The rotation of the polarization plane of light, quadratic in the magnetic field strength, and circular dichroism are observed in two-sublattice tetragonal noncentrosymmetrical antiferromagnetic crystals CoF$_2$ and FeF$_2$. Experiments were carried out on antiferromagnetically homogeneous samples. The effects change their signs with the reversal of the antiferromagnetic vector direction. Quadratic rotation constants are measured to be $1.3 \times 10^{-2}$ deg/cm-Oe$^2$ for CoF$_2$ and $(7.0 \pm 1.5) \times 10^{-6}$ deg/cm-Oe$^2$ for FeF$_2$ for light propagating along the tetragonal [001] axis, with the light wavelength being 6328 Å and a magnetic field oriented along the [110] direction. It was shown experimentally that the spectra of linear and quadratic in H magnetic circular dichroism differed qualitatively. The former was obtained for $H \parallel k \parallel [001]$ and the latter for $k \parallel [001], H$.

I. INTRODUCTION

The crystal magnetic subsystem ordering results in new allowed optical effects symmetry forbidden in magnetically disordered media [1]. Among such effects are an even-parity in the magnetic field strength nonreciprocal rotation of the polarization plane of light and related circular dichroism. Both effects must not change their signs with the reversal of the magnetic field direction, but are to change them with the inversion of the directions of all the crystal elementary magnetic moments. The appearance of these effects in media nonsymmetrical with respect to the anti-inversion operation $A = 1 \cdot 1$ was reported [2], [3]. The possibility of magnetic gyration quadratic in field follows from generalized to magnetically ordered media Onsager relations for kinetic coefficients [4] which lift the prohibition against the H-even in terms of the expansion of antisymmetric dielectric tensor components

$$\varepsilon_{ij}^a = f_{ij} \cdot \mathbf{H} + f_{ij\gamma} \cdot H_\gamma \cdot H_\beta$$

(Gyration properties, quadratic in $H$, can be described by a fourth-rank polar c-tensor $F_{ijk\delta}$, antisymmetric in the first pair of indices and symmetric in the second one, or by dual to it third-rank axial c-tensor $G_{ijk\delta} = e_{ijk\delta} \cdot F_{ijk\delta}$. The linear magneto-optic effect (linear in a magnetic field birefringence $b$ linearly polarized light) [2] is also described by a third-rank axial c-tensor $q_{ijk\delta}$). But since the symmetries of $G_{ijk\delta}$ and $q_{ijk\delta}$ about the permutation of indices are different, the coincidence of magnetic classes of crystals where these effects are allowed is not complete. The $G_{ijk\delta}$ tensor is symmetric with respect to the permutation of all indices. Both tensors vanish in centroantisymmetric crystals having the anti-inversion center $\overline{1}$ among operations of the magnetic point group and in crystal classes 432, 43m, m3m without the anti-inversion center. Besides, $G_{ijk\delta}$ becomes zero in crystals with symmetries 422, 4mm, 42m, 4/mmm, 622, 6mm, 6m2 and 6/mm where the linear magneto-optic effect is allowed. The $G_{ijk\delta}$ tensor is allowed in 27 antiferromagnetic crystal classes in which quadratic in $H$ magnetization is allowed [5].

In the present work quadratic in field rotation of the polarization plane of light and circular dichroism are reported to be observed experimentally in antiferromagnetic (APM) crystals. The well studied two-sublattice APM CoF$_2$, FeF$_2$ and MnF$_2$, were taken as objects under investigation. The structure of these fluorides is described by the magnetic symmetry point group $D_{4h}$. The absence of the symmetry center in ligand surroundings of magnetic ions belonging to different sublattices of a magnetically ordered crystal results in the lift of the prohibition against the existence of nonzero components $G_{xxy} = G_{xzy} = G_{yxz}$. 

ABSTRACT

The rotation of the polarization plane of light, quadratic in the magnetic field strength, and circular dichroism are observed in two-sublattice tetragonal noncentrosymmetrical antiferromagnetic crystals CoF$_2$ and FeF$_2$. Experiments were carried out on antiferromagnetically homogeneous samples. The effects change their signs with the reversal of the antiferromagnetic vector direction. Quadratic rotation constants are measured to be $1.3 \times 10^{-2}$ deg/cm-Oe$^2$ for CoF$_2$ and $(7.0 \pm 1.5) \times 10^{-6}$ deg/cm-Oe$^2$ for FeF$_2$ for light propagating along the tetragonal [001] axis, with the light wavelength being 6328 Å and a magnetic field oriented along the [110] direction. It was shown experimentally that the spectra of linear and quadratic in H magnetic circular dichroism differed qualitatively. The former was obtained for $H \parallel k \parallel [001]$ and the latter for $k \parallel [001], H$. 

