zeta}\Delta s_{\alpha}$, and thus it is completely determined by the quantum reduction of the magnetizations of sublattices specified by expression (14) and depends on the field.

Let us demonstrate that, even in the case of small single-ion anisotropy, the allowance for Δs_{α} can result in qualitative changes in the conclusions of the phenomenological theory which, as is known [14,20], states that the stable phase is the collinear antiferromagnetic one with $\mathbf{l} \parallel Z$ under the condition $DI > E^2$ and the symmetric spin-flop (or weakly ferromagnetic) phase with spins located in the XY plane and the angle $2\varphi_D$ between them for $DI < E^2$. Taking the second-order corrections into account, energies (20) of different spin configurations take the following form:

i) antiferromagnetic collinear phase –

$$E_0^{AFM} = -IS^2 - 2S^2D - (2S-1)\frac{E^2}{I};$$

ii) weakly ferromagnetic phase –

$$E_0^{WAF} = -IS^2 - SD - \frac{2S-1}{4}\frac{D^2}{I} - \frac{(2S-1)^2}{2}\frac{E^2}{I};$$

$$\varphi_D = \frac{\pi}{2} - {\rm arctg}\frac{2S-1}{S}\frac{E}{I}\left[1+\frac{1}{2S}\left(\frac{D}{I}+\frac{2S-1}{S}\frac{E^2}{I^2}\right)\right].$$

Comparing the presented energies, it is easy to find that the collinear spin configuration is stable under the condition $2SDI > (2S-3)E^2$. The last inequality qualitatively agrees with the conclusions of the quasiclassical theory starting from $S=2$. In this case, the antiferromagnetic phase for the spins $S=1$ and $S=3/2$ remains stable if $2DI > -E^2$, whereas, for $S=3/2$, the term with E^2 disappears at all, and it is necessary to consider the terms of higher orders. Crystals with the spin $S=3/2$ were specially studied in [23], where it was shown that, in this case, the collinear phase boundary is determined by a fourth-order parabola or, to be more precise, by the condition $DI^3 > E^4$. This result is explained by different spin "reductions" Δs_{α} in each of the structures, so that $\Delta s_{\alpha}^{AFM} \sim (E/I)^2$, and $\Delta s_{\alpha}^{WAF} \sim (D/I)^2,\ (E/I)^4$. As is known, at a sufficiently large single-ion anisotropy, the difference between the results of the quasiclassical and quantum theories becomes even more significant (see [3–8]).

It is also worth noting that there exists a possibility of the formation of one more weakly ferromagnetic phase – non-symmetric, in which $\mathbf{l} \parallel \mathbf{m} \parallel X$ (or Y), where (in the same way as above) $\mathbf{m}$ is the ferromagnetism vector. Here, the longitudinal moment is also caused by different spin reductions: $\Delta s_{1,2} = (2S-1)S^{-1}(D \pm E)^2/I^2$, i.e. $m \sim DE/I^2$, but it is easy to see that the energy of this phase $E_{0{\rm non-sym}}^{\rm WAF} = -IS^2 - SD - (2S-1)(D^2-E^2)/4I$ is always higher than the energy $E_0^{\rm WAF}$ of the symmetric weakly ferromagnetic phase.

5. Spin Wave Spectrum

As far as we know, in spite of the rather extensive data on AFMR and spin wave spectra in uniaxial and biaxial magnetic crystals with two sublattices [14,15,20,24], calculations of resonance properties of tetragonal antiferrodielectrics with the Dzyaloshinskii interaction are absent in the literature. At the same time, such information seems to be useful, as it enables the interpretation

of numerous experimental data. The corresponding consideration of spin wave energies will be performed with the use of the Hubbard operators [3,4,8] $B_{\mathbf{n}\alpha}$ and $B^{+}_{\mathbf{n}\alpha}$ that allow us to write the operators of spin projections as

$$S^{+}_{\mathbf{n}\alpha} = \sqrt{2S}(x_\alpha B_{\mathbf{n}\alpha} + y_\alpha B^{+}_{\mathbf{n}\alpha});$$

$$S^{\zeta}_{\mathbf{n}\alpha} - s_\alpha = \sqrt{2S} z_\alpha (B_{\mathbf{n}\alpha} + B^{+}_{\mathbf{n}\alpha}); \tag{21}$$

