

## Investigation of the Origin of the Anomalous Faraday Rotation of $\text{Bi}_x\text{Ca}_{3-x}\text{Fe}_{3.5+0.5x}\text{V}_{1.5-0.5x}\text{O}_{12}$ by Means of the Magneto-optical Kerr Effect

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(Received 18 January 1972)

The polar magneto-optic Kerr effect of  $\text{Bi}_{0.8}\text{Ca}_{2.2}\text{Fe}_{3.9}\text{V}_{1.1}\text{O}_{12}$  has been measured between 0.5 and 0.24  $\mu\text{m}$ . A strong magneto-optical transition is found at 0.47  $\mu\text{m}$  which is not observed in  $\text{Y}_3\text{Fe}_5\text{O}_{12}$ . This transition is concluded to be the origin of the anomalous large Faraday rotation of  $\text{Bi}_x\text{Ca}_{3-x}\text{Fe}_{3.5+0.5x}\text{V}_{1.5-0.5x}\text{O}_{12}$  recently reported and is interpreted as a charge transfer of an electron from an oxygen  $p$  orbital to an antibonding  $e$  orbital of the tetrahedral iron complex. The large rotation is attributed to a mixing of O and Bi orbitals.

It has recently been found<sup>1,2</sup> that for garnets of composition  $\text{Bi}_x\text{Ca}_{3-x}\text{Fe}_{3.5+0.5x}\text{V}_{1.5-0.5x}\text{O}_{12}$  (CaVBIG) with  $0.5 \leq x \leq 1$  the Faraday rotation for near infrared and visible radiation is much larger than for the rare-earth iron garnets like  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  (YIG). The experimental data on different crystals indicate that the Faraday rotation in this wavelength region, where the electric dipole part is predominant over the magnetic dipole part, increases linearly with the concentration of  $\text{Bi}^{3+}$  ions on the dodecahedral sites.<sup>1</sup>

This effect is surprising since previous experiments on garnets and other magnetic ferrioxides lead to the conclusion that this electric dipole part of the Faraday rotation is mainly determined by the  $\text{Fe}^{3+}$  ions and their local oxygen surroundings. The presence of other ions, e.g., different types of rare-earth ions or yttrium in the garnets<sup>3,4</sup> and orthoferrites,<sup>4</sup> or Li and Mg in the spinel ferrites<sup>5</sup> had little influence on this rotation. For these compounds a satisfactory explanation of the strong magneto-optical transitions occurring in the ultraviolet region, which are the origin of the Faraday rotation, can be given by using a molecular orbital model of  $\text{Fe}^{3+}$  oxygen complexes. Evidence for such an explanation, first suggested by Clogston,<sup>6</sup> was given by the magneto-optical Kerr-effect measurements of Kahn, Pershan, and Remeika.<sup>4</sup>

To investigate the anomalous behavior of CaVBIG we have measured the spectrum of its magneto-optical transitions at energies up to 5 eV, using the polar Kerr effect. Figure 1 shows the Kerr rotation spectrum of  $\text{Ca}_{2.2}\text{Bi}_{0.8}\text{Fe}_{3.9}\text{V}_{1.1}\text{O}_{12}$  between 0.6  $\mu\text{m}$  (2 eV) and 0.24  $\mu\text{m}$  (5.2 eV) in a saturating magnetic field. For comparison the

spectrum of YIG was also measured. The results for the latter crystal were in good agreement with those given previously by Kahn, Pershan, and Remeika.<sup>4</sup> The measurements were obtained with a Kerr spectrometer employing polarization modulation described elsewhere.<sup>7</sup> The accuracy of the measured rotations is about 0.001°.