I. INTRODUCTION

The crystal magnetic subsystem ordering results in new allowed optical effects symmetry forbidden in magnetically disordered media [1]. Among such effects are an even-parity in the magnetic field strength nonreciprocal rotation of the polarization plane of light and related circular dichroism. Both effects must not change their signs with the reversal of the magnetic field direction, but are to change them with the inversion of the directions of all the crystal elementary magnetic moments. The appearance of these effects in media nonsymmetrical with respect to the anti-inversion operation $1 = 1 \cdot 1$ was reported [2], [3]. The possibility of magnetic gyration quadratic in field follows from generalized to magnetically ordered media Onsager relations for kinetic coefficients [4] which lift the prohibition against the H-even in terms of the expansion of antisymmetric dielectric tensor components

$$\varepsilon_{ij}^a = f_{ij} \cdot \mathbf{H} + f_{ij\gamma} \cdot H_\gamma \cdot H_\beta$$

(Gyration properties, quadratic in $H$, can be described by a fourth-rank polar c-tensor $F_{ijk\delta}$, antisymmetric in the first pair of indices and symmetric in the second one, or by dual to it third-rank axial c-tensor $G_{ijk\delta} = e_{ijk\delta} \cdot F_{ijk\delta}$. The linear magneto-optic effect (linear in a magnetic field birefringence $b$ linearly polarized light) [2] is also described by a third-rank axial c-tensor $q_{ijk\delta}$). But since the symmetries of $G_{ijk\delta}$ and $q_{ijk\delta}$ about the permutation of indices are different, the coincidence of magnetic classes of crystals where these effects are allowed is not complete. The $G_{ijk\delta}$ tensor is symmetric with respect to the permutation of all indices. Both tensors vanish in centroantisymmetric crystals having the anti-inversion center $\overline{1}$ among operations of the magnetic point group and in crystal classes 432, 43m, m3m without the anti-inversion center. Besides, $G_{ijk\delta}$ becomes zero in crystals with symmetries 422, 4mm, 42m, 4/mmm, 622, 6mm, 6m2 and 6/mm where the linear magneto-optic effect is allowed. The $G_{ijk\delta}$ tensor is allowed in 27 antiferromagnetic crystal classes in which quadratic in H magnetization is allowed [5].

In the present work quadratic in field rotation of the polarization plane of light and circular dichroism are reported to be observed experimentally in antiferromagnetic (APM) crystals. The well studied two-sublattice APM CoF$_2$, FeF$_2$ and MnF$_2$, were taken as objects under investigation. The structure of these fluorides is described by the magnetic symmetry point group $D_{4h}$. The absence of the symmetry center in ligand surroundings of magnetic ions belonging to different sublattices of a magnetically ordered crystal results in the lift of the prohibition against the existence of nonzero components $G_{xxy} = G_{xzy} = G_{yxz}$.
In the crystals studied the most easily detected quadratic effects of magnetic gyration can manifest themselves by the polarization plane rotation or dichroism of the circularly polarized light propagating along the \( C_2 \) -axis in a field \( H \) \([110]\). Similar geometry was used in experiments. The experimental geometry \( k \parallel C_2 \perpendicular H \) is favorable since linear in \( H \) magnetic rotation of the polarization plane of light (the Faraday effect) and related circular dichroism are absent in it. The linear magneto-optic effect does not manifest itself in this geometry either. The latter can lead to splitting of the optical axis due to the appearance of components \( C_{XZ} \) and \( C_{YX} \) in the dielectric tensor, but in this case the rotation of the indicatrix axis \( X_1 \) occurs so that one of the optical axes remains coincident with the \( C_2 \) -axis. Magnetic birefringence of the linearly polarized light due to the Cotton-Mouton effect would give rise to some experimental difficulties. But the influence of the linear birefringence on the polarization plane rotation can be eliminated by using a proper procedure. The problem was substantially simplified also by the fact that the values and signs of the linear birefringence due to the linear magneto-optic effect do not manifest themselves by the value of magnetic linear dichroism in the exciton-magnon absorption related to symmetry requirements.