$$\left\{ \begin{array}{c} x_\alpha \\ y_\alpha \end{array} \right\} = \frac{1}{\sqrt{2S}} \langle \Psi^{*(0)}_{\mathbf{n}\alpha}(S;S) | S^{\pm}_{\mathbf{n}\alpha} | \Psi^{(1)}_{\mathbf{n}\alpha}(S;S-1) \rangle;$$

$$z_\alpha = \frac{1}{\sqrt{2S}} \langle \Psi^{*(0)}_{\mathbf{n}\alpha}(S;S) | S^{\zeta}_{\mathbf{n}\alpha} | \Psi^{(1)}_{\mathbf{n}\alpha}(S;S-1) \rangle,$$

where $\Psi^{(0)}_{\mathbf{n}\alpha}(S;S-1)$ is the function of the first excited state from collection (9). We note that the appearance of the quantity z_α which is finite due to the single-ion anisotropy in transformations (21) causes the dispersion of quasiparticles and determines the probability of transitions corresponding to the second excited state of ions, which is impossible in the framework of the phenomenological approach. However, the question about the excitation and properties of these states will not be considered here.

In representation (21), operator (4) is as follows:

$$H_{\mathbf{n}\alpha} = \varepsilon_\alpha B^{+}_{\mathbf{n}\alpha} B_{\mathbf{n}\alpha};$$

$$\varepsilon_\alpha = e^{(1)}_\alpha - e^{(0)}_\alpha = -(2S-1)D(\vartheta_\alpha) + H^{\zeta}_\alpha -$$

$$-2(2S-1)\frac{F^2(\vartheta_\alpha)}{H^{\zeta}_\alpha} - \frac{(2S-1)(2S-3)}{2}\frac{E^2(\vartheta_\alpha)}{H^{\zeta}_\alpha}. \tag{22}$$

In these formulas and below, we set $\varphi_\alpha = \pi/4$. Therefore, expressions (7) are transformed into $D(\vartheta_\alpha) = D(\pi/4;\vartheta_\alpha)$; $E(\vartheta_\alpha) = E(\pi/4;\vartheta_\alpha)$; $F(\vartheta_\alpha) = F_{\xi\zeta}(\pi/4;\vartheta_\alpha)$, a $F_{\xi\eta}(\pi/4;\vartheta_\alpha) = F_{\eta\zeta}(\pi/4;\vartheta_\alpha) = 0$.

After passing to the **k**-representation, the complete operator of the considered excited spin states of antiferrodielectrics in the harmonic approximation can be presented in the standard form as

$$H = \sum_{\mathbf{k}} \Bigg\{ \sum_{\alpha} [\varepsilon_\alpha + \Gamma_\alpha(\mathbf{k})] B^{+}_{\mathbf{k}\alpha} B_{\mathbf{k}\alpha} +$$

$$+ \frac{1}{2}[\Gamma_{\alpha+3}(\mathbf{k}) B_{\mathbf{k}\alpha} B_{-\mathbf{k}\alpha} + \text{h.c.}] \Bigg\} +$$

$$+ \sum_{\mathbf{k}} [\Gamma_3(\mathbf{k}) B^{+}_{\mathbf{k}1} B_{\mathbf{k}2} + \Gamma_6(\mathbf{k}) B_{\mathbf{k}1} B_{-\mathbf{k}2} + \text{h.c.}], \tag{23}$$

where the parameters of the kinetic interaction between different sublattices are determined in terms of the parameters of operator (1) as follows:

$$\Gamma_\alpha(\mathbf{k}) = \Bigg\{ JS(x^2_\alpha + y^2_\alpha) + \frac{1}{2}\Delta JS(x_\alpha + y_\alpha)^2 +$$

$$+ \frac{(-1)^\alpha}{2} J_D S(x_\alpha - y_\alpha)^2 - \frac{(-1)^\alpha}{2} J_D S(x_\alpha + y_\alpha)^2 \cos^2\vartheta_\alpha +$$

$$+ [\Delta JS + (-1)^\alpha J_D S](x_\alpha + y_\alpha) z_\alpha \sin 2\vartheta_\alpha \Bigg\} \gamma_1(\mathbf{k});$$