The rotation maxima in these spectra indicate approximately the energies of optical transitions which are magneto-optically active, i.e., show a different response for left- and right-handed circular polarized light. It is more precise to state

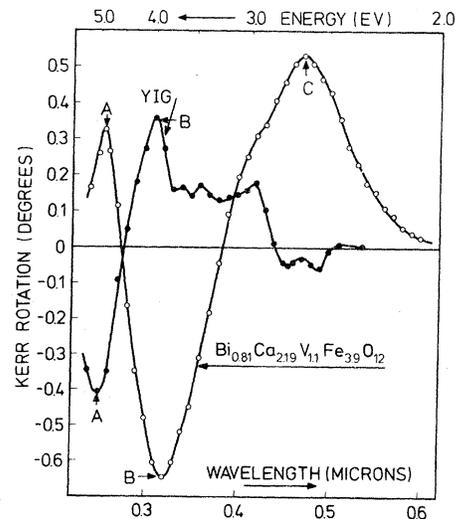


FIG. 1. Kerr rotation spectra of  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  and  $\text{Bi}_{0.81}\text{Ca}_{2.19}\text{V}_{1.1}\text{Fe}_{3.9}\text{O}_{12}$ . Rotation peaks A and B have in YIG the opposite sign compared with CaVBIG because of a different orientation of the sublattice magnetizations (see text).

that at the energies of these transitions  $\epsilon_1'$ , the imaginary part of the off-diagonal element  $i\epsilon_1$  of the dielectric tensor, shows a peak, but it has been found<sup>4,7</sup> that large peaks of the Kerr rotation are close to the maxima of  $\epsilon_1'$ .

When comparing the two spectra in Fig. 1 it must be realized that, in a saturating magnetic field, the magnetizations of the tetrahedral and octahedral iron sublattices in YIG are opposite to those of CaVBIG ( $x=0.8$ ). In YIG the magnetization of the tetrahedral ferric ions is predominant and aligns parallel to  $H_0$  whereas in CaVBIG ( $x=0.8$ ) the larger magnetization of the octahedral ions is parallel to the field.

It can be seen from Fig. 1 that the two transitions *A* and *B* which occur in YIG at 5 and 4 eV are also present in CaVBIG. While peak *A* is slightly lower in CaVBIG than in YIG ( $0.33^\circ$  and  $0.42^\circ$ ) peak *B* at 4 eV is much larger in CaVBIG ( $0.65^\circ$ ) than in YIG ( $0.33^\circ$ ). The most remarkable effect is, however, that in CaVBIG a strong transition *C* occurs at about 2.6 eV. In this energy region the YIG spectrum shows only a weak structure of low intensity.

This new transition *C* is especially interesting since it has recently been found<sup>1</sup> that the wavelength dependence of the Faraday rotation for  $\lambda > 0.53 \mu\text{m}$  can be explained by assuming a strong magneto-optical transition at about  $0.45 \mu\text{m}$  in CaVBIG. Therefore one can conclude that where-

as in YIG the long-wavelength Faraday rotation is caused by transitions in the ultraviolet region (4 and 5 eV) in CaVBIG this Faraday rotation is caused by a different type of transition in the visible spectral region at about 2.6 eV.

We will discuss the measured Kerr-effect spectra, especially the new transition *C* in CaVBIG, within the framework of the molecular orbital theory of  $\text{Fe}^{3+}$  oxygen complexes which has been reasonably successful<sup>4</sup> in explaining the Kerr-effect spectra of other magnetic ferric oxides. Figure 2 shows the qualitative energy-level scheme of both octahedral and tetrahedral  $\text{Fe}^{3+}$  oxygen complexes as derived from estimations of the overlap of the oxygen *p* orbitals ( $\sigma$  and  $\pi$ ) and the metal-ion  $3d$  and  $4s$  orbitals. Including higher metal orbitals like  $4p$  does not essentially change the scheme of Fig. 2 except for the occurrence of levels at higher energy which are not important for the present discussion. The schemes have been given earlier by several authors.<sup>8,9</sup>

The electric-dipole-allowed transitions in these complexes are of the charge transfer type in which an electron is transferred from an orbital mainly oxygen *p* in character, to a so-termed antibonding orbital mainly metal ion in character. For the present purpose it is sufficient to consider only the transitions to the lowest antibonding orbitals (marked by an asterisk in Fig. 2) having symmetry  $e_g^*$  or  $t_{2g}^*$  for the octahedral complex