All the experiments should be performed with homogeneously ordered AFM samples. Quadratic in \( H \) magnetization which is also susceptible to the crystal states with opposite orientations of magnetic sublattices \([5]\) was used for the sample monodomainization and remagnetization of its AFM state. In a field \( H \parallel [110] \) AFM crystals of the type of \( \text{CoF}_2 \), are magnetized along the \( C_6 \) -axis. The sign of \( M_z \) is unambiguously connected with the direction of the AFM vector \( \mathbf{L} = \mathbf{M}_z - \mathbf{M}_\perp \). An additional field applied along the \( z \)-axis results in energy inequivalence of time-reversed AFM states: \( \mathbf{B}^+ - \mathbf{B}^- = C_{XZ} H_x H_y H_z \). If \( \mathbf{B}^+ - \mathbf{B}^- \) achieves a critical value defined by coercitivity of an AFM domain wall, the wall motion results in an increase of the AFM domain, more efficient in energy. In such a way AFM samples of cobalt, iron and manganese fluorides can be monodomainized and remagnetized. A required component of a field \( H_z \) was obtained with an additional solenoid. Homogeneity of the AFM state of samples \( \text{CoF}_2 \) and \( \text{FeF}_2 \) was checked visually by the linear magneto-optic effect which permitted visualizing the AFM \( 180^\circ \) -domains in a longitudinal \( (H \parallel C_6) \) magnetic field of 5 kOe for \( \text{CoF}_2 \) and 15 kOe for \( \text{FeF}_2 \). A small value of the linear magneto-optic effect did not make it possible to visualize AFM domains in \( \text{MnF}_2 \). Homogeneity of the AFM state in \( \text{MnF}_2 \) can be evidenced by the value of magnetic linear dichroism in the exciton-magnon absorption related to the linear magneto-optic effect.

3. RESULTS AND DISCUSSION

Fig.1 shows the results of the polarization plane rotation of the linearly polarized light propagating along the \( C_2 \) -axis in a \( \text{CoF}_2 \) sample in both AFM+ and AFM− states. A magnetic field is applied along \([110]\), \( T = 15 \) K, \( t = 0.5 \text{mm}, \lambda = 6328 \AA \). Solid lines indicate the dependences \( \Phi = \pm RH^2 \) describing the experiment well. At \( T = 0 \) K the constant \( R \) is equal to \( 1.4 \times 10^{-8} \text{deg/cm.Oe}^2 \). Similar dependences are obtained for \( \text{FeF}_2 \). For this crystal the quadratic rotation constant is \( (7.0 \pm 1.5) \times 10^{-10} \text{deg/cm.Oe}^2 \). In \( \text{MnF}_2 \) the quadratic rotation is not observed for the experimental sensitivity about \( 10^{-11} \text{deg/cm.Oe}^2 \). The temperature dependence of the rotation in Fig.2 indicates the disappearance of the effect at the transition of \( \text{CoF}_2 \) and \( \text{FeF}_2 \) crystals to the paramagnetic state. The effect disappears in a AFM crystal as well in a field oriented along \( H \parallel [100] \) due to symmetry requirements.

Of some interest is comparison between quadratic and linear in \( H \) rotations normalized to the same value of \( z \)-projections of linear and quadratic magnetizations. If a crystal is considered to be affected by magnetic vectors of ferromagnetism \( \mathbf{M} \) and antiferromagnetism \( \mathbf{L} \) rather than by a magnetic field, the non-zero component of the quadratic magnetic gyration vector can be expressed as the sum.
For the z-projection of quadratic magnetization similar expression can be written according to [6] as follows

\[
\psi_{z}^{\text{quad}} = G_{zxy} \cdot H_{x} H_{y} = G_{zxy}^{(LL)} L_{x} L_{y} L_{z} + G_{zxy}^{(ML)} M_{x} M_{y} L_{z}
\]

(2)

Hence, the rotation of the quadratic rotation, quadratic magnetization and magnetic vectors \( \vec{M} \) and \( \vec{L} \) can be of the form

\[
\Phi_{z}^{\text{quad}}/\ell = B^{\text{(M)}} M_{z}^{\text{quad}} + \alpha L_{x} L_{y} L_{z} + \beta M_{x} M_{y} L_{z}
\]

(3)

