



# **Charge Transfer Transitions and Circular Magnetooptics in Ferrites**

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### Highlights:

- Critical overview of the "first-principles" DFT-based band models of the optical and magnetooptical responses.
- Cluster model and charge transfer transitions in ferrites: the theory of the circular MOE and comparisons with experiments.
- Elucidation of the Bi-substitution-induced effects in ferrites.
- Exchange-relativistic "spin-other-orbit" interaction V<sub>SoO</sub> as the main, if not the only source of circular MOE for weak ferromagnets.
- Nonlinear **m**-dependence of the circular MOE in ferrites as an explicit indication of the V<sub>SoO</sub> contribution.

Abstract: The concept of charge transfer (CT) transitions in ferrites is based on the cluster approach and takes into account the relevant interactions, such as the low-symmetry crystal field, spin–orbital, Zeeman, exchange and exchange-relativistic interactions. For all its simplicity, this concept yields a reliable qualitative and quantitative microscopic explanation of spectral, concentration, temperature and field dependencies of optic and magneto-optic properties ranging from the isotropic absorption and optical anisotropy to circular magneto-optics. In this review paper, starting with a critical analysis of the fundamental shortcomings of the "first-principles" density functional theory (DFT-based) band theory, we present the main ideas and techniques of the cluster theory of the CT transitions to be main contributors to circular magneto-optics of ferrites. Numerous examples of comparison of cluster theory with experimental data for orthoferrites, iron garnets and other ferrites are given.

Keywords: cluster model; charge transfer transitions; circular magnetooptics; ferrites

# 1. Introduction

Over the past 175 years since Michael Faraday's discovery of the relation between light and electromagnetism, magneto-optics has become a broad field of fundamental and applied research. On the one hand, magneto-optics is aimed at the experimental study of the electronic and magnetic structure, magnetic anisotropy, magnetic phase transitions, spin–orbital, exchange and exchange-relativistic effects; and on the other hand, toward the search for new materials with high magneto-optical characteristics, improvement and development of new magneto-optical applications. Various ferrites, especially bismuth-substituted iron garnets,  $R_3Fe_5O_{12}$  (R = Y, or rare-earth ion), occupy a special place among magneto-optical (MO) materials. They are the main objects of fundamental research and basic materials for creating various devices for applied magneto-optical modulators, optical sensors and visualizers, terahertz isolators, circulators, magneto-optical modulators, optical magnetoelectric sensors and nonreciprocal elements of the integrated optics, to promising applications in high density MO data-storage and low-power consumption spintronic nanodevices.



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**Copyright:** © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Rare-earth orthoferrites, RFeO<sub>3</sub>, which have been studied since the 60s of the last century, have attracted the attention of researchers for several decades, and continue to attract it, owing to their weak ferromagnetism, remarkable magneto-optical properties, different spin-reorientation transitions, high velocity of domain walls and many other physical properties [1]. Orthoferrites remain a focus of considerable research due to promising applications in innovative spintronic devices.

The problem of describing the optical and magneto-optical properties of ferrites is one of the most challenging tasks in the theory of strongly correlated 3d compounds. Despite many years of experimental and theoretical research, the nature of their optical, and especially, magneto-optical, response, remains a subject of debate. This concerns both the identification of electronic transitions responsible for the formation of the main optical and magneto-optical properties, and the comprehensive calculation of their contributions to the optical and magneto-optical response functions. The solution of this problem largely depends on the choice of the optimal strategy for taking into account the effects of charge transfer and strong local correlations, which can be formulated as the compromise between the one-electron band and atomic–molecular descriptions of electronic states.

In this review paper, we present a critical analysis of band approaches to describing the optical and magneto-optical responses of 3d ferrite-type compounds based on the use of density functional theory (DFT) (see, e.g., [2–4]) and argue that the traditional physically transparent atomic–molecular cluster approach (see, e.g., [5–8]) based on local symmetry, strong covalence and charge transfer (CT) effects with strong local correlations, provides consistent descriptions and explanations of the optical and magneto-optical responses of various ferrites in a wide spectral range. The review was stimulated by the lack of detailed and reliable studies of electron–hole excitations and of a proper understanding of the relative roles of different transitions in the optical and magneto-optical responses of ferrites.

