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MAGNETIC DAVYDOV SPLITTING IN ANTIFERRODIELECTRICS

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Electron excitations of an antiferrodielectric (AFD) in the case of a non-collinear arrangement of the spins on the sublattices are investigated by means of exciton theory. It is shown that magnetic Davydov splitting (MDS) for magnetic-dipole optical transitions in an AFD can be observed only when the arrangement of the spins of inequivalent magnetic ions is noncollinear. Formulas are obtained for the magnitude of the MDS as a function of the external magnetic field and for the intensity of the components of the Davydov doublet. The theory is compared with experiment for the crystal $RbMnF_3$.

1. INTRODUCTION

A number of experimental papers on the investigation of light absorption by magnetic ions of an antiferrodielectric (AFD) have appeared recently; in this work, a doublet splitting of the narrow magnetic-dipole lines of optical transitions has been detected and is associated with the collective properties of the magnetic ions of the AFD's (Cr_2O_3, $YCrO_3$ and $RbMnF_3$ crystals). By analogy with the splitting which reflects the collective properties of molecules in molecular crystals,[1] this splitting has been called magnetic Davydov splitting (MDS)[2-6] in order to distinguish it from the Bethe splitting of the levels of a magnetic ion in a crystal ligand field.

In AFD's possessing weak ferromagnetism (the four-sublattice AFD's Cr_2O_3[2,5] and $YCrO_3$[4]), the magnitude of the MDS in the absence of a constant external magnetic field depends on Dzyaloshinskiĭ's exchange constant, whereas for an ideal two-sublattice AFD, such as $RbMnF_3$,[3,6] the MDS is entirely induced by a constant external magnetic field.

The first attempt to explain MDS theoretically was undertaken by van der Ziel.[2] However, as Sugano et al.[7] have shown, the combined quadrupole-quadrupole and spin-orbit mechanism used by van der Ziel for the transfer of the excitation between sublattices leads to a magnitude for the MDS of 10^{-2} cm^{-1}, which clearly does not agree with the experimental data. In [7], the transfer of the excitation between inequivalent magnetic ions as a result of the antisymmetric exchange interaction between a virtual magnon and an exciton is investigated. Although the order of magnitude of the MDS turns out to be correct, in the presence of an external magnetic field H_0 the mechanism proposed in [7] for the appearance of the MDS explains neither the quadratic dependence of the splitting on H_0 nor the intensity of the components of the Davydov doublet. This same objection applies to the explanation of MDS given by Allen et al. in [5]. The correct dependence of the magnitude of the MDS on the external field was obtained by the author in [8].

In the present paper, the electron excitations of an AFD in the case of a non-collinear arrangement of the spins S_1 and S_2 of the sublattices are investigated using the exciton theory[1] developed for an AFD,[9-11] and the conditions for which MDS occurs are found. By way of an example, we compare the theory with an experimental observation of MDS in a crystal of $RbMnF_3$.

2. HAMILTONIAN FOR AN AFD ELECTRONIC EXCITATION

The lowest optical electronic excitations of an AFD magnetic ion are accompanied by a change of the ion spin by unity. In collinear AFD's, this leads to a rigorous spin exclusion on the transfer of excitation energy from one sublattice to another[1)][10, 11]. The spin exclusion is weakened for AFD's under the influence of a strong external constant magnetic field in a phase with reversed moments, and for AFD's with weak ferromagnetism. It is in these cases that we should expect Davydov splitting to appear.[11]

We shall consider the lowest electronic excitations of an AFD whose sublattices have spins with non-collinear equilibrium values (Fig. 1). In the case of an AFD with "easy-axis" anisotropy, the spins of the sublattices are oriented along the direction of the z_1 and z_2 axes, which form an angle $\theta = \theta_1 = -\theta_2$ with one of the anisotropy axes z, along which the external magnetic field $\mathbf{H}_0$ is applied. Then $\cos\theta = H_0/H_E$, if $\sqrt{H_A H_E} < H_0 < H_E$ (H_A and H_E are the anisotropy magnetic field and exchange magnetic field respectively). In the case of an AFD with weak ferromagnetism in the absence of an external magnetic field, $\cos\theta = H_D/H_E$, where H_D is the Dzyaloshinskiĭ exchange magnetic field. To obtain the AFD Hamiltonian describing the electronic excitations, we start from the fact that the interaction of AFD magnetic ions reduces to the interaction between electrons of unfilled 3d or 4f shells.[12,13]

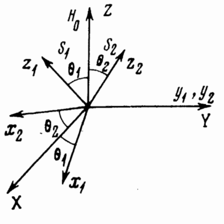

FIG. 1. Equilibrium spin configuration for $H_0 > H_C$.

[1)] The transfer of excitation energy becomes possible in the second order of perturbation theory, if virtual magnons are included [7].

