Nature of high magnetooptic activity of crystals with Fe^{3+} ions

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A disproportionately large Faraday effect of isolated octahedral FeO_6^{9-} complexes has been observed for the first time. It is explained theoretically. The approach taken here leads to a consistent description of the magnetooptic activity of paramagnetic and magnetically ordered crystals, including weak ferromagnets.

In an effort to explain the Faraday effect in magnetically ordered oxide crystals with Fe^{3+} ions, with a high magnetooptic activity, an experimental and theoretical study has been carried out to find the contributions from the magnetic moment of Fe^{3+} ions and from the effective magnetic fields acting on excited states of octahedral complexes. The magnetooptic activity constants of octahedral FeO_6^{9-} complexes in paramagnetic and magnetically ordered crystals are significantly higher than the corresponding constants for the Mn^{2+}, Gd^{3+}, and Eu^{2+} S ions. The theoretical work is based on the assumption that the Faraday effect stems from allowed electric dipole ${}^6A_{1g}-{}^6T_{1u}$ transitions with charge transfer. The anomalously large Faraday effect in weak ferromagnets stems from strong Dzyaloshinskiĭ–Moriya exchange-relativistic interactions, which are not manifested in the formation of the spin magnetic structure.

The Faraday effect of the octahedral FeO_6^{9-} complexes was measured on a $Ca_3Fe_{0.15}Ga_{1.85}Ge_3O_{12}$ single crystal, in which the Fe^{3+} ions occupy only octahedral positions, and the octahedral complexes can be assumed to be essentially noninteracting. It turns out that the Faraday effect increases in absolute value more rapidly than the magnetization with increasing magnetic field. Figure 1 shows the field dependence of the Faraday effect at $\omega = 3.1$ eV (solid line) and that of the magnetization (dashed line). Taking the gyromagnetic component $C_m m$ into account, we can thus write the Faraday effect as

$$\theta = (C_A + C_m)m + C_H H, \tag{1}$$

where H is the magnetic field, m is the reduced magnetization, and C_i are the magnetooptic activity constants. When referred to a concentrated $Ca_3Fe_2Ge_3O_{12}$ crystal, in which all the octahedral positions are occupied by Fe^{3+} ions, these constants can be approximately satisfactorily by

$$C_A = -(4{,}3 \pm 0.8) \cdot 10^5 \cdot F(\omega, \omega_A)\ \text{deg/cm},\ C_H = -(16 \pm 8)F(\omega, \omega_H)\ \text{deg/cm/kOe}$$

$$F(\omega, \omega_i) = \omega^2(\omega_i^2 - \omega^2)^{-2}, \tag{2}$$

where $\omega_A = 5.9$, $\omega_H = 3.5$ eV, and $C_m = 170 \pm 30$ deg/cm.

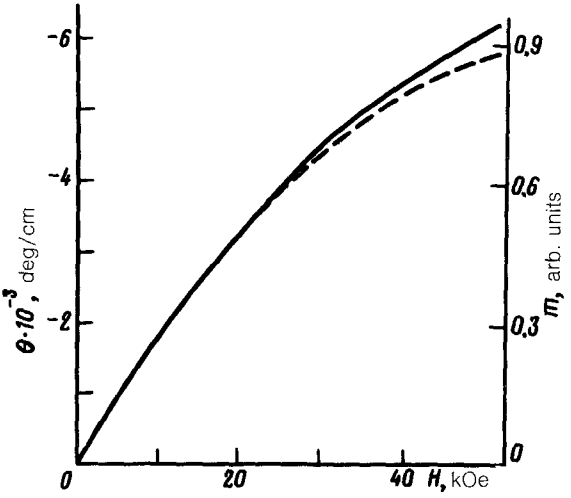

FIG. 1.

The value of the constant C_A per ion is more than an order of magnitude greater than C_A for the Gd^{3+} S ion,[1] which is an analog of the Fe^{3+} ion from the standpoint of the effect of the strongest allowed interconfigurational transitions on the formation of the Faraday effect. This circumstance is even more surprising, since the frequencies of the $3d$–$4p$ interconfigurational transitions in Fe^{3+} ions are at considerably higher energies than those of $4f$–$5d$ transitions in Gd^{3+} ions, and the values of the spin-orbit splitting in the excited states are about an order of magnitude smaller. Although the field component does correspond in order of magnitude to the Faraday effect in diamagnetic materials, its sign is unusual and cannot be explained on the basis of classical considerations. Specifically, according to the Becquerel formula, the magnitude of the Faraday effect would be proportional to the dispersion of the refractive index, $dn/d\omega$. At frequencies below the frequencies of the transitions which determine the refractive index, the sign of the rotation should be positive. The large value of the Faraday effect and the sign of the field component point to a strong effect of transitions with change transfer on the formation of the magnetooptic activity. The frequencies of the effective transitions, ω_A and ω_H, indicate the frequency region in which they lie.