The rest of the paper is organized as follows. In Section 2, we present a critical overview of the DFT-based approaches [9,10] for descriptions of the optical and magnetooptical properties of strongly correlated 3d compounds and point to the cluster model as a comprehensive, physically clear alternative to the DFT approach. In Section 3, we address the CT states and CT transitions in octahedral  $[FeO_6]^{9-}$  and tetrahedral  $[FeO_4]^{5-}$  clusters as basic elements of crystalline and electronic structure for most ferrites. Here we also show that the CT transitions provide adequate descriptions of the optical spectra for a wide range of ferrites and other 3d oxides. In Section 4, we discuss different interactions for the CT states, with a specific focus on so-called exchange-relativistic interactions—in particular, the novel "spin-other-orbit" interaction. In Section 5, we analyze the polarizability tensor for the octahedral [FeO<sub>6</sub>]<sup>9-</sup> cluster and argue that its contribution to the optical and magnetooptical anisotropy is determined by different interactions in excited states. In Section 6, we overview different points of the microscopic theory of circular magneto-optics for ferritegarnets and weak ferromagnets, including Bi-substituted garnets; the specific role of the "spin-other-orbit" coupling in weak ferromagnetic ferrites; the temperature dependence of circular magneto-optics; and the role of the 4f-5d transitions in rare-earth ions. A brief summary is given in Section 7.

#### 2. Density Functional Theory or Cluster Model?

## 2.1. So-Called "Ab Initio" DFT Based Approaches

The electronic states in strongly correlated 3d oxides manifest both significant localization and dispersional features. One strategy to deal with this dilemma is to restrict oneself to proper, small, many-electron clusters embedded to a whole crystal, then creating model effective lattice hamiltonians whose spectra may reasonably well represent the energy and dispersion of the important excitations of the full problem [7,8,11]. Despite some shortcomings, the method did provide a clear physical picture of the complex electronic structure and the energy spectrum, along with the possibility of a quantitative modeling. However, the last few decades, the condensed matter community faced an expanding avalanche of the DFT-based papers with the so-called ab initio calculations of electronic structure and physical properties for strongly correlated systems, such as 3d compounds. Only in recent years has a series of papers been published on ab initio calculations of the electronic structure, and optical and magneto-optical spectra of iron garnets (see, e.g., [3,4]).

However, DFT [9,10] still remains, in some sense, ill-defined: many DFT statements were ill-posed or not rigorously proved [8,11]. All efforts to account for the correlations beyond LDA (local density approximation) encounter an insoluble problem of double counting of interaction/correlation terms, which were just included into Kohn–Sham single-particle potential [9,10].

Most widely used DFT computational schemes start with "metallic-like" approaches making use of approximate energy functionals: firstly, the LDA scheme, which is constructed as an expansion around the homogeneous electron gas limit and fails quite dramatically to capture the properties of strongly correlated systems. The LDA+U and LDA+DMFT (DMFT, dynamical mean-field theory) [12] methods are believed to correct the inaccuracies of approximate DFT exchange correlation functionals. The main idea of these computational approaches consists of selective descriptions of the strongly correlated electronic states, typically, d or f orbitals, using the Hubbard model, while all the other states continue to be treated at the level of standard DFT functionals. Despite the fact that the LDA+U and LDA+DMFT methods are now considered as the most powerful methods for studying strongly correlated systems, they retain many of the shortcomings of the DFT+LDA approach.