$$\Gamma_{\left\{ \begin{array}{c} 3 \\ 6 \end{array} \right\}}(\mathbf{k}) = \Bigg\{ \frac{1}{2} IS \Big[(x_1 + y_1)(x_2 + y_2)\cos(\vartheta_1 - \vartheta_2) \pm$$

$$\pm (x_1 - y_1)(x_2 - y_2) \Big] + \frac{1}{2}\Delta IS(x_1 + y_1)(x_2 + y_2) \times$$

$$\times \sin\vartheta_1 \sin\vartheta_2 + IS \Big[z_1(x_2 + y_2) - (x_1 + y_1) z_2 \Big] \times$$

$$\times \sin(\vartheta_1 - \vartheta_2) - \Delta IS[z_1(x_2 + y_2)\cos\vartheta_1 \sin\vartheta_2 +$$

$$+ (x_1 + y_1) z_2 \sin\vartheta_1 \cos\vartheta_2 \Big] \Bigg\} \gamma_2(\mathbf{k}); \tag{24}$$

$$\Gamma_{\alpha+3}(\mathbf{k}) = \Bigg\{ 2JS x_\alpha y_\alpha + \frac{1}{2}\Delta JS(x_\alpha + y_\alpha)^2 \sin^2\vartheta_\alpha -$$

$$- (-1)^\alpha J_D S(x_\alpha + y_\alpha)^2 - (-1)^\alpha J_D S(x_\alpha + y_\alpha)^2 \cos^2\vartheta_\alpha +$$

$$+ [\Delta J - (-1)^\alpha J_D] S(x_\alpha + y_\alpha) z_\alpha \sin 2\vartheta_\alpha \Bigg\} \gamma_1(\mathbf{k}),$$

while $\gamma_1(\mathbf{k})$ and $\gamma_2(\mathbf{k})$ denote the intra- and intersublattice structural factors, respectively. The eigenenergies of Hamiltonian (23) are calculated in a common way and have a form

$$\Omega^2_{\pm}(\mathbf{k};\mathbf{H}) = \frac{1}{2}\sum_{\alpha} \{ [\varepsilon_\alpha + \Gamma_\alpha(\mathbf{k})]^2 - \Gamma^2_{\alpha+3}(\mathbf{k}) \} +$$