Therefore, the total Hamiltonian $\mathscr{H}$ of a system of interacting magnetic ions, leaving the number of electrons at each ion unchanged, can be written, using the results of paper [14], in the form

$$\mathscr{H}=\mathscr{H}_0+\mathscr{H}_{int}; \tag{1}$$

$$\mathscr{H}_0=\sum_{n\alpha}\mathscr{H}_{n\alpha}, \tag{2}$$

$$\mathscr{H}_{n\alpha}=\sum_{\lambda\sigma}\varepsilon_{\lambda\sigma}\overset{+}{a}_{n\alpha;\,\lambda\sigma}a_{n\alpha;\,\lambda\sigma}$$
$$+\frac{1}{2}\sum_{(\lambda,\sigma)}\langle n\alpha\lambda_1;n\alpha\lambda_2|V|n\alpha\lambda_3;n\alpha\lambda_4\rangle\cdot\overset{+}{a}_{n\alpha;\,\lambda_1\sigma_1}\overset{+}{a}_{n\alpha;\,\lambda_2\sigma_2}a_{n\alpha;\,\lambda_3\sigma_2}a_{n\alpha;\,\lambda_4\sigma_1};$$

$$\mathscr{H}_{int}=\frac{1}{2}\sum_{n\alpha,\,m\beta}V_{n\alpha;\,m\beta},$$

$$V_{n\alpha;\,m\beta}=\sum_{(\lambda,\sigma)}\langle n\alpha\lambda_1;m\beta\lambda_2|V|n\alpha\lambda_3;m\beta\lambda_4\rangle$$
$$\times\sum_{\sigma_1'\sigma_2'}\overset{*}{\chi}_{\alpha\sigma_1}(\sigma_1')\overset{*}{\chi}_{\beta\sigma_2}(\sigma_2')\chi_{\alpha\sigma_3}(\sigma_2')\chi_{\beta\sigma_4}(\sigma_1')\overset{+}{a}_{n\alpha;\,\lambda_1\sigma_1}\overset{+}{a}_{m\beta;\,\lambda_2\sigma_2}a_{n\alpha;\,\lambda_3\sigma_3}a_{m\beta;\,\lambda_4\sigma_4}$$
$$+\sum_{(\lambda,\sigma)}\langle n\alpha\lambda_1;m\beta\lambda_2|V|m\beta\lambda_3;n\alpha\lambda_4\rangle \tag{3}$$
$$\times\sum_{\sigma_1'\sigma_2'}\chi_{\alpha\sigma_1}^{*}(\sigma_1')\chi_{\beta\sigma_2}^{*}(\sigma_2')\chi_{\beta\sigma_3}(\sigma_2')\chi_{\beta\sigma_4}(\sigma_1')\;\overset{+}{a}_{n\alpha;\,\lambda_1\sigma_1}\overset{+}{a}_{m\beta;\,\lambda_2\sigma_2}a_{m\beta;\,\lambda_3\sigma_3}a_{n\alpha;\,\lambda_4\sigma_4},$$

where the index (λ,σ) under the summation sign denotes summation over all λ_i and σ_j.

In the formulas (2) and (3), $\overset{+}{a}_{n\alpha;\,\lambda\sigma}$ and $a_{n\alpha;\,\lambda\sigma}$ are creation and destruction operators for an electron in the λ-th orbital with spin projection σ in the α-th magnetic ion at the n-th lattice site;

$$\langle n_1\lambda_1;n_2\lambda_2|V|n_3\lambda_3;n_4\lambda_4\rangle$$
$$=\int\varphi^{*}_{n_1;\,\lambda_1}(\mathbf{r}_1)\varphi^{*}_{n_2;\,\lambda_2}(\mathbf{r}_2)\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\varphi_{n_3;\,\lambda_3}(\mathbf{r}_2)\varphi_{n_4;\,\lambda_4}(\mathbf{r}_1)\,d\mathbf{r}_1\,d\mathbf{r}_2,$$

where $\varphi_{n\alpha;\,\lambda}(\mathbf{r})$ is the electron wavefunction (in the XYZ coordinate system) which is the solution of the Schrödinger equation for an electron situated in a self-consistent Hartree-Fock field and in the electrostatic crystal field of the ligands surrounding the magnetic ion; $\chi_{\alpha\sigma}(\sigma')$ are the spin wavefunctions of the electron, defined in the coordinate system x_α, y_α, z_α. Taking into account that the operator for a rotation through angle θ_α about the y-axis for a spin $S = 1/2$ has the form

$$R(\theta_\alpha)=I\cos(\theta_\alpha/2)+i\sigma_y\sin(\theta_\alpha/2)$$

(I is the unit matrix, and σ_y a Pauli matrix), we obtain the explicit dependence of the operator $V_{n\alpha;\,m\beta}$ of the interaction between the magnetic ions on the angles θ_α and θ_β at which the electron spins of the magnetic ions are inclined:

$$V_{n\alpha;\,m\beta}=\sum_{(\lambda,\sigma)}\langle n\alpha\lambda_1;m\beta\lambda_2|V|n\alpha\lambda_3;m\beta\lambda_4\rangle$$
$$\times\Phi_{\sigma_1\sigma_4}\left(\frac{\theta_\alpha-\theta_\beta}{2}\right)\Phi_{\sigma_2\sigma_3}\left(\frac{\theta_\beta-\theta_\alpha}{2}\right)\overset{+}{a}_{n\alpha;\,\lambda_1\sigma_1}\overset{+}{a}_{m\beta;\,\lambda_2\sigma_2}a_{n\alpha;\,\lambda_3\sigma_3}a_{m\beta;\,\lambda_4\sigma_4}$$
$$+\sum_{(\lambda,\sigma)}\langle n\alpha\lambda_1;m\beta\lambda_2|V|m\beta\lambda_3;n\alpha\lambda_4\rangle\overset{+}{a}_{n\alpha;\,\lambda_1\sigma_1}\overset{+}{a}_{m\beta;\,\lambda_2\sigma_2}a_{m\beta;\,\lambda_3\sigma_2}a_{n\alpha;\,\lambda_4\sigma_1}, \tag{4}$$

$$\Phi_{\sigma\sigma'}\left(\frac{\theta_\alpha-\theta_\beta}{2}\right)=\delta_{\sigma\sigma'}\cos\left(\frac{\theta_\alpha-\theta_\beta}{2}\right)+(\delta_{\sigma\downarrow}\delta_{\sigma'\uparrow}-\delta_{\sigma\uparrow}\delta_{\sigma'\downarrow})\sin\left(\frac{\theta_\alpha-\theta_\beta}{2}\right). \tag{5}$$

The first term in expression (4) describes the exchange interaction of the ions $n\alpha$ and $m\beta$ and depends essentially on the direction of the spins of the interacting electrons in the crystal, whereas the second term, which describes the Coulomb interaction, does not depend on the direction of the electron spins.

To write down the Hamiltonian $\Delta\mathscr{H}^f$ of an excited state of the AFD, it is necessary to define Bose operators $B^+_{n\alpha}(f)$ which create an electron excitation f at an ion when the ion undergoes a transition from the ground state $|\varphi^0_{n\alpha}\rangle$ to the excited state $|\varphi^f_{n\alpha}\rangle$. Defining the operator $B^+_{n\alpha}(f)$ by means of the relation[1, 11]

$$|\varphi_{n\alpha}{}^f\rangle=B_{n\alpha}{}^+(f)|\varphi_{n\alpha}{}^0\rangle$$

and confining ourselves to quadratic terms in the operators $B^+_{n\alpha}$, $B_{n\alpha}$, we obtain for the quantity $\Delta\mathscr{H}^f$ an expression of the usual form[2]

$$\Delta\mathscr{H}^f=\sum_{n\alpha}(\Delta\varepsilon_\alpha{}^f+D^f)B_{n\alpha}{}^+(f)B_{n\alpha}(f)+\sideset{}{'}\sum_{n\alpha;\,m\beta}M^f_{n\alpha;\,m\beta}B_{n\alpha}{}^+(f)B_{m\beta}(f), \tag{6}$$

where

$$\Delta\varepsilon_\alpha{}^f=\langle\varphi_{n\alpha}{}^f|\mathscr{H}_{n\alpha}|\varphi_{n\alpha}{}^f\rangle-\langle\varphi_{n\alpha}{}^0|\mathscr{H}_{n\alpha}|\varphi_{n\alpha}{}^0\rangle$$

is the optical excitation energy of an ion in a crystal ligand field, comprising the energies $\epsilon_{\lambda\sigma}$ of the individual electrons and the configurational interaction energy of the electrons;

$$D^f=\sideset{}{'}\sum_{m\beta}\{\langle\overset{f}{\varphi}_{n\alpha};\overset{0}{\varphi}_{m\beta}|V_{n\alpha;\,m\beta}|\overset{0}{\varphi}_{m\beta};\overset{f}{\varphi}_{n\alpha}\rangle$$
$$-\langle\overset{0}{\varphi}_{n\alpha};\overset{0}{\varphi}_{m\beta}|V_{n\alpha;\,m\beta}|\overset{0}{\varphi}_{m\beta};\overset{0}{\varphi}_{n\alpha}\rangle\}$$

is the change in the interaction energy of all the ions of the AFD with one ion when the latter undergoes a transition to an excited state.[1, 11] The matrix elements for transfer of the f-th electronic excitation

$$M^f_{n\alpha;\,m\beta}=\langle\overset{f}{\varphi}_{n\alpha};\overset{0}{\varphi}_{m\beta}|V_{n\alpha;\,m\beta}|\overset{f}{\varphi}_{m\beta};\overset{0}{\varphi}_{n\alpha}\rangle \tag{7}$$

are determined by the exchange interaction contained in the operator $V_{n\alpha;\,m\beta}$.