The values of effective on-site Coulomb parameters  $U_{eff} = U - J$ , where U represents the Hubbard on-site Coulomb repulsion parameter and J the intra-atomic Hund's exchange integral, are ordinarily determined by seeking good agreement of the calculated properties, such as band gaps, with the experimental results. The values of  $U_{eff}$  strongly affect the calculated material properties. Recent studies have attempted to calculate these parameters directly based on first principles approaches. Nevertheless, the calculated values differ widely, even for the same ionic state in a given material, due to a number of factors, such as the choice of the DFT scheme or the underlying basis set. Although it has become a common practice that a certain U<sub>eff</sub> value is chosen a priori during the setup of a first principles-based calculation, it is also well known that a certain  $U_{eff}$  value may not work definitively for all calculation methods and DFT schemes. By independently constraining the field on the Fe atoms at the octahedral and tetrahedral sites in YIG (yttrium iron garnet), the authors [4] obtained two different values of  $U_{eff}$ , i.e., 9.8 eV for octa-Fe and 9.1 eV for tetra-Fe. These values are considerably different from those used for iron garnets in previous works; e.g., U = 3.5 eV and J = 0.8 eV [13] using the orthonormalized linear combination of atomic orbitals basis set within constrained LDA approach, and  $U_{eff} = 5.7 \text{ eV} [14]$ , U = 4 eV [3,15]. The Hubbard and Hund *U* and *J* parameters were chosen as  $U_{eff} = 2.7$  eV for YIG, 4.7 eV for LuIG and 5 eV for Bi-substituted garnet  $Bi_xLu_{3-x}Fe_5O_{12}$  [16].

Despite many examples of seemingly good agreement with experimental data claimed by the DFT community, both the questionable starting points and many unsolved and even unsoluble problems give rise to serious doubts in quantitative and even qualitative predictions made with the DFT-based techniques [8,11].

Strictly speaking, the DFT is designed for description of ground rather than excited states, and there is no good scheme for excitations. As an excited-state density does not uniquely determine the potential, there is no general analog of the Hohenberg–Kohn functional [9,10] for excited states. The standard functionals are inaccurate both for on-site crystal field and for charge transfer excitations [17]. The DFT-based approaches cannot provide the correct atomic limit and the term and multiplet structure [18,19], which is crucial for descriptions of the optical responses for 3d compounds. Although there are efforts to obtain correct results for spectroscopic properties depending on spin and orbital density, this problem remains an open one in DFT research. Clearly, all these difficulties stem from unsolved foundational problems in DFT. Given these background problems,

the DFT-based models should be addressed as semi-empirical approximate ones rather than ab initio theories. M. Levy introduced in 2010 the term DFA to define density functional approximation instead of DFT, which is believed to quite appropriately describe contemporary DFT [20].

A basic drawback of the spin-polarized approaches to descriptions of electronic structures for spin-magnetic systems, especially in a simple LSDA scheme [2], is that these start with a local density functional in the form

$$\mathbf{v}(\mathbf{r}) = v_0[n(\mathbf{r})] + \Delta v[n(\mathbf{r}), \mathbf{m}(\mathbf{r})](\hat{\boldsymbol{\sigma}} \cdot \frac{\mathbf{m}(\mathbf{r})}{|\mathbf{m}(\mathbf{r})|}),$$

where  $n(\mathbf{r})$  and  $\mathbf{m}(\mathbf{r})$  are the electron and spin magnetic density, respectively;  $\hat{\sigma}$  is the Pauli matrix. That is, these imply the presence of a large fictious local *one-electron* spin-magnetic field  $\propto (v^{\uparrow} - v^{\downarrow})$ , where  $v^{\uparrow,\downarrow}$  are the on-site LSDA spin-up and spin-down potentials. The magnitude of the field is considered to be governed by the intra-atomic Hund exchange, and its orientation by the effective molecular or inter-atomic exchange fields. Despite the supposedly spin nature of the field, it produces an unphysically giant spin-dependent rearrangement of the charge density that cannot be reproduced within any conventional technique operating with spin Hamiltonians [11]. Furthermore, a direct link with the orientation of the field makes the effect of the spin configuration on the charge distribution unphysically large. However, in reality, long-range spin-magnetic coupling has no significant influence on the redistribution of the charge density. In such a case, the straightforward application of the LSDA scheme can lead to an unphysical effect of a breaking of spatial symmetry induced by a spin configuration. The DFT-LSDA community needed many years to understand such a physically clear point.