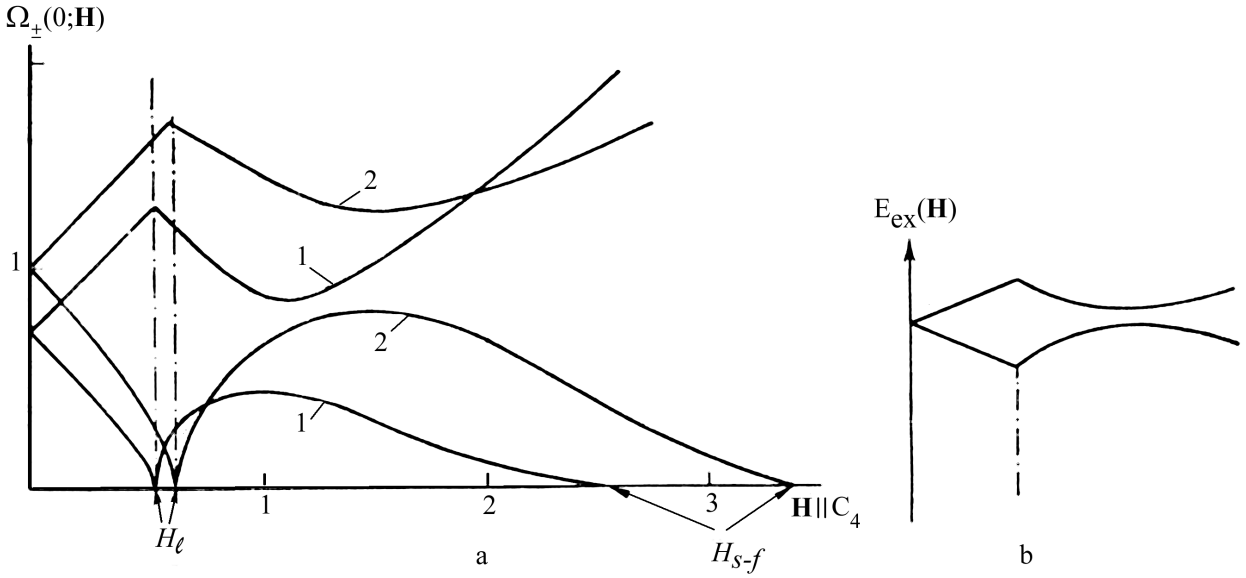

Fig. 1. Field dependence (in units of I) of AFMR frequencies (a) and exciton absorption lines (b) at $E \neq 0$: *1* – $\Delta I = 0.5$; $(2S-1)D = -0.25$; $(2S-1)E = 0.2$; *2* – $\Delta I = 1$; $(2S-1)D = -0.5$; $(2S-1)E = 0.5$

$$+\Gamma_3^2(\mathbf{k}) - \Gamma_6^2(\mathbf{k}) \pm T(\mathbf{k});$$

$$T^2(\mathbf{k}) = \frac{1}{4}\left\{\sum_\alpha (-1)^\alpha \{[\varepsilon_\alpha + \Gamma_\alpha(\mathbf{k})]^2 - \Gamma_{\alpha+3}^2(\mathbf{k})\}\right\}^2 +$$

$$+\left\{\sum_\alpha \{\Gamma_6(\mathbf{k})\Gamma_{\alpha+3}(\mathbf{k}) - \Gamma_3(\mathbf{k})[\varepsilon_\alpha + \Gamma_\alpha(\mathbf{k})]\}\right\}^2 -$$

$$-\left\{\sum_\alpha (-1)^\alpha \{\Gamma_3(\mathbf{k})\Gamma_{\alpha+3}(\mathbf{k}) - \Gamma_6(\mathbf{k})[\varepsilon_\alpha + \Gamma_\alpha(\mathbf{k})]\}\right\}^2. \tag{25}$$

It is also worth adding that expression (25) remains valid in the case of an arbitrary spin configuration, though with the use of the corresponding parameters of the kinetic interaction of type (24).

Let us consider explicit expressions for some individual cases where the general formula (25) is simplified. For example, in the absence of single-ion anisotropy, the AFMR frequencies corresponding to spin excitations with $\mathbf{k} \approx 0$ in the longitudinal phase are equal to

$$\Omega_\pm^{\|}(0;\mathbf{H}) = S\left\{\left[\sqrt{(\Delta I - \Delta J)(2I + \Delta I - \Delta J)} \pm \right.\right.$$

$$\left.\left. \pm \mu_B g \frac{H}{S}\right]^2 - J_D^2\right\}^{1/2}. \tag{26}$$

From here, it is easy to obtain expression (16) for the field H_l. If the parameters D, $E \neq 0$, the most significant addition resulting from the quantum approach consists in the appearance of the resonance intersublattice interaction ($\Gamma_3(\mathbf{k}) \sim EH$ from set (24)) that causes a nonlinear behavior of the AFMR frequency as a function of the longitudinal field. Calculating all $\Gamma_j(\mathbf{k})$ with regard for quantum corrections, one can conclude that the AFMR frequency is described by the expression

$$\Omega_\pm^{\|}(0;\mathbf{H}) = \left\{\left[\sqrt{\Omega^2(0;0) + (2S-1)^2E^2} \pm \right.\right.$$

$$\left.\left. \pm \mu_B g H\right]^2 - (2S-1)^2E^2\right\}^{1/2}, \tag{27}$$

where $\Omega(0;0)$ denotes the uniform precession frequency in the absence of a field determined by formula (19); the field H_l that follows from (27) is also given there. One can see that $\Omega(0;0)$ depends on the intrasublattice exchange that, as is known, does not contribute in phenomenology. Formulas (26) in the case of $D = E = 0$ and (27) in the case of $\Delta I = \Delta J = J_D = 0$ actually coincide, though they were obtained within different approaches. In the region of the non-symmetric oblique phase, formula (25) practically cannot be simplified in either case. The form of the dependences $\Omega_\pm(0;\mathbf{H})$ for some sets of parameters and arbitrary fields $\mathbf{H} \parallel Z$ is given in Fig. 1. For the sake of comparison,