In order to theoretically derive the parameters of the magnetooptic activity of a system of noninteracting octahedral FeO_6^{9-} complexes, we need to know the energies of the ${}^6A_{1g}$–${}^6T_{1u}$ transitions, the corresponding oscillator strengths f, and the half-widths of the transition lines, Γ, which determine the splitting and mixing of the ${}^6T_{1u}$ terms with an effective orbital angular momentum $L = 1$. The calculated transition energies[2] in orthoferrites agree well with Ref. 3, so the values of the parameters f and Γ can be found simultaneously through an analysis of optical absorption spectra. The positions of the charge-transfer bands depend strongly on the nature of the cation surroundings of the FeO_6^{9-} complexes. In the garnet $Ca_3Fe_2Ge_3O_{12}$, these bands lie at an energy 1.4 eV above those in orthoferrites. The values of g_L are determined by the comparable contributions of $3d$ electrons and $2p$ holes, and they may be substantially different (to the point of having the opposite sign!) from the classical value $g_L = 1$. A

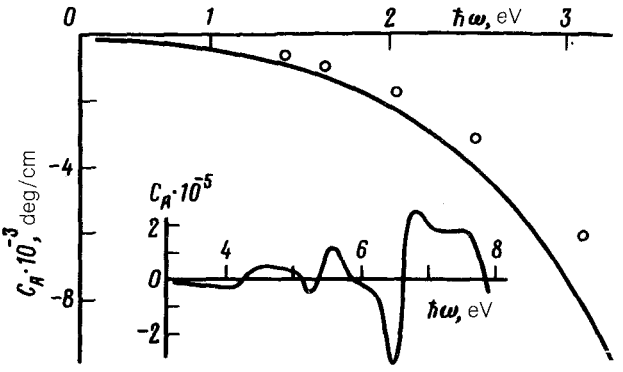

FIG. 2.

model-based calculation of the magnetooptic activity parameters of octahedral FeO_6^9 complexes in the paramagnet $Ca_3Fe_2Ge_3O_{12}$ has been carried out with allowance for splitting and mixing. Figure 2 shows experimental values and a theoretical functional dependence $C_A(\omega)$ in the long-wavelength region; the inset shows the same results directly in the region of the ${}^6A_{1g}-{}^6T_{1u}$ absorption band. The good agreement with the experimental values of C_A in the interval 1.4–3.1 eV is evidence in favor of model that we used. The agreement with experiment in terms of the parameters C_H is also completely satisfactory.

The calculation of the magnetooptic constants of isolated paramagnetic complex can be extended to magnetically ordered crystals. It has been found that the Faraday effect of the real antiferromagnetic garnet $Ca_3Fe_2Ge_3O_{12}$ is "constructed" from the constants of an isolated complex with a 10% error. In addition, a calculation of the components of the octahedral $Y_3Fe_5O_{12}$ sublattice yields the values $C_A(1\text{ eV}) = -3000$ deg/cm and $C_H(1\text{ eV}) = -0.5$ deg/(cm·kOe), in satisfactory agreement with the known experimental values $C_A = -2500$ deg/cm and $C_H = -0.3$ deg/(cm·kOe). The theoretical values of the quantity $d\theta/dH(2\text{ eV}) = C_A\chi_\perp + C_H$ ($\chi_\perp$ is the transverse susceptibility) for $YFeO_3$ (-6 deg/(cm·kOe) and for $FeBO_3$ (-5 deg/(cm·kOe) also agree satisfactorily with the experimental values [-3 deg/(cm·kOe)]. In all cases the negative sign of C_H is a consequence of the negative sign of the effective orbital g-factor for the ${}^6T_{1u}$ term, of lower energy.

For weak ferromagnets we would have $m \ll 1$, and the ferromagnetic component $C_A m$ of the Faraday effect would be small. In this case, a particular role would be played by the antiferromagnetic component, determined by the anisotropic interactions in charge-transfer states, in particular, the spin-orbit analog of the Dzyaloshinskiĭ–Mori interaction,

$$V = \sum_{m,n} \vec{\lambda}(m,n)[\mathbf{L}(m) \times \mathbf{S}(n)], \tag{3}$$

which is the only mechanism which can explain the nature of the Faraday effect in orthorhombic weak ferromagnets. The value of the orbital analog of the Dzyaloshinskiĭ field, $\mathbf{H}_D(L) \sim [\vec{\lambda} \times \langle \mathbf{S} \rangle]$, averaged over the various ${}^6T_{1u}$ terms, can be esti-

mated from

$$\theta = C_H H_D(L). \tag{4}$$

The effective field $H_D(L)$ is about an order of magnitude greater than the Dzyaloshinskiĭ spin field $H_D(S)$, since it is determined by the strong direct cation-anion exchange. This circumstance explains the anomalously high magnetooptic activity of weak ferromagnets. A preliminary analysis[4] of the spectra of the Kerr effect directly in the region of the ${}^6A_{1g}-{}^6T_{1u}$ absorption bands supports this conclusion.

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