Overall, the LSDA approach seems to be more or less justified for a semi-quantitative description of exchange coupling effects for materials of classical Néel-like collinear magnetic order. However, it can lead to erroneous results for systems and high-order perturbation effects where the symmetry breaking and quantum fluctuations are of a principal importance, such as: (i) noncollinear spin configurations, particularly in quantum s = 1/2 magnets; (ii) relativistic effects, such as the symmetric spin anisotropy and antisymmetric DM coupling [21]; (iii) spin-dependent electric polarization [22,23]; and (iv) linear and circular magneto-optical effects. There are some intractable problems with match-making between the conventional formalism of a spin Hamiltonian and LSDA approach to the exchange and exchange-relativistic effects. Visibly plausible numerical results for different exchange and exchange-relativistic parameters reported in many LSDA investigations (see, e.g., [24]) evidence only a potential capacity of the LSDA-based models for semiquantitative estimations, rather than for reliable quantitative data [21–23].

It is rather surprising how little attention has been paid to the systematic DFT-based calculations of the optical response for the transition metal oxides (TMO). The available examples, upon closer examination, only once again indicate the fundamental problems that the DFT approach encounters when trying to describe the optical responses of strongly correlated systems in a wide spectral range. Let us turn to a recent paper by Roedl and Bechstedt [25] on NiO and other TMOs, whose approach is typical for the DFT community. The authors calculated the dielectric function  $\epsilon(\omega)$  for NiO with the DFT-GGA+U+ $\Delta$  technique and claimed: "The experimental data agree very well with the calculated curves." However, this agreement is a result of a simple fitting when the two model parameters U and  $\Delta$  are determined (U = 3.0,  $\Delta$  = 2.0 eV) such that the best possible agreement concerning the positions and intensities of the characteristic peaks in the experimental spectra is obtained. In addition, the authors arrived at an absolutely unphysical conclusion: "The optical absorption of NiO is dominated by intra-atomic  $t_{2g} \rightarrow e_g$  transitions."

There are still many people who think the DFT+LDA has provided a very successful ab initio framework to successfully tackle the problem of the electronic structures of materials. However, both the starting point and realizations of the DFT approach have raised serious

unresolved questions [8]. The HK "theorem" of the existence of a mythical universal density functional that can resolve everything looks like a way into Neverland; the DFT heaven is probably unattainable. Various DFAs, local or nonlocal, will never be exact. Users are willing to pay this price for simplicity, efficacy and speed, combined with useful (but not yet chemical or physical) accuracy [17,26]. The most popular DFA fail for the most interesting systems, such as strongly correlated oxides—in particular, ferrites. The standard DFT approximations over-delocalize the 3d electrons, leading to highly incorrect descriptions. Some practical schemes, in particular, DMFT, can correct some of these difficulties, but none has yet become a universal tool with known performances for such systems [17].