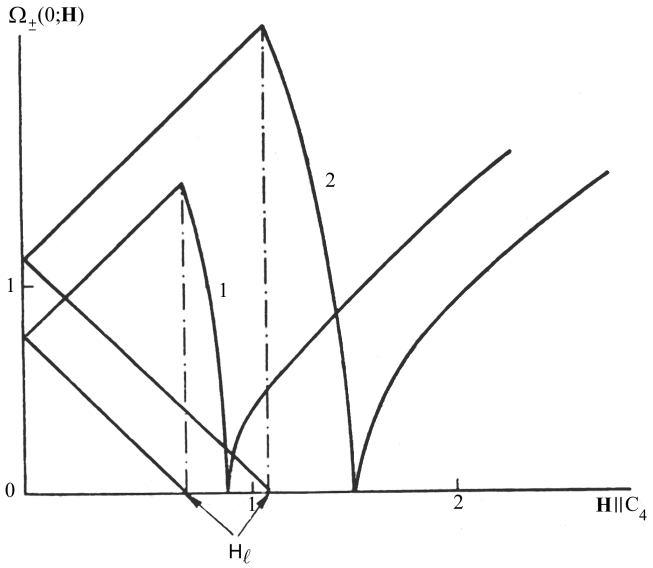

Fig. 2. Field dependence (in units of I) of AFMR frequencies at $E = 0$ in the case where the spin flop occurs via two second-order phase transitions: *1* – $\Delta I = 0.5$; $(2S-1)D = -0.25$; *2* – $\Delta I = 1$; $(2S-1)D = -0.5$

Fig. 2 presents the AFMR frequency for the case of $E = J_D = 0$. It is worth noting that the point $H = H_l$ corresponds to the equality $\Omega_-^{\parallel}(0;\mathbf{H}_l) = 0$; after that, the both non-zero AFMR frequencies do not cross, and $\Omega_-^{\parallel}(0;\mathbf{H}) < \Omega_+^{\parallel}(0;\mathbf{H})$. The end of the turn ($\mathbf{H} = \mathbf{H}_{\rm s-f}$) corresponds to the "adhesion" of the spin sublattices; in this case, $\Omega_-(0;\mathbf{H}_{\rm s-f}) = 0$.

Let us consider the AFMR frequency in the case of a symmetric spin configuration (setting $D = E = 0$ for the sake of simplicity). Then

$$H = \sum_{\mathbf{k}} \Bigg\{ [\varepsilon_\perp + \Gamma^\perp \gamma_1(\mathbf{k})] \sum_\alpha B^+_{\mathbf{k}\alpha} B_{\mathbf{k}\alpha} +$$

$$+ \Bigg\{ \sum_\alpha [\Gamma_1^\perp - i(-1)^\alpha \kappa] \gamma_1(\mathbf{k}) B_{\mathbf{k}\alpha} B_{-\mathbf{k}\alpha} + (\Gamma_2^\perp - i\kappa) \times$$

$$\times \gamma_2(\mathbf{k}) B^+_{\mathbf{k}1} B_{\mathbf{k}2} + \Gamma_3^\perp \gamma_2(\mathbf{k}) B_{\mathbf{k}1} B_{-\mathbf{k}3} + \text{h.c.} \Bigg\} \Bigg\}; \qquad (28)$$

$$\varepsilon_\perp = (I_0 - J)S; \quad I_0 = \sqrt{I^2 + J_D^2}; \quad \kappa = I J_D S / I_0;$$

$$\Gamma^\perp = JS + \frac{1}{2}(\Delta J S + J_D S \sin 2\varphi_D) \sin^2 \vartheta;$$

$$\Gamma_1^\perp = \Gamma^\perp - JS - J_D S \sin 2\varphi_D;$$

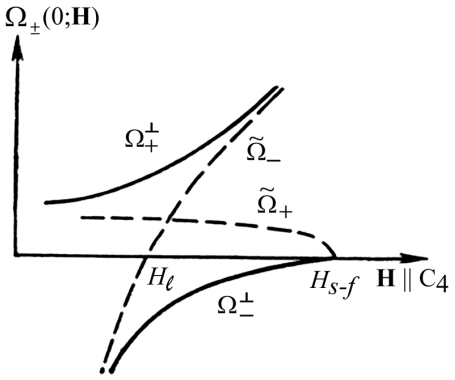

Fig. 3. Optically active ($\mathbf{k} = 0$) eigenenergies of Hamiltonian (27)