To find the analytic dependence of the quantities $M^f_{n\alpha,\,m\beta}$ on the angle of inclination θ_α of the spins of the sublattices, we examine the structure of the wavefunctions $|\varphi^0_{n\alpha}\rangle$ and $|\varphi^f_{n\alpha}\rangle$. Since in the coordinate representation the functions $|\varphi^0_{n\alpha}\rangle$ and $|\varphi^f_{n\alpha}\rangle$ are linear combinations of Slater determinants and transform respectively according to the ${}^{2S+1}\Gamma_1$ and ${}^{2(S-1)+1}\Gamma_f$ representations of the crystal symmetry group,[13] in the second quantization representation these wavefunctions have the form

$$|\overset{0}{\varphi}_{n\alpha}\rangle=\overset{+}{a}_{n\alpha;\,\lambda_1\uparrow}\overset{+}{a}_{n\alpha;\,\lambda_2\uparrow}\ldots\overset{+}{a}_{n\alpha;\,\lambda_j\uparrow}|0\rangle, \tag{8}$$
$$|\overset{f}{\varphi}_{n\alpha}\rangle=C_1{}^f\overset{+}{a}_{n\alpha;\,\lambda_1\downarrow}\overset{+}{a}_{n\alpha;\,\lambda_2\uparrow}\ldots\overset{+}{a}_{n\alpha;\,\lambda_j\uparrow}|0\rangle$$
$$+C_2{}^f\overset{+}{a}_{n\alpha;\,\lambda_1\uparrow}\overset{+}{a}_{n\alpha;\,\lambda_2\downarrow}\ldots\overset{+}{a}_{n\alpha;\,\lambda_j\uparrow}|0\rangle+\ldots$$
$$+C_j{}^f\overset{+}{a}_{n\alpha;\,\lambda_1\uparrow}\overset{+}{a}_{n\alpha;\,\lambda_2\uparrow}\ldots\overset{+}{a}_{n\alpha;\,\lambda_j\downarrow}|0\rangle.$$

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[2] Here we confine ourselves to the Heitler-London approximation [1] for the optical excitations of the AFD. In treating spin excitations of an AFD, one must add a term proportional to $B^+_{n\alpha}B^+_{m\beta}$ to the operator $\Delta\mathscr{H}^f$.

Here $|0\rangle$ is the vacuum electron function, j is the number of magnetic electrons in the 3d or 4f shell of the ion, and C_i^f are numbers determined from the normalization of the function $|\varphi_{n\alpha}^f\rangle$ and its symmetry.

It follows from the form of the functions (8) that the excitation $|\varphi_{n\alpha}^0\rangle \rightarrow |\varphi_{n\alpha}^f\rangle$ takes place by way of a transition of one of the electrons from a state with spin projection $+1/2$ to a state with spin projection $-1/2$. Consequently, the matrix elements for transfer of the excitation, according to (4), (5), (7), and (8), are written as

$$M_{n\alpha;\,m\beta}^{f} = \mathcal{M}_{n\alpha;\,m\beta}^{f}\left\{\delta_{\alpha\beta} + (1-\delta_{\alpha\beta})\cos^2\left(\frac{\theta_\alpha-\theta_\beta}{2}\right)\right\}$$

$$\mathcal{M}_{n\alpha;\,m\beta}^{f} = \sum_{\lambda_1\ldots\lambda_4}\langle n\alpha\lambda_1;\, m\beta\lambda_2|V|n\alpha\lambda_3;\, m\beta\lambda_4\rangle$$
$$\times\langle\varphi_{n\alpha}^{f};\,\varphi_{m\beta}^{0}|\overset{+}{a}_{n\alpha;\,\lambda_1\downarrow}\overset{+}{a}_{m\beta;\,\lambda_2\uparrow}a_{n\alpha;\,\lambda_3\uparrow}a_{m\beta;\,\lambda_4\downarrow}\,|\varphi_{m\beta}^{f};\,\varphi_{n\alpha}^{0}\rangle. \tag{9}$$

The transformation

$$B_{n\alpha}(f) = \frac{1}{\sqrt{N}}\sum_{\mathbf{k}\mu} e^{i\mathbf{kn}}\,u_{\alpha\mu}(\mathbf{k};f)B_\mu(\mathbf{k};f),$$

where N is the number of cells in the crystal, μ is the exciton band index, and **k** is the wave-vector, brings the Hamiltonian (6) to the form

$$\mathcal{H}_{ex}^{f} = \sum_{\mu\mathbf{k}} E_\mu(\mathbf{k};f)B_\mu^{+}(\mathbf{k};f)B_\mu(\mathbf{k};f). \tag{10}$$