The presence of two last terms in Eq. (4) shows that the quadratic rotation can appear at \( M_{z}^{\text{quad}} = 0 \) as well. If \( \alpha = 0 \) and \( \beta = 0 \) we obtain \( B^{\text{(M)}} = 2.0 \text{ deg/cm·CGSM} \) units at \( T = 4.2 \text{ K} \) when \( C_{zxy} = 6.8 \times 10^{-7} \text{ CGSM/Oe}^{2} \). The value of \( C_{zxy} \) is found from [7] where \( M_{z} = 360 \text{ CGSM/mol} \) at \( H_{[110]} = 50 \text{kOe} \). The proportionality factor \( V^{\text{(M)}} \) which relates the rotation and magnetization in the experimental Faraday geometry

\[
\Phi_{z}^{\text{quad}}/\ell = V^{\text{(M)}} M_{z}
\]

(5)

appeared to be equal to 2.4 deg/cm·CGSM units. The calculation was performed using magnetic susceptibility \( \chi_{z}^{X} = 6.0 \times 10^{-4} \text{ CGSM units/cm}^{3} \) [8]. The values of \( B^{\text{(M)}} \) and \( V^{\text{(M)}} \) are similar. Moreover, the possibility of their equality cannot be ruled out since errors related with using different results can be essential. It should be noted that the equality of \( B^{\text{(M)}} \) and \( V^{\text{(M)}} \) can be only approximate or accidental since in these cases the nature of the appearance of magnetization and energy level perturbation of a crystal is different. This difference is clearly observed in the spectra of magnetic circular dichroism obtained for both experimental geometries.

In CoF$_{2}$ dichroism was measured in the visible spectrum on the absorption band frequencies due to exciton-magnon and some other collective excitations of the 3d-shell of Co$^{2+}$ ions. Figs. 3 and 4 show the circular dichroism spectra recorded at \( \vec{H} \parallel [110] \) and \( \vec{H} \parallel [001] \) for \( \vec{H} \parallel [001] \). (Dashed lines indicate absorption spectra). In both cases AFM states and z-projection signs of magnetic moments \( M_{z} = X_{z} H_{z} \) and \( M_{z}^{\text{quad}} = C_{zxy} \cdot H_{x} H_{y} \) were consistent. Experiments were performed on the AFM state which during monodomainization occupied the entire sample for the given transverse field \( \vec{H} \parallel [110] \) direction and for the applied additional longitudinal field \( \vec{H} \parallel [001] \). It can be seen in the spectra obtained that the signs of linear and quadratic in \( H \) magnetic circular dichroism \( (\psi_{z} - \psi_{-z})/(\psi_{z} + \psi_{-z}) \) are different in the exciton-magnon band at 22 769 cm$^{-1}$ and 13 283 cm$^{-1}$ and 23 047 cm$^{-1}$. Besides the dichroism band spectra near 22 900 cm$^{-1}$ are different. It should be also noted that the spectrum of magnetic circular dichroism of the exciton-magnon band at 22 769 cm$^{-1}$ appeared more complicated than that reported earlier [9]. Quadratic dichroism dispersive curves show that the main mechanism of the dichroism origin is the removal of sublattice degeneracy and absorption band splitting.

The difference between the linear and quadratic in \( H \) spectra of magnetic circular dichroism is more prominent under simultaneous actions of the transverse and longitudinal field components. Fig. 5 shows the dichroism spectrum evolution with an increase in the field z-component. At \( H_{z} \approx 5 \text{kOe} \) and \( H_{[110]} = 24 \text{kOe} \).
the dichroism compensation occurs during the transition at 23 047 cm\(^{-1}\) and 13 283 cm\(^{-1}\). An incomplete compensation revealing the band structure is observed in the exciton-magnon absorption at 22 769 cm\(^{-1}\). The above results indicate that at the inclined field direction when both components \(H_2\) and \(H_{[110]}\) are nonzero, dichroism and rotation of the polarization plane can be nonlinearly dependent on magnetization in relatively weak fields. In such weak fields the linear relation of magnetization and dichroism (or the rotation of the polarization plane of light) still exists at symmetry field orientations along [001] or [110].

4. CONCLUSION

The experiments described above showed that the quadratic magnetic rotation and circular dichroism in AFM can be of easily measurable value. Susceptibility of these effects to the crystal magnetic structure symmetry and to the reversal of the directions of elementary magnetic moments makes them attractive for defining the magnetic point symmetry of multisublattice AFM and for visualization of time-reversed AFM domains. Undoubtedly, quadratic magnetic dichroism spectra can be useful for the identification of transitions in the AFM optical spectra.

REFERENCES