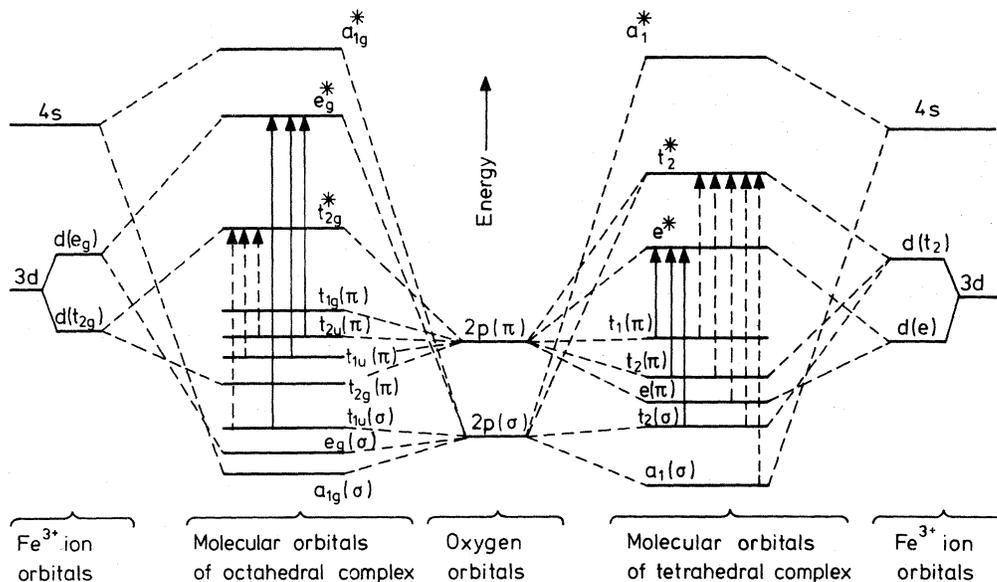


FIG. 2. Molecular orbitals of octahedral  $\text{FeO}_6$  and tetrahedral  $\text{FeO}_4$  complexes. The  $\sigma$  and  $\pi$  indications reflect the main origin of the antibonding and nonbonding orbitals. The dashed and solid arrows indicate allowed optical transition with, respectively, the antibonding  $t_2^*$  ( $t_{2g}^*$ ) or the  $e^*$  ( $e_{2g}^*$ ) levels as final states.

and  $e^*$  or  $t_2^*$  for the tetrahedral complex. The allowed transitions to these states are indicated by arrows in Fig. 2.

The magnetic circular dichroism and thus the Kerr rotation of such a transition is proportional to the effective spin-orbit coupling  $\zeta_{\text{eff}}$  of the final state, which is the sum of the spin-orbit coupling of the excited electron  $\zeta_{\text{el}}$  and that of the hole left behind in the oxygen orbital  $\zeta_{\text{hole}}$ :

$$\Phi_{\text{Kerr}} \sim \zeta_{\text{eff}} \sim \zeta_{\text{el}} + \zeta_{\text{hole}}. \quad (1)$$

First the Kerr spectrum of YIG will be discussed briefly with the aid of the level diagram in Fig. 2 and then the new rotations in CaVBIG.

In YIG the largest spin-orbit coupling occurs for electrons in a  $t_{2g}^*$  or  $t_2^*$  orbital where  $\zeta_{\text{el}} = 350 \text{ cm}^{-1}$  according to spectroscopic data.<sup>10</sup> The  $e_g^*$ ,  $e^*$ ,  $a_{1g}^*$ , and  $a_1^*$  orbitals have for symmetry reasons no orbital momentum so that  $\zeta_{\text{el}} = 0$ , while it can be argued that  $\zeta_{\text{hole}}$  for the oxygen  $p$  orbitals is considerably smaller than  $350 \text{ cm}^{-1}$ .<sup>4,6</sup> Consequently, for the Kerr-effect peaks of YIG we need to consider only the transitions to the  $t_{2g}^*$  and  $t_2^*$  levels, indicated by the dashed arrows.