Here $B_\mu^+(\mathbf{k}, f)$ and $B_\mu(\mathbf{k}, f)$ are Bose operators which create and destroy an exciton f in the band μ with wave wave-vector **k** and having energy $E_\mu(\mathbf{k}; f)$. For crystals with a center of symmetry,

$$E_\mu(\mathbf{k};f) = \Delta\varepsilon^f + D^f + L_1^f(\mathbf{k}) - (-1)^\mu L_2^f(\mathbf{k})\cos^2\left(\frac{\theta_1-\theta_2}{2}\right),$$
$$L_1^f(\mathbf{k}) = \sum_{\mathbf{n}}\mathcal{M}_{0\alpha;\,\mathbf{n}\alpha}^{f}\,e^{i\mathbf{kn}},$$
$$L_2^f(\mathbf{k}) = \sum_{\mathbf{n}}\mathcal{M}_{01;\,\mathbf{n}2}^{f}\exp\{i\mathbf{k}(\mathbf{n}+\boldsymbol{\rho}_1-\boldsymbol{\rho}_2)\}, \tag{11}$$

where $\boldsymbol{\rho}_\alpha$ is the radius-vector from the center of the cell to the α-th magnetic ion.

It follows from expression (10) and (11) that two bands $E_1(\mathbf{k}; f)$ and $E_2(\mathbf{k}; f)$ of excited states correspond to one optical excitation $\Delta\epsilon^f$ in the crystal. For $\mathbf{k} = 0$, the AFD electronic excitation branches differ from one another by an amount

$$\Delta\nu_D(f) = 2|L_2^f(0)|\cos^2\left(\frac{\theta_1-\theta_2}{2}\right), \tag{12}$$

which we can call the magnetic Davydov splitting in the AFD. (This optical splitting should not be confused with the splitting of two exciton branches that is characterized by the separation between the minimum energy of the upper branch and the maximum of the lower branch.) The splitting $\Delta\nu_D(f)$ is absent in the case of an antiparallel arrangement of the spins of the sublattices in the ground state, when $\theta_1 = \theta$ and $\theta_2 = \pi + \theta$. Thus, the formula (12) also reflects the law for lifting the spin exclusion on transfer of an excitation from one sublattice to another as a function of the angle between the spins of the magnetic ions in the ground state.

3. INTENSITY OF SINGLE-ION OPTICAL TRANSITIONS

For a full elucidation of the nature of MDS in AFD's it is necessary to consider the polarization of the lines of the Davydov doublets, $E_1(\mathbf{k}; f)$ and $E_2(\mathbf{k}; f)$. Single-ion optical transitions in an AFD under the influence of the magnetic field component $\mathbf{h}_0$ of an electromagnetic wave of frequency ω and wave-vector **Q** are defined in the exciton representation by the operator

$$\mathcal{H}_{ex-\gamma}(t) = \mathbf{M}_\mu(f)\mathbf{h}_0 e^{-i\omega t}B_\mu^{+}(\mathbf{Q};f) + \text{h.c.},$$
$$\mathbf{M}_\mu(f) = \mu_B\sqrt{N}\sum_\alpha\left\langle\varphi_{n\alpha}^{f}\left|\sum_i \mathbf{s}_{n\alpha i}\exp(i\mathbf{Q}\mathbf{r}_{n\alpha i})\right|\varphi_{n\alpha}^{0}\right\rangle u_{\alpha\mu}(\mathbf{Q};f),$$

where $\mathbf{s}_{n\alpha i}$ and $\mathbf{r}_{n\alpha i}$ are the operators of the spin and coordinates of the i-th electron in the α-th ion of the **n**'th cell, and μ_B is the Bohr magneton.

Here we are interested in magnetic-dipole transitions between states with the same orbital electronic configuration in crystals with O_h symmetry[2,6] i.e., in the transitions ${}^{2s+1}A_g \rightarrow {}^{2(s-1)+1}E_g$, and for the magnetic-dipole transition moment we obtain the expression

$$\mathbf{M}_\mu(f) = \frac{i\mu_B\sqrt{N}}{e}Q^j\sum_\alpha\sum_{\substack{\lambda\lambda'\\ \sigma\sigma'}}\langle\varphi_{n\alpha}^{f}|\overset{+}{a}_{n\alpha;\,\lambda\sigma}a_{n\alpha;\,\lambda'\sigma'}|\varphi_{n\alpha}^{0}\rangle$$
$$\times\langle\sigma|\mathbf{S}_\alpha|\sigma'\rangle\langle\lambda|\mathbf{d}_\alpha^{j}|\lambda'\rangle\,\tilde{u}_{\alpha\mu}, \tag{13}$$

where

$$\tilde{u}_{\alpha\mu} = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix},$$

and $\mathbf{d}_\alpha$ is the operator of an electric-dipole transition in the α-th ion of the cell; in the case when the crystal environments of the magnetic ions are equivalent (which is the case for most AFD's), $\mathbf{d}_\alpha$ does not depend on the sublattice index α, i.e., $\mathbf{d}_1 = \mathbf{d}_2 \equiv \mathbf{d}$. We now take into account that the spin operator $\mathbf{s}_\alpha$ of an electron in its own system of coordinate x_α, y_α, z_α (Fig. 1) is related to the spin operator $\mathbf{S}_{(\alpha)}$ in the XYZ system of coordinates by the transformation

$$S_{(\alpha)}^{X} = s_{z_\alpha}\sin\theta_\alpha + s_{x_\alpha}\cos\theta_\alpha,\qquad S_{(\alpha)}^{Y} = s_{y_\alpha},$$
$$S_{(\alpha)}^{Z} = s_{z_\alpha}\cos\theta_\alpha - s_{x_\alpha}\sin\theta_\alpha. \tag{14}$$