#### 2.2. Cluster Model Approach

At variance with the DFT theory, the cluster model approach does generalize and advance crystal-field and ligand-field theory. The method provides a clear physical picture of the complex electronic structure and the energy spectrum, and the possibility of a quantitative modeling. The cluster calculations might provide a better description of the overall electronic structure of insulating 3d oxides than the band structure calculations [27,28], mainly due to a better account of correlation effects; electron-lattice coupling; and relatively weak interactions, such as spin-orbital and exchange coupling. Moreover, the cluster model has virtually no competitors in the description of impurity or dilute systems. Cluster models do widely use the symmetry for atomic orbitals; point group symmetry; and advanced technique, such as Racah algebra and its modifications for point group symmetry [7,8,29]. On the other hand, the cluster model is an actual proving-ground for various calculation techniques, from simple quantum chemical MO-LCAO (molecular orbital linear combination of atomic orbitals) to the more elaborate LDA + MLFT (MLFT, multiplet ligand-field theory) [30] approach. The LDA + MLFT technique implies a sort of generalization of the conventional ligand-field model with the DFT-based calculations. Haverkort et al. [30] started by performing a DFT calculation for the proper, infinite crystal using a modern DFT code, which employs an accurate density functional and basis set (e.g., linear augmented plane waves (LAPWs)). From the (self-consistent) DFT crystal potential, they then calculated a set of Wannier functions that were suitable for the single-particle basis of the cluster calculation. The authors compared the theory with experimental spectra (XAS, nonresonant IXS, photoemission spectroscopy) for different 3d oxides and found overall satisfactory agreement, indicating that their ligand-field parameters are over 90% correct. However, the authors were forced to treat on-site correlation parameter  $U_{dd}$  and orbitally averaged  $\Delta_{pd}$  as adjustable ones. Despite the involvement of powerful calculation techniques, the numerical results of the LDA + MLFT approach seem to be more like semiquantitative ones. Nevertheless, any comprehensive physically valid description of the electron and optical spectra for strongly correlated systems, as we suggest, should combine simple physically clear cluster ligand-field analysis with a numerical calculation technique such as LDA+MLFT [30], and a regular appeal to experimental data.

It is now believed that the most intensive low-energy electron–hole excitations in insulating 3d oxides correspond to the charge transfer (CT) transitions [7,8,31–49]. Namely, the CT transitions are considered as a likely source of the optical and magneto-optical response of the 3d metal-based oxide compounds, in particular, ferrites, in a wide spectral range of 1–10 eV, primarily of the fundamental absorption edge. The low-energy, dipole-forbidden *d*–*d* orbital excitations, or phonon-assisted crystal field transitions, are characterized by the oscillator strengths which are smaller by a factor  $10^2-10^3$  than those for the dipole-allowed *p*–*d* CT transitions, and usually correspond to contributions to the dielectric function  $\varepsilon''$  in the order of 0.001–0.01.

Despite CT transitions being a well established concept in the solid state physics, their theoretical treatment remains rather naive and hardly progressed during the last few decades. Usually, it is based on the *one-electron* approach with some 2p-3d or, at best,  $2p \rightarrow 3d t_{2g}$ ,  $2p \rightarrow 3d e_g$  CT transitions in 3d oxides. In terms of the Hubbard model, this is a CT transition from the nonbonding oxygen band to the upper Hubbard band. However, such

a simplified approach to CT states and transitions in many cases appears to be absolutely insufficient and misleading, even for qualitative explanation of the observed optical and magneto-optical properties. First, one should generalize the concept of CT transitions taking into account the conventional transition between the lower and upper Hubbard bands, which corresponds to an inter-site d-d CT transition, or inter-site transition across the Mott gap.

Several important problems are hardly addressed in the current analysis of optical spectra, including the relative roles of different initial and final orbital states and respective CT channels, strong intra-atomic correlations, effects of strong electron and lattice relaxation for CT states, the transition matrix elements or transition probabilities, probable changes in crystal fields and correlation parameters accompanying the charge transfer. One of the central issues in the analysis of electron–hole excitations is whether low-lying states are comprised of free charge carriers or excitons.

Despite all their shortcomings, the cluster models have proven themselves to be reliable working models for strongly correlated systems- such as 3d compounds. These have a long and distinguished history of applications in electron, optical and magneto-optical spectroscopy, magnetism and magnetic resonance. The author and his colleagues has successfully demonstrated the great potential of the cluster model for description of the *p*–*d* and *d*–*d* charge transfer transitions and their contributions to optical and magneto-optical responses of various 3d oxides, such as ferrites [31–40], cuprates [41–45], manganites [40,46,47] and nickelates [48,49].