$$\Gamma_2^\perp = IS(\cos^2\varphi_D - \sin^2\varphi_D \cos^2\vartheta) + \frac{1}{2}\Delta I S \sin^2\vartheta;$$

$$\Gamma_3^\perp = IS(\sin^2\varphi_D \sin^2\vartheta) + \frac{1}{2}\Delta I S \sin^2\vartheta;$$

$$\cos\vartheta = \frac{H}{H_{\rm s-f}},$$

where the field $H_{\rm s-f}$ of the spin-flip transition is given in (17). The AFMR frequencies that correspond to Hamiltonian (27) can be presented in the form

$$\Omega_\pm^\perp(0;\mathbf{H}) = \Bigg\{ \frac{1}{2}(\tilde\Omega_+^2 + \tilde\Omega_-^2) \pm$$

$$\pm \Bigg[\frac{1}{4}(\tilde\Omega_+^2 - \tilde\Omega_-^2)^2 + 4\kappa^2(\varepsilon_\perp + \Gamma^\perp + \sum_j \Gamma_j^\perp) \times$$

$$\times (\varepsilon_\perp + \Gamma^\perp - \Gamma_1^\perp - \Gamma_2^\perp + \Gamma_3^\perp) \Bigg]^{1/2} \Bigg\}^{1/2}. \qquad (29)$$

In the obtained expression (29), we used the notations

$$\tilde\Omega_+^2 = 2J_D^2 S^2 \left(1 + \frac{I + \Delta I - \Delta J}{I_0}\right)\left(1 - \frac{H^2}{H_{\rm s-f}^2}\right);$$

$$\tilde\Omega_-^2 = 2I_0 S \Bigg\{ \left[\mu_B g H - 2\left(\frac{J_D^2}{I_0} + \Delta J\right) S\right] \cos^2\vartheta -$$

$$-(\Delta I - \Delta J + I - I_0) S \Bigg\}$$

for the frequencies of operator (28) at $\kappa = 0$ which are depicted in Fig. 3 by dashed lines. From formula (29), it is easy to find that $\Omega_-^\perp(0;\mathbf{H}) = 0$ only if

$\tilde{\Omega}_-^2 = 4I^2S^2\cos^2\vartheta$, hence $H = H_{\mathrm{s-f}}$. Thus, $\Omega_-^{\perp} < 0$ (see solid lines in Fig. 3) in the whole range of existence of the symmetric spin configuration demonstrating its absolute instability in tetragonal antiferrodielectrics with the Dzyaloshinskii interaction. This fact was noted in [25], though without calculation of the AFMR frequencies. Finally, it is worth saying that, with the help of the substitutions $\Delta IS \to -(2S-1)D$ and $J_D S \to (2S-1)E$, the expressions for $\Omega_{\pm}^{\perp}(0;\mathbf{H})$ can be transformed to those describing the AFMR in NiF_2 crystal in a longitudinal field, which, as far as we know, have not been presented in the literature.

6. Comparison with Experiment and Conclusions

Based on the considered approach and the obtained results, let us try to discuss the known experimental data concerning FeF_2 antiferromagnetic dielectric in the field $\mathbf{H}||Z||C_4$ [16, 17, 19, 26, 27]. We recall that it is a tetragonal easy-axis antiferrodielectric that can be described by Hamiltonian (1), whereas the AFMR frequencies can be given by expression (27). In correspondence with measurements [16,26], here $\Omega(0;0) = 52.7$ cm $^{-1}$, $IS = (60 \div 62)$ cm^{-1}, $D = (6 \div 9)$ cm^{-1}, and $g = (2.2 \div 2.25)$. Moreover, the Dzyaloshinskii interaction E does not manifest itself in low fields, which agrees with the data on the EPR spectra of Fe^{2+} ZnF_2 ions [25], which also results in the inequality $E \ll D$.