Then, according to (8), (13), and (14), the quantities $M^i(f)$, which determine the probability of single-ion magnetic-dipole transitions in an AFD for a given polarization vector $\mathbf{h}_0$, acquire the form

$$M_{1(2)}^{Z}(f) = \frac{iQ\mu_B}{2}\sqrt{\frac{NF}{2m\omega_0}}\left(\sin\theta_1 \underset{(-)}{+} \sin\theta_2\right),\quad \mathbf{h}_0\parallel Z,$$
$$M_{1(2)}^{\perp}(f) = \frac{iQ\mu_B}{2}\sqrt{\frac{NF}{2m\omega_0}}\left(\cos\theta_1 \underset{(-)}{+} \cos\theta_2\right),\quad \mathbf{h}_0\perp Z,$$
$$F = \frac{2m\omega_0}{e^2\hbar}\left|\sum_{\lambda\lambda'}\langle\lambda|d^j|\lambda'\rangle\langle\varphi_{n\alpha}^{f}|\overset{+}{a}_{n\alpha;\lambda\downarrow}a_{n\alpha;\lambda'}\ \ |\varphi_{n\alpha}^{0}\rangle\right|^2, \tag{15}$$

where F is the oscillator strength of the optical transition under consideration, ω_0 is the transition frequency, and m is the electron mass. We remark that the matrix elements of a dipole transition $\langle\lambda|d^j|\lambda'\rangle$ of polarization j are taken between states λ and λ' belonging to the same 3d (or 4f) shell. Therefore, for the transitions ${}^{2s+1}A_g \rightarrow {}^{2(s-1)+1}E_g$ to occur, it is necessary to include high-lying odd electron states.[12]

The MDS problem is completely solved by the formulas (11), (12) and (15), if the connection between the angle $\theta = \theta_1 = -\theta_2$ and the external magnetic field H_0 and Dzyaloshinskiĭ exchange magnetic field is taken into account. Here we shall say a few more words about what happens to the AFD excitation branches $E_1(\mathbf{k}; f)$ and $E_2(\mathbf{k}; f)$ in the case of large fields H_0, when the AFD becomes a ferrodielectric. On increase of H_0, the spins on the sublattices form a smaller and smaller angle between themselves. Because of this, the resonance transfer $M^f_{n1;\, m2}$ of an excitation between sublattices increases and the Davydov splitting gets bigger, although the intensity of the second exciton-excitation branch falls (like $\sin^2 \theta$). So long as two sublattices of the AFD exist (i.e., up to fields $H_0 \leq H_E$), we can speak of two branches of the same AFD electronic excitation, $E_1(\mathbf{k}; f)$ and $E_2(\mathbf{k}; f)$. For fields $H_0 = H_E$, an abrupt change of the crystal symmetry occurs. If the crystal possesses cubic symmetry, the unit cell now contains only one magnetic ion and the lattice constant becomes smaller by a factor of two. The branch $E_2(\mathbf{k}; f)$, which had earlier its own independent physical meaning, is now a continuation of the branch $E_1(\mathbf{k}; f)$, since the Brillouin zone of the crystal has grown larger by a factor of two. Thus, at $H_0 = H_E$, two antiferromagnetic branches become one electronic-excitation branch $E(\mathbf{k}; f)$[3)] of a ferrodielectric, with

$$E(\mathbf{k}; f) = \Delta\varepsilon^f + D^f + \mathcal{L}^f(\mathbf{k}), \quad \mathcal{L}^f(\mathbf{k}) = \sum_{\mathbf{n}} \mathcal{M}^{\,f}_{0n}\, e^{i\mathbf{kn}}. \tag{16}$$

(The summation over $\mathbf{n}$ in (16) is performed over the sites of a lattice whose lattice constant is half that of the crystal in its antiferromagnetic phase.) Here we have a complete analogy with typical Davydov splitting in molecular crystals, for which the splitting is totally absent when the molecules acquire the same spatial orientation[1]—one of the branches becomes a continuation of the other branch, since the Brillouin zone has been doubled.

