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MAGNETOOPTICAL EFFECT IN JAHN-TELLER CRYSTALS WITH KRAMERS RARE-EARTH IONS

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The investigation of the Faraday effect in $DyVO_4$-type Jahn-Teller crystals, containing two Kramers doublets E' and E'' in the low-energy part of the electron spectrum, is performed. The components of the tensor of linear magnetooptical effect are obtained in the mean field approximation. The ionic contributions into the effect are separated, the features of their temperature dependencies are studied. The estimate of the so-called crystalline contributions into the Faraday effect is performed. It is shown that the crystalline contributions increase and can be of the same order as the ionic one when we approach to the absorption edge.

One of the most topical problems of physics is the investigation of the structural phase transitions (SPT) which are interesting both theoretically and from the point of view of searching for the new physical effects promising in their practical use.

The investigators attention is increasingly drawn by the SPT in which Jahn-Teller effect is evident. Such transitions are observed, particularly in the rare-earth vanadate crystals. The change of the lattice symmetry in the crystals of this type is accompanied by the homogeneous deformation and considerable restructuring of the electron subsystem which results, as a rule, in the anomalies of their elastic, magnetic and optical properties [1–4]. The microscopic theory of the magnetooptical effect in dielectric ionic crystals was developed in [5,6]. The methods suggested in them is used in this paper to investigate the Faraday effect in Jahn-Teller crystals of the $DyVO_4$ type with Kramers rare-earth ions.

The linear magnetooptical effect is described by the component of the tensor of dielectric permeability proportional to the external magnetic field $\vec{H}$. For tensor $\varepsilon_{\alpha\beta}(\omega)$ as a starting we assume the expression in terms of the two time retarding Green functions $\langle\langle \hat{P}^{\alpha}|\hat{P}^{\beta}\rangle\rangle_{0,\omega}$, were

$$\hat{P}^{\alpha} = \sum_{n,k}(e\hat{D}^{\alpha}_{nk} + z_k u^{\alpha}_{nk}) \tag{1}$$

is the operator of the total electric dipole moment of the crystal ($\alpha = x, y.z$) which includes electric and ionic components.

$$\hat{D}^{\alpha}_{nk} = \sum_{ss'} \mu^{ss'}_{k\alpha} \hat{X}^{ss'}_{nk} \tag{2}$$

is the operator of the electron dipole moment of the ion k in the unit cell n; $\hat{X}_{nk}^{ss'}$ are the Hubbard operators acting in the space of s electron states of the k-th ion; $\mu_{k\alpha}^{ss'}$ are the corresponding matrix elements; u_{nk}^{α} are the vector components of ionic displacements; e, z_k are the electron and ion charges, respectively.

In the Hamiltonian of the problem, the electronic excitations of separate ions, their multipole interactions both with each other and with the lattice deformation, phonon vibrations as well as the interaction of the crystal with the external magnetic field were taken into account. The investigations were carried out at the frequencies corresponding to the crystal transparence region near the short-wave absorption edge. In this case one can only deal with the electron components of the Green function. The function

$$\langle\langle \hat{P}^{\alpha}|\hat{P}^{\beta}\rangle\rangle_{0,\omega} = e^2 \sum_{kk'} \langle\langle D_k^{\alpha}|D_{k'}^{\beta}\rangle\rangle_{0,\omega} \tag{3}$$

is determined using the equations of motion, decoupled in the random phase approximation. As a result, for the component of the tensor of the linear magnetooptical effect the following expression is achieved:

$$B_{\alpha\beta,\delta}^{\text{ion}}(\omega) = -\frac{8\pi^2 e^2}{\hbar v} \sum_{kk'} (G'_{\delta})_{kk'}^{\alpha\beta} \tag{4}$$

where $\hat{G}'_{\delta} = \frac{1}{i}(\frac{\partial}{\partial H_{\delta}}\langle\langle \hat{D}|\hat{D}\rangle\rangle)_{H_{\delta}=0}$. It is shown that apart from the main ion contributions $B_{\alpha\beta,\delta}^{\text{ion}}(\omega)$ in Faraday effect caused by the change of the electron dipole susceptibility of ions

$$Z_{\alpha\beta}^{k}(\omega) = \sum_{\nu\nu'} \frac{\tilde{\mu}_{k\alpha}^{\nu\nu'}\tilde{\mu}_{k\beta}^{\nu'\nu}}{\hbar\omega - \tilde{\lambda}_{k\nu'} + \tilde{\lambda}_{k\nu}} \langle \tilde{X}_k^{\nu\nu} - \tilde{X}_k^{\nu'\nu'}\rangle \tag{5}$$

under the influence of the magnetic field there exist additional, so-called crystal, contributions, connected with the interactions of the electronics dipole and quadrupole moments of neighbouring ions ($\tilde{\lambda}_{\nu}$ is the energy of the electron state of $|\nu\rangle$ in the crystal field).