The results of measurements of Kahn, Pershan, and Remeika<sup>4</sup> on rare-earth iron garnets with different concentrations of tetrahedral iron show that peak  $B$  of Fig. 1 corresponds to an octahedral transition while the peak  $A$  and the weaker peaks between 2.5 and 3.5 eV are from tetrahedral transitions. From the work of Ref. 4 it can be concluded that peak  $B$  corresponds to the transitions  $t_{2u}(\pi) \rightarrow t_{2g}^*$  or  $t_{1u}(\pi) \rightarrow t_{2g}^*$ , probably an overlapping combination of both. For the tetrahedral transitions no assignments have been given in Ref. 4. From the right-hand side of Fig. 2 it can be seen that a possible assignment is that the transition  $a_1(\sigma) \rightarrow t_2^*$  accounts for peak  $A$  (at 5 eV) whereas the other transitions to the  $t_2^*$  level account for the weaker peaks below 3.5 eV.

When considering CaVBIG one must question what the effect is of substituting  $\text{Bi}^{3+}$  for  $\text{Y}^{3+}$ . We suggest that an important effect can result from a mixing of the  $6p$  orbitals of the rather covalent bismuth ion with the oxygen orbitals. This mixing will lead to a strong increase of the spin-orbit coupling  $\zeta$  of an electron in an oxygen  $2p$  orbital due to the large spin-orbit coupling for bismuth  $6p$  electrons which is about  $17\,000 \text{ cm}^{-1}$  for the free ion.<sup>11</sup> Therefore  $\zeta_{\text{hole}}$  will contribute significantly to the total spin-orbit coupling  $\zeta_{\text{eff}}$  of the final state of a transition [see Eq. (1)] in CaVBIG, in contrast to the case of YIG. As a re-

sult, substitution of  $\text{Bi}^{3+}$  will have two effects: The Kerr rotations of the transitions found in YIG will change, but more important, some transitions which do not show resolvable Kerr rotation in YIG, for instance those having  $e_g^*$  or  $e^*$  as a final state (see Fig. 2) will do so for CaVBIG.

To explain with this effect the strong rotation peak  $C$  one should search in Fig. 2 for this type of transition at lower energies than the peaks found in YIG. The transitions  $t_1(\pi) \rightarrow e^*$  and  $t_2(\pi) \rightarrow e^*$  of the tetrahedral complex satisfy this requirement. We therefore suggest that the strong peak  $C$ , causing the long-wavelength Faraday rotation of CaVBIG can be assigned to one of these tetrahedral transitions. There is an indication in the experimental spectrum that peak  $C$  is split (note the weak change of slope at  $0.42 \mu\text{m}$ ) which is compatible with the idea of two transitions.

Within this model the difference between the Kerr rotation of the octahedral peak  $B$  in YIG and CaVBIG is attributed to an increase of  $\zeta_{\text{hole}}$  of the  $t_{1u}(\pi)$  and  $t_{2u}(\pi)$  oxygen orbitals due to mixing with the Bi  $6p$  orbitals. For the tetrahedral transition  $A$  (at 5 eV) we do not observe an appreciable increase of the rotation when comparing YIG and CaVBIG even if we account for the different concentration of tetrahedral iron. This is in agreement with the assignment of this peak to the  $a_1(\sigma) \rightarrow t_2^*$  transition, given before, since the  $a_1(\sigma)$  orbital has no orbital angular momentum and therefore no spin-orbit coupling, even when mixing with Bi orbitals occurs.

Obviously a rigorous proof of the suggested explanation can be given only after a molecular orbital calculation of both the iron-oxygen and bismuth-oxygen complexes have been given. Nevertheless the model presented above gives a rather natural explanation of the observed rotation spectra of CaVBIG since it is based upon existing theoretical and experimental evidence for YIG and there is no need of introducing new types of optical transitions as is necessary for other models.<sup>1</sup>

Further work on this problem is in progress in our laboratories.

We would like to thank Dr. R. P. van Staple, Dr. T. J. A. Popma, Dr. P. F. Bongers, and Dr. H. I. Ralph for valuable discussions and Mr. F. R. van der Valk for technical assistance.