It follows from what has been said that the explanation of MDS given by Sugano et al. for an AFD with collinear sublattices with reflection symmetry is incorrect. Taking account of virtual magnons can, as pointed out in [7], lead to a spin-forbidden transfer of an excitation between different sublattices. However, the fulfillment of this condition alone is not sufficient for the observation of MDS, since the intensity of one of the components of the doublet goes to zero. A necessary condition for the observation of the MDS of magnetic-dipole transitions is that the spins of the AFD sublattices be non-collinear. Passing over to the study of MDS by means of the formulas (11), (12), and (15) for specific crystals, it is necessary to remember that MDS in AFD's with complicated magnetic structure (such as that in crystals of Cr_2O_3 and $YCrO_3$) requires in addition a treatment of the electric-dipole optical transitions (occurring with inclusion of spin-orbit interaction), since, because of the inequivalence of the crystalline environments of the magnetic ions, it is possible to observe combined magnetic and electric Davydov splitting.

4. MDS IN A CRYSTAL OF $RbMnF_3$

The MDS of magnetic-dipole optical transitions should be observed most clearly in collinear two-sublattice AFD's. Eremenko and Novikov[6] observed the MDS of the 25 144.5 cm^{-1} line of the ${}^6A_{1g} \to {}^4E_g$ transition in the ion Mn^{2+} in the ideal cubic two-sublattice AFD, $RbMnF_3$. Because of the smallness of the anisotropy field $H_A \approx 4$ Oe and the large magnitude of the exchange field $H_E \approx 9 \times 10^5$ Oe, non-collinearity of the sublattice spins, necessary for the observation of MDS, is achieved at fields $H_0 > H_C = \sqrt{H_A H_E} \approx 18 \times 10^3$ Oe. This is seen clearly experimentally. Figure 2 illustrates the MDS of this optical transition. The 25 144.5 cm^{-1} line splits under the influence of the magnetoelastic interaction into a and b orbitally nondegenerate states. Each of the a and b states undergoes a further splitting in a field $H_0 > H_C$ into a_1, a_2 and b_1, b_2 components, which are associated only with the collective properties of the crystal.[6]

The formulas (11), (12), and (15) are in full agreement with the MDS pattern in a crystal of $RbMnF_3$. In fact, knowing the equilibrium spin configurations as a function of the magnitude of the external field H_0 [16] and the selection rules for magnetic-dipole optical transitions[6] to the states a and b, we have, according tc (11), the following expression for the exciton-excitation energies

$$E_{1,2}(\mathrm{Q} \approx 0;\, f) = \Delta\varepsilon^f + D^f + L_1^f(Q \approx 0)$$
$$\pm L_2^f(Q \approx 0)\cos^2\theta, \quad f = a, b. \tag{17}$$

(To obtain (17), we took into account that, for a crystal of $RbMnF_3$ for equilibrium non-collinear spin states,[16] $\theta_1 = -\theta_2 = \theta$ and $\cos\theta = H_0/H_E$.) We note now that the electronic excitation energy $\Delta\epsilon^f$ of an ion is composed of the energy of a purely electronic excitation $\Delta\epsilon^f_0$ and the Zeeman excitation energy $\mu_{\mathrm{eff}} H_0 \{gS - g^f(S-1)\} \times \cos\theta$, where g and g^f are the g-factors in the ground and excited states in a cubic field $\mathbf{O_h}$. Calculating too the quantity D^f, we find

$$\Delta\varepsilon^f + D^f = \Delta\varepsilon_0{}^f + D_0{}^f - \left(1 - \frac{g^f}{g}\right)(S-1)\frac{\mu_{\mathrm{eff}} H_0{}^2}{H_E},$$
$$D_0{}^f = -\frac{1}{2}\sum_{m\beta;\, j}\ \sum_{\lambda\lambda'\lambda''\sigma} \langle n\alpha\lambda;\, m\beta\lambda' | V | n\alpha\lambda;\, m\beta\lambda'' \rangle$$
$$\times\, \delta_{\lambda\lambda_j} \langle \varphi_{m\beta}{}^f | \overset{+}{a}_{m\beta;\, \lambda'\sigma}\, a_{m\beta;\, \lambda''\sigma} | \varphi_{m\beta}{}^f \rangle.$$

Thus, for the exciton-excitation branches $E_1(\mathbf{Q} \approx 0; f)$ and $E_2(\mathbf{Q} \approx 0; f)$ we have, finally:

$$E_{1,2}(\mathrm{Q} \approx 0;\, f) = \Delta\varepsilon_0{}^f + D_0{}^f + L_1{}^f(\mathrm{Q} \approx 0)$$
$$+ \left\{ \frac{\mu_{\mathrm{eff}}(S-1)(g^f - g)}{gH_E} + \frac{L_2{}^f(\mathrm{Q} \approx 0)}{H_E{}^2} \right\} H_0{}^2. \tag{18}$$

It can be seen from formula (18) that the coefficients of H_0^2 have different magnitudes for the excitations f_1 and f_2 (f = a, b). Experimentally this is manifested in the