It should be noted that ionic contributions $B_{\alpha\beta,\delta}^{\text{ion}}$, in which the crystal field effect is taken into account, are, as in the case of isolated molecules [7], the sum total of three components caused by

1) the change of the wave functions of electronic states

$$B_{\alpha\beta,\delta}^{(1)\text{ion}}(\omega) = -\frac{4\pi e^2}{iv} \sum_{k} \sum_{\nu\nu'} \frac{\partial}{\partial H_{\delta}} \left(\tilde{\mu}_{k\alpha}^{\nu\nu'}\tilde{\mu}_{k\beta}^{\nu'\nu}\right)_0 \frac{\langle X_k^{\nu\nu} - X_k^{\nu'\nu'}\rangle}{\hbar\omega - \tilde{\lambda}_{k\nu'} + \tilde{\lambda}_{k\nu}} \tag{6}$$

2) the change of the energy spectrum

$$B_{\alpha\beta,\delta}^{(2)\text{ion}}(\omega) = -\frac{4\pi e^2}{iv} \sum_{k} \sum_{\nu\nu'} \tilde{\mu}_{k\alpha}^{\nu\nu'}\tilde{\mu}_{k\beta}^{\nu'\nu}) \frac{\langle X_k^{\nu\nu} - X_k^{\nu'\nu'}\rangle}{(\hbar\omega - \tilde{\lambda}_{k\nu'} + \tilde{\lambda}_{k\nu})^2} \frac{\partial}{\partial H_{\delta}} \left(\tilde{\lambda}_{k\nu'} - \tilde{\lambda}_{k\nu}\right)_0 \tag{7}$$

3) the change of the population of electron levels

$$B^{(3)\text{ion}}_{\alpha\beta,\delta}(\omega) = -\frac{4\pi e^2}{iv}\sum_k\sum_{\nu\nu'}\frac{\tilde{\mu}^{\nu\nu'}_{k\alpha}\tilde{\mu}^{\nu'\nu}_{k\beta}}{\hbar\omega - \tilde{\lambda}_{k\nu'} + \tilde{\lambda}_{k\nu}}\frac{\partial}{\partial H_\delta}\left\langle \tilde{X}^{\nu\nu}_k - \tilde{X}^{\nu'\nu'}_k\right\rangle_0 \quad (8)$$

The $DyVO_4$-type crystals in the high-temperature phase have a tetragonal structure with the space symmetry D^{19}_{4h}. The unit cell contains two ions Dy^{3+} connected by the inversion operation and posses D_{2d} site symmetry. At the decreasing of temperature ($T_c \approx 14$ K) the crystals turn into the orthorhombic phase with the appearance of the spontaneous deformation u_{xy} of the B_{1g} symmetry (here the system of co-ordinates turned at $\pi/4$ around the z axe in relation to the crystallographic axes of lattice is used). The low-energy part of the electron spectrum of Dy^{3+} ions consists of two Kramers doublets $E', E''(\Gamma_3, \Gamma_6)$ the distance between which is $\Delta \sim 9$ cm^{-1}.

Let us consider the magnetooptical effect in the crystals with the above pattern of the electronic states of the active ions when the magnetic field is directed along the z axe. The mean field Hamiltonian has the following expression on the basis of wave-functions of the doublets E' and E'':

$$\hat{H}_{MF} = \left\| \begin{array}{cccc} \lambda_{E'} + h^z_1 & & -i\eta & \\ & \lambda_{E'} - h^z_1 & & i\eta \\ i\eta & & \lambda_{E''} + h^z_2 & \\ & -i\eta & & \lambda_{E''} - h^z_2 \end{array} \right\| \quad (9)$$

where $\eta = \mu F_z + qP_{xy}$ is the parameter characterising the internal fields F_z and P_{xy} influenced on the electronic dipoles and quadrupoles, respectively; $h^z_1 = \frac{e}{2mc}m^{E'E'}_z H_z$, $h^z_2 = \frac{e}{2mc}m^{E''E''}_z H_z$; μ, q, $m^{\nu\nu'}_z$ are the matrix elements of the dipole, quadrupole and magnetodipole moments, respectively. The upper unpopulated electron levels as well as the influence of the magnetic field on them is not taken into account.