With these values without regard for the constant E, the critical flop field is determined from the equality $\mu_B g H_l = \Omega(0;0)$, or $H_l = 44$ T. The allowance for the value $E \approx 0.1D \approx (0.6 \div 1)$ cm^{-1} [16, 17, 26] results in the reduction of this field by $(2.0 \div 2.5)$ T. Thus, in a field somewhat higher than 40 T, there must take place a first-order transition to the oblique phase (a second-order transition requires the fulfillment of the condition $E > E_{\mathrm{cr}} \approx 2.5$ cm^{-1}). It seems that such a picture is confirmed by work [27] that dealt with measurements of the magnetization of FeF_2 in longitudinal fields $H \leq 45$ T and testified to its rather significant jump in a field of the order of 40 T. On the other hand, optical data [19] demonstrate that, in much smaller fields (~ 25 T), there also take place changes in the magnetic subsystem of this magnet. If we make an assumption about a second-order transition, then the estimates according to formulas (19) and (27) require the fulfillment of the inequality $E > D$, which is impossible to coordinate with magnetostatic and resonance experiments [16, 17, 26]. In particular, such a high value of the Dzyaloshinskii interaction constant would result in much larger $\chi_{\|}$ than the observed one (see (18)). The nature of the relatively considerable jump of the magnetization in a field > 40 T also becomes obscure. In addition, it is worth noting that the Zeeman splitting of exciton absorption lines in FeF_2 also does not agree with their expected behavior demonstrated in Fig. 1,*b*. All these considerations testify to the fact that even the developed quantum theory cannot provide a consistent description of the set of experimental data and eliminate the arising contradictions. For today, there are no measurements of the field dependences of AFMR frequencies that would simplify the determination of the lability fields of a certain phase and the order of phase transformations. We hope that such experiments are easy to perform.

Summing up, it is worth saying that one of the most significant results of the quantum approach consists in an increase of the number of equations used for the determination of spin configurations. In contrast to the phenomenological approach that is usually reduced to the solution of the Landau–Lifshits equation (or equations in the case of many-sublattice systems) in a certain approximation, the quantum theory additionally includes the equation for the average spin s in the proper coordinate system. Of basic importance is the fact that this equation appears to be different depending on the value of the initial spin S at a site. The solution of the corresponding system of equations substantially changes the quasiclassical results (for example, by that it includes the so-called singlet phases, the relation between the angles and magnetization, *etc.*). As was mentioned, such problems have been analyzed till now only in the case where $S = 1$.

On the whole, the problem of the description of magnets with a large contribution of the spin-orbit interaction, or strong single-ion anisotropy, and an arbitrary value of S remains urgent. The application of the quantum theory, which is the only right way for such systems, is restricted by several examples mainly concerning the CoF_2 crystal, where $S = 3/2$ [23, 27]. In this case, a satisfactory agreement between theory and experiment can be reached only with regard for the magnetostriction that results in the breaking of smooth turns of spin vectors, by transforming second-order transitions into first-order ones. There is no doubt that the contribution of the elastic coupling in magnetic crystals with relatively weak single-ion anisotropy (among which, one considers FeF_2 with $S = 5/2$) also can be considerable. The latter necessarily decreases the longitudinal susceptibility making the effective value of quantities of the E type lower than the initial one. However,

the quantum approach with regard for magnetostriction effects is only at the beginning of its development (see, e.g., [9]), and it is too early to make final conclusions about the description of the available experiments.

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КВАНТОВА ТЕОРІЯ МАГНІТНИХ ДІЕЛЕКТРИКІВ ІЗ СЛАБКОЮ ОДНОІОННОЮ АНІЗОТРОПІЄЮ

В.М. Локтєв

Р е з ю м е

Розвинуто мікроскопічну квантову теорію спінових конфігурацій, спін-орієнтаційних фазових переходів та спінових збуджень у тетрагональних антиферомагнітних діелектриках з взаємодією Дзялошинського, що має одноіонне походження. Показано, що в кутовій несиметричній фазі не відбувається перетинання частот АФМР, які відштовхуються саме в міру величини константи Дзялошинського. Обговорено наявні експериментальні дані по антиферомагнітному фториду заліза.