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## Jahn-Teller Effect in the Emission of KI:Tl-Type Phosphors; Coexistence of Two Kinds of Minima on the ${}^3T_{1u}$ Adiabatic Potential-Energy Surfaces

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(Received 31 January 1972)

By an accurate analysis it is demonstrated how Fukuda's model, which is based on the coexistence of two kinds of minima on the  ${}^3T_{1u}$  and  ${}^3A_{1u}$  adiabatic potential-energy surfaces, is not tenable in the framework of Russell-Saunders coupling. A generalized calculation to the intermediate-coupling case shows that two kinds of minima can coexist on the  ${}^3T_{1u}$  adiabatic potential-energy surfaces if the spin-orbit interaction is of a suitable value as compared with the Jahn-Teller interaction and the exchange energy.

The problem of the interpretation of emission spectra of KI:Tl-type phosphors is a formidable task, and many efforts have been made by several researchers in order to interpret them. Although several schemes have been advanced to explain these phenomena, a complete understanding has not yet been reached.<sup>1</sup>

Recently, Fukuda<sup>2</sup> proposed a model which is able to explain most of the observed features concerning the luminescence excitable in the  $A$  absorption band. This model is based on the coexistence, in the  $\epsilon_g(Q_2, Q_3)$  subspace, of two kinds of minima on the  ${}^3T_{1u}$  and  ${}^3A_{1u}$  adiabatic potential-energy surfaces (APES's). The two emission bands  $A_T$  and  $A_x$ , in the low temperature spectrum,<sup>3,4</sup> are considered to be due to transitions from these minima to the ground state  ${}^1A_{1g}$ .

Some cross sections of  ${}^3T_{1u}$  and  ${}^3A_{1u}$  APES's, along the  $Q_3$  axis, were computed by Fukuda, assuming Russell-Saunders (RS) coupling. They seem to confirm the existence of two kinds of minima when the spin-orbit coupling constant  $\zeta$  is of suitable value as compared with the electron-lattice coupling parameter  $b = \langle t_{1u,x} | V_2 | t_{1u,x} \rangle$ .

We have performed a more careful analysis of these minima in the whole  $\epsilon_g$  subspace taking into account also the  $Q_2$  coordinate. The results of our computations, reported in this Letter, show

that two kinds of minima cannot coexist if Russell-Saunders coupling is assumed.

In the  $\epsilon_g$  subspace, the APES's  $E(Q_2, Q_3)$  are obtained by diagonalizing the electron-lattice interaction matrix  $H_{ei}$  for  $Q_1 = Q_4 = Q_5 = Q_6 = 0$ , taking into account the lattice potential energy  $Q_2^2 + Q_3^2$  and the diagonal matrix element of the spin-orbit interaction. Using the same symbols as Fukuda, for the  $\Gamma_4^-(Y.\theta_x - X.\theta_y)$  or  ${}^3T_{1u,z}$  state we obtain (taking the positive root)

$$y = 2x_3 - (12x_2^2 + \frac{1}{4})^{1/2} + A(x_2^2 + x_3^2). \quad (1)$$

Here  $y = E/\zeta$ ,<sup>5</sup>  $x_{2,3} = (-b/2\sqrt{3}\zeta)Q_{2,3}$ , and  $A = 12\zeta(1 - \beta)/b^2$ , where  $\beta$  is the difference in curvature between the excited and the ground APES's. By putting  $x_2 = 0$  in Eq. (1), the cross section of Ref. 2 is obtained.

The coordinates of the stationary points are obtained from the equations  $\partial y/\partial x_3 = 0$  and  $\partial y/\partial x_2 = 0$ , and the results are  $x_3 = -1/A$ ,  $x_2 = 0$ , or  $x_2 = \pm(3/A^2 - \frac{1}{48})^{1/2}$ ; the latter  $x_2$  are real only if  $A \leq 12$ .

In order to check whether these points are actually minima, the second derivatives must be considered. It is easily seen that the point of the coordinates  $x_3 = -1/A$ ,  $x_2 = 0$  is a minimum ( $T$  minimum) if  $A \geq 12$ , while it is a saddle point if  $A < 12$ . On the contrary, the points of the coordi-