The eigenvalues of the mean-field Hamiltonian (9)

$$\tilde{\lambda}_{1,2} = \frac{\lambda_{E'} + h^z_1 + h^z_2 + \lambda_{E''}}{2} \pm \sqrt{\left(\frac{\lambda_{E'} + h^z_1 - h^z_2 - \lambda_{E''}}{2}\right)^2 + \eta^2} \quad (10)$$

$$\tilde{\lambda}_{3,4} = \frac{\lambda_{E'} - h^z_1 - h^z_2 + \lambda_{E''}}{2} \pm \sqrt{\left(\frac{\lambda_{E'} - h^z_1 + h^z_2 - \lambda_{E''}}{2}\right)^2 + \eta^2} \quad (11)$$

show that the H_z field splits the doublets E', E'' eliminating spin degeneration. They cause the contributions (7), (8) into the magnetooptical effect (population of the sublevels of the doublets E' and E'' are determined as $\langle \tilde{X}^{\nu\nu}\rangle = e^{-\beta\tilde{\lambda}_\nu}/\sum_{\nu'} e^{-\beta\tilde{\lambda}_{\nu'}}$).

To calculate the contribution (6) let us introduce an unitary matrix $\hat{U}$. By solving the system of equations

$$\begin{cases} \hat{U}\hat{H}_{MF}\hat{U}^{-1} = \hat{\tilde{H}}_{MF} \\ \hat{U}\hat{U}^{-1} = \hat{1} \end{cases} \quad (12)$$

we come to a new wave function basis corresponding the diagonal Hamiltonian H_{MF} which determines the matrix elements of the electron dipole moments changed by the magnetic field

$$\hat{\tilde{\mu}}_\alpha = \hat{U}\hat{\mu}_\alpha\hat{U}^{-1} \quad (13)$$

The temperature and field dependencies of parameter η, which is included into the expressions for eigenvalues and components of the unitary matrix U, are determined from the minimum of the crystal free energy.

As the result, the following expressions for components of the tensor of linear magnetooptical effect at $T > T_c$ have been obtained:

$$B^{(1)\mathrm{ion}}_{xy,z} = 0$$

$$B^{(2)\mathrm{ion}}_{xy,z}(\omega) = \sum_\alpha C_\alpha(\omega) I^{(2)}_\alpha(\omega) \frac{1}{Z} e^{-\beta\lambda_\alpha} \tag{14}$$

$$B^{(3)\mathrm{ion}}_{xy,z}(\omega) = \beta \sum_\alpha C_\alpha(\omega) I^{(3)}_\alpha(\omega) \frac{1}{Z} e^{-\beta\lambda_\alpha} \tag{15}$$

where $C_\alpha(\omega) = 4\pi e^3 \hbar\omega m^{\alpha\alpha}_z/(mcv)$; $Z = \sum_\alpha e^{-\beta\lambda_\alpha}$; $\alpha = E', E''$.

Factors $I_\alpha(\omega)$ describe electron dipole transitions from the occupied states α into the symmetry allowed upper free states and have the following from

$$I^{(2)}_\alpha(\omega) = \sum_n \frac{|\mu^{\alpha n}_x|^2(\lambda_n - \lambda_\alpha)}{[\hbar^2\omega^2 - (\lambda_n - \lambda_\alpha)^2]^2}; \quad I^{(3)}_\alpha(\omega) = \sum_n \frac{|\mu^{\alpha n}_x|^2}{\hbar^2\omega^2 - (\lambda_n - \lambda_\alpha)^2} \tag{16}$$

In the transparence region near the short-wave absorption edge the following estimates $I^{(2)}_\alpha(\omega) \ll \beta I^{(3)}_\alpha(\omega)$ and $I^{(3)}_{E'} \approx I^{(3)}_{E''} \equiv I_3$ are obtained for the wide temperature range (when $kT \ll \lambda_n - \lambda_E$). Therefore, the magnetooptical effect is, in general, determined by the contribution (15).

In the low-temperature phase ($T < T_c$) all contributions (6)-(8) are nonzero but the main are only two of them

$$B^{(1)\mathrm{ion}}_{xy,z}(\omega) = \frac{2C(\omega)}{W^2} I_1(\omega)\eta_0 \sin(2\varphi_0)\, \mathrm{th}\left(\frac{1}{2}\beta W\right) \tag{17}$$

and

$$B^{(3)\mathrm{ion}}_{xy,z}(\omega) = \frac{\beta C(\omega)}{W} I_3(\omega)(\lambda_{E''} - \lambda_{E'}) \tag{18}$$

where $W = \sqrt{(\lambda_{E''} - \lambda_{E'})^2 + 4\eta_0^2}$, $\varphi = \frac{1}{2}\,\mathrm{arctg}\,\frac{2\eta_0}{\lambda_{E''} - \lambda_{E'}}$, $\eta_0 = \tilde{t}(B_{1g})\langle q_0\rangle$, $\tilde{t}(B_{1g})$ is the quadrupole-quadrupole interaction constant renormalized due to the lattice deformation as well as dipole interaction; $\langle q_0\rangle$ is the averaged quadrupole moment (the order parameter) determined from the minimum of the lattice free energy.