#### 3. Cluster Model: The CT Configurations and CT Transitions in Ferrites

# 3.1. Electronic Structure of Octahedral [FeO<sub>6</sub>]<sup>9–</sup> Clusters in Ferrites

The slightly distorted octahedral  $[FeO_6]^{9-}$  clusters are main optical and magnetooptical centers in weak ferromagnetic orthoferrrites, RFeO<sub>3</sub>; hematite,  $\alpha$  -Fe<sub>2</sub>O<sub>3</sub>; borate, FeBO<sub>3</sub>; cubic antiferromagnetic garnets such as Ca<sub>3</sub>Fe<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>; and tetrahedral  $[FeO_4]^{5-}$ complexes in other ferrites as well.

Five Me 3d and eighteen oxygen O2p atomic orbitals in the octahedral MeO<sub>6</sub> complex with the point symmetry group  $O_h$  form hybrid Me 3d-O2p bonding and antibonding  $e_g$ and  $t_{2g}$  molecular orbitals, and purely oxygen nonbonding  $a_{1g}(\sigma)$ ,  $t_{1g}(\pi)$ ,  $t_{1u}(\sigma)$ ,  $t_{1u}(\pi)$ and  $t_{2u}(\pi)$  orbitals (see, e.g., [5,8,29,46]). Nonbonding  $t_{1u}(\sigma)$  and  $t_{1u}(\pi)$  orbitals with the same symmetry are hybridized due to the oxygen–oxygen O2p $\pi$ -O2p $\pi$  transfer. The relative energy positions of different nonbonding oxygen orbitals are of primary importance for the spectroscopy of the oxygen–3d–metal charge transfer. This is firstly determined by the bare energy separation  $\Delta \epsilon_{2p\pi\sigma} = \epsilon_{2p\pi} - \epsilon_{2p\sigma}$  between O2p $\pi$  and O2p $\sigma$  electrons.

Since the O2p $\sigma$  orbital points towards the two neighboring positive 3d ions, an electron in this orbital has its energy lowered by the Madelung potential as compared with the O2p $\pi$  orbitals, which are oriented perpendicular to the respective 3d–O–3d axes. Thus, Coulomb arguments favor the positive sign of the  $\pi - \sigma$  separation  $\epsilon_{p\pi} - \epsilon_{p\sigma}$ , whose numerical value can be easily estimated in frames of the well-known point charge model, and appears to be in the order of 1.0 eV. In a first approximation, all the  $\gamma(\pi)$  states  $t_{1g}(\pi), t_{1u}(\pi), t_{2u}(\pi)$  have the same energy. However, the  $O2p\pi$ - $O2p\pi$  transfer yields the energy correction to bare energies with the largest value and positive sign for the  $t_{1g}(\pi)$ state. The energy of the  $t_{1u}(\pi)$  state drops due to a hybridization with the cation  $4p t_{1u}(\pi)$ state. In other words, the  $t_{1g}(\pi)$  state is believed to be the highest in energy non-bonding oxygen state [46]. For illustration, in Figure 1 we show the energy spectrum of the 3d–2p manifold in the octahedral complexes  $MeO_6$  with the relative energy positions of the levels according to the quantum chemical calculations [50] for the  $[FeO_6]^{9-}$  octahedral complex in a lattice environment typical for perovskites such as LaFeO<sub>3</sub>. It should be emphasized once more that the top of the oxygen electron band is composed of  $O2p\pi$  nonbonding orbitals that predetermine the roles of the oxygen states in many physical properties of 3d perovskites.

The *conventional* ground state electronic structure of octahedral  $\text{Fe}^{3+}O_6$  clusters is associated with the configuration of the completely filled O 2p shells and half-filled Fe 3d shell. The typical high-spin ground state configuration and crystalline term for  $\text{Fe}^{3+}$  in the octahedral crystal field or for the octahedral [FeO<sub>6</sub>]<sup>9–</sup> center are  $t_{2g}^3 e_g^2$  and  ${}^6A_{1g}$ , respectively.

The excited CT configuration  $\underline{\gamma}_{2p}^1 3d^{n+1}$  arises from the spin-conserving transition of an electron from the predominantly anionic molecular orbitals  $\gamma_{2p}$  into an empty 3d-type MO ( $t_{2g}$  or  $e_g$ ). The transition between the ground and the excited configuration can be presented as the intra-center p–d CT transition  $\gamma_{2p} \rightarrow 3d(t_{2g}, e_g)$ .