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[3)] For AFD spin-excitation branches $E_1(\mathbf{k})$ and $E_2(\mathbf{k})$ in strong magnetic fields (cf., e.g. [15]), the splitting $\Delta\nu = E_1(\mathbf{k}) - E_2(\mathbf{k})$ also increases with increase of the field H_0, but at $H_0 = H_E$ for crystals of cubic symmetry the branch $E_2(\mathbf{k})$ is a continuation of the branch $E_1(\mathbf{k})$. The branches $E_1(\mathbf{k})$ and $E_2(\mathbf{k})$ become one spin-excitation branch of a ferrodielectric. In the general case there are two excitation branches when $H_0 \geqslant H_E$, for both electronic and spin excitations.

different curvatures of the parabolas f_1 and f_2; Fig. 2 shows that for a $RbMnF_3$ crystal

$$L_2^f(Q\approx 0) > 0, \quad \mu_{\mathrm{eff}}(g^f/g-1) < 0,$$
$$L_2^f(Q\approx 0) > \left|\mu_{\mathrm{eff}}\frac{g^f-g}{g}\right|(S-1)H_E,$$

i.e., the resonance interaction energy is positive and exceeds the Zeeman excitation energy in absolute magnitude. A numerical value of $L_2^f(Q\approx 0)$ is found by comparing the theoretical formula for the MDS

$$\Delta\nu_D(f) = 2L_2^f(Q\approx 0)H_0^2/H_E^2, \tag{19}$$

obtained from expression (12) with the experimental formula found in paper [6] (H_0 is in Oersteds and $\Delta\nu_D$ in cm^{-1}

$$\Delta\nu_D(f) = 1{,}27\cdot 10^{-10}H_0^2. \tag{20}$$

An estimate of the magnitude of the exchange interaction $M^f_{n1;n2}$ between neighboring ions on opposite sublattices is also of interest. It follows from the definitions (9) and (11) that

$$M^f_{n1;n2} \approx \frac{L_2^f(Q\approx 0)}{\delta}\cos^2\left(\frac{\theta_1-\theta_2}{2}\right),$$

where δ is the number of nearest neighbors for a crystal of cubic symmetry. Therefore, for an $RbMnF_3$ crystal, according to (19) and (20) we obtain

$$M^f_{n1} \approx 9\ [\mathrm{cm}^{-1}]\cos^2\theta.$$

Thus, the exchange is a maximum for excitation of ions with parallel spins and equal to zero for excitation of ions with antiparallel spins (the spin exclusion on the transfer of an electronic excitation between sublattices of the AFD).

The intensity of the components of the Davydov doublet is easily evaluated using the formulas (15), if we note that the light absorption corresponding to the first and second components of the doublet is proportional to $\cos^2\theta$ and $\sin^2\theta$. For fields $H_0 < H_I \sim 1.4\times 10^5$ Oe, the intensity of the first component is small, but on increase of the field it rises sharply, while the intensity of the second component falls sharply (proportionally to $1-(H_0/H_E)^2$). This conclusion is in full agreement with the experimental picture of the absorption. In Fig. 2 the dashed portions of the parabolas a_1 and b_1 exactly characterize the low-intensity components of the doublet.

To conclude the comparison of the theory with experiment for the AFD $RbMnF_3$, we emphasize again that the good agreement is obtained as a result of the fact that the $RbMnF_3$ crystal has a clearly defined cubic symmetry, for which the crystalline ligand environments of magnetic ions of the first and second sublattices are the same. In this sense, this crystal can be considered to be ideal for the study of MDS.

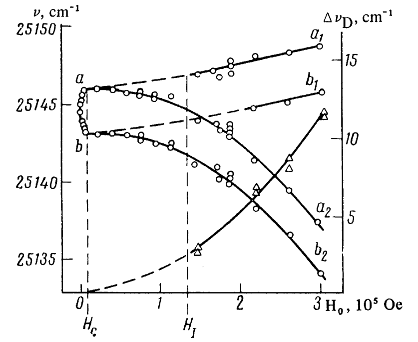

FIG. 2. Exciton absorption in the transition $^6A_{1g}\rightarrow{}^4E_g$ in $RbMnF_3$ (from the data of [6]); Δ is the dependence of the MDS on the magnitude of the external magnetic field H_0.

For an AFD with weak ferromagnetism at zero magnetic fields H_0, the magnitude of the MDS can be obtained in an elementary way, if we put $\theta_1 = -\theta_2 = \theta$ and $\cos\theta = H_D/H_E$ in the general formula (12). The resulting expression for the MDS coincides exactly with the results of paper [7] for $H_0 = 0$.

5. CONCLUSION

The theory of MDS in AFD's developed in the present paper is applicable to magnetic-dipole transitions in magnetic ions. However, the exciton model used to describe the excited states of an AFD can be applied to the study of electric-dipole transitions, and this enables us to describe electric Davydov splitting (EDS) in an AFD both at the frequencies of single-ion optical transitions in ions and at the frequencies of pair optical transitions. A detailed account of the theory of EDS for an AFD will be given in a separate paper.

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