In fig. 1 the temperature dependencies of the reduced component $\tilde{B}^{\mathrm{ion}}_{xy,z}(T) = \left(B^{(1)\mathrm{ion}}_{xy,z} + B^{(3)\mathrm{ion}}_{xy,z}\right) / \left(B^{(1)\mathrm{ion}}_{xy,z} + B^{(3)\mathrm{ion}}_{xy,z}\right)_{T_c}$ calculated at $\tilde{t}(B_{1g}) = 11.2\ \mathrm{cm}^{-1}$, $\lambda_{E''} - \lambda_{E'} = 9\ \mathrm{cm}^{-1}$, $T_c = 14$ K [8] and for different values of I_1/I_3 are shown. At $T > T_c$ the component $\tilde{B}^{\mathrm{ion}}_{xy,z}(T)$ decreases monotonously. In the low-temperature phase the component $\tilde{B}^{\mathrm{ion}}_{xy,z}(T)$ achieves minimum for $I_1/I_3 < 1$ and increases monotonously for $I_1/I_3 \geq 1$ with the temperature decrease. In the vicinity of T_c function $\tilde{B}^{\mathrm{ion}}_{xy,z}(T)$ possess peak-like anomaly.

The obtained temperature and frequency dependencies of $\tilde{B}^{\mathrm{ion}}_{xy,z}(\omega, T)$ components for $DyVO_4$ crystals are in qualitative agreement with the results

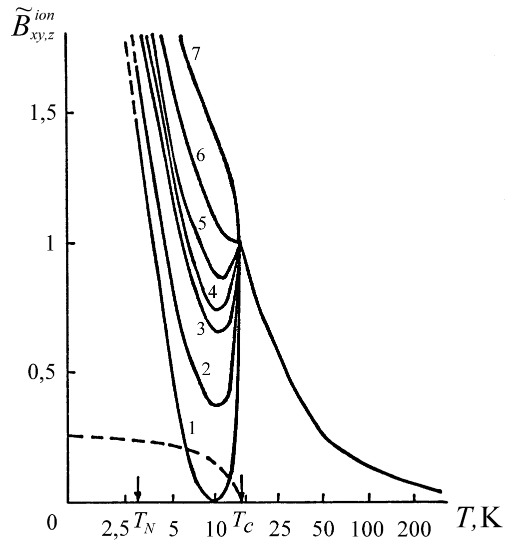

Figure 1. Temperature dependence of the $\tilde{B}^{\rm ion}_{xy,z}$ components for $DyVO_4$ crystals at different $N = I_1/I_3$ ratio values: (1) $N = -2$; (2) $N = -1$; (3) $N = 0$; (4) $N = 0.2$; (5) $N = 0.5$; (6) $N = 1$; (7) $N = 2$. Dashed line corresponds to the $B^{(1)\rm ion}_{xy,z}$ contribution.

of the experimental investigations of $KMnF_3$ crystals which also possess SPT [9]. At $T = T_c$ the dependence $\tilde{B}^{\rm ion}_{xy,z}(T)$ for $KMnF_3$ crystal has peak-like anomaly similar to the one presented by curves 1–3 in fig. 1.

The crystalline contributions in the Faraday effect for the rare-earth vanadate crystals are also analysed. It is shown that in transparence region of the $DyVO_4$ crystals at the frequencies distant by 2 eV and more from the short-wave absorption edge crystalline contributions is up to 50% of the ionic contribution and are caused mainly by the electronic dipole moment interactions. In the crystals with the non-Kramers rare-earth ions ($TbVO_4$, $TmAsO_4$, etc.) crystalline contributions are small and can be observed only in the close vicinity of the absorption edge.

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МАГНІТООПТИЧНИЙ ЕФЕКТ У ЯН-ТЕЛЛЕРІВСЬКИХ КРИСТАЛАХ З КРАМЕРСІВСЬКИМИ РІДКОЗЕМЕЛЬНИМИ ІОНАМИ

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Проведено дослідження ефекту Фарадея в ян-теллерівських кристалах типу $DyVO_4$, де низькоенергетична частина електронного спектра іонів Dy^{3+} містить два крамерсівські дублети E' та E''. В наближенні середнього поля одержано вирази для компонент тензора лінійного магнітооптичного ефекту, виділено іонні внески в ефект, вивчено особливості їх температурних залежностей. Проведено оцінку так званих кристалічних внесків у ефект Фарадея. Показано, що при наближенні до краю поглинання кристалічні внески зростають і можуть бути співвимірними з іонними внесками.