The p–d CT configuration consists of two partly filled molecular-orbital subshells, localized predominantly on the 3d cation and ligands, respectively. The excited cation configuration (3d<sup>6</sup>) nominally corresponds to the Fe<sup>2+</sup> ion. Strictly speaking, the many-electron p–d CT configuration should be written as  $t_{2g}^{n_1}e_g^{n_2}\underline{\gamma}_{2p}$  with  $n_1 + n_2 = 6$ , or  $((t_{2g}^{n_1}e_g^{n_2})^{2S'+1}\Gamma'_{g'};\underline{\gamma}_{2p})^{2S+1}\Gamma$  ( $S = S' \pm \frac{1}{2}, \Gamma \in \Gamma'_g \times \gamma_{2p}; ^{2S+1}\Gamma$  is a crystal term of the CT configuration), if we make use of the spin and orbital quasi-momentum addition technique [29].



**Figure 1.** The diagram of Me 3d-O 2p molecular orbitals for the MeO<sub>6</sub> octahedral center. The O 2p-Me 3d charge transfer transitions are shown by arrows: strong dipole-allowed  $\sigma - \sigma$  and  $\pi - \pi$  by thick solid arrows; weak dipole-allowed  $\pi - \sigma$  and  $\sigma - \pi$  by thin solid arrows; weak dipole-forbidden low-energy transitions by thin dashed arrows. Adapted from reference [40].

# 3.2. Intra-Center Electric-Dipole p-d CT Transitions

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The conventional classification scheme of the intra-center electric-dipole p–d CT transitions in the octahedral [FeO<sub>6</sub>]<sup>9–</sup> clusters first of all includes the electric-dipole allowed transitions from the odd-parity oxygen  $\gamma_u = t_{1u}(\pi), t_{2u}(\pi), t_{1u}(\sigma)$  orbitals to the even-parity iron  $3dt_{2g}$  and  $3de_g$  orbitals, respectively. These one-electron transitions generate the many-electron ones,  ${}^6A_{1g} \rightarrow {}^6T_{1u}$ , which differ by the crystalline term of the respective  $3d^6$  configuration:

$$(t_{2g}^{3}{}^{4}A_{2g}; e_{g}^{2})^{6}A_{1g} \to ((t_{2g}^{4}; e_{g}^{2})^{5}T_{2g}; \underline{\gamma_{u}})^{6}T_{1u},$$

$$(1)$$

$$(t_{2g}^{3}{}^{4}A_{2g}; e_{g}^{2})^{6}A_{1g} \to ((t_{2g}^{3}; e_{g}^{3})^{5}E_{g}; \underline{\gamma_{u}})^{6}T_{1u},$$
<sup>(2)</sup>

for  $\gamma_u \rightarrow 3dt_{2g}$  and  $\gamma_u \rightarrow 3de_g$  transitions, respectively. We see that in contrast to the manganese centers Mn<sup>3+</sup>O<sub>6</sub><sup>9-</sup> [46], each one-electron  $\gamma_u \rightarrow 3dt_{2g}$  transition generates one many-electron CT transition.

The  $MeO_6$  octahedral center can be written with the aid of the Wigner–Eckart theorem [29] as follows (see [46] for details):

$$\langle \gamma_u \mu | \hat{d}_q | \gamma_g \mu' \rangle = (-1)^{j(\gamma_u) - \mu} \left\langle \begin{array}{cc} \gamma_u & t_{1u} & \gamma_g \\ -\mu & q & \mu' \end{array} \right\rangle^* \langle \gamma_u \| \hat{d} \| \gamma_g \rangle , \tag{3}$$

where  $\langle \cdot \cdot \cdot \rangle$  is the Wigner coefficient for the cubic point group  $O_h$  [29],  $j(\Gamma)$  is

the so-called quasi-momentum number and  $\langle \gamma_u \| \hat{d} \| \gamma_g \rangle$  is the one-electron dipole moment submatrix element. The 3d–2p hybrid structure of the even-parity molecular orbital  $\gamma_g \mu = N_{\gamma_g} (3d\gamma_g \mu + \lambda_{\gamma_g} 2p\gamma_g \mu)$  and a more simple form of purely oxygen odd-parity molecular orbital  $\gamma_u \mu \equiv 2p\gamma_u \mu$ , both with a symmetry superposition of the ligand O 2p orbitals, point to a complex form of the submatrix element in (3) to be a sum of *local* and *nonlocal* terms composed of the one-site and two-site (*d*–*p* and *p*–*p*) integrals, respectively. In the framework of a simple "local" approximation that implies the full neglect of all many-center integrals,

$$\langle t_{2u}(\pi) \| \hat{d} \| e_g \rangle = 0; \ \langle t_{2u}(\pi) \| \hat{d} \| t_{2g} \rangle = -i\sqrt{\frac{3}{2}}\lambda_{\pi}d;$$

$$\langle t_{1u}(\sigma) \| \hat{d} \| t_{2g} \rangle = 0; \ \langle t_{1u}(\sigma) \| \hat{d} \| e_g \rangle = -\frac{2}{\sqrt{3}}\lambda_{\sigma}d;$$

$$\langle t_{1u}(\pi) \| \hat{d} \| e_g \rangle = 0; \ \langle t_{1u}(\pi) \| \hat{d} \| t_{2g} \rangle = \sqrt{\frac{3}{2}}\lambda_{\pi}d.$$

$$(4)$$

where  $\lambda_{\sigma} \sim t_{pd\sigma} / \Delta_{pd}$  and  $\lambda_{\pi} \sim t_{pd\pi} / \Delta_{pd}$  are *effective* covalence parameters for  $e_g, t_{2g}$  electrons, respectively;  $d = eR_0$  is an elementary dipole moment for the cation–anion bond length  $R_0$ . We see that the "local" approximation results in an additional selection rule: it forbids the  $\sigma \to \pi$  and  $\pi \to \sigma$  transitions,  $t_{1u}(\sigma) \to t_{2g}$  and  $t_{1,2u}(\pi) \to e_g$ , respectively, though these are dipole-allowed. In other words, in frames of this approximation, only  $\sigma$ -type ( $t_{1u}(\sigma) \rightarrow e_g$ ) or  $\pi$ -type ( $t_{1,2u}(\pi) \rightarrow t_{2g}$ ) CT transitions are allowed. Hereafter, we make use of the terminology of "strong" and "weak" transitions for the dipole-allowed CT transitions going on the  $\sigma - \sigma$  and  $\pi - \pi$  and  $\pi - \sigma$  and  $\sigma - \pi$  channels, respectively. It should be emphasized that the "local" approximation, if non-zero, is believed to provide a leading contribution to transition matrix elements with corrections of the first order in the cation-anion overlap integral [40,46]. Moreover, the nonlocal terms are neglected in standard Hubbard-like approaches. Given typical cation-anion separations  $\mathbf{R}_{MeO} \approx 4$  a.u., we arrive at values less than 0.1 a.u. even for the largest two-site integral; however, neglecting them should be done carefully. Equations (3) and (4) point to likely extremely large dipole matrix elements and oscillator strengths for strong p-d CT transitions, mounting to  $d_{ii}$ ~eÅ and  $f \sim 0.1$ , respectively.

Hence, starting with three nonbonding purely oxygen orbitals,  $t_{1u}(\pi)$ ,  $t_{1u}(\sigma)$ ,  $t_{2u}(\pi)$ , as initial states for one-electron CT, we arrive at six many-electron dipole-allowed CT transitions  ${}^{6}A_{1g} \rightarrow {}^{6}T_{1u}$ . There are two transitions  $t_{1u}(\pi)$ ,  $t_{2u}(\pi) \rightarrow t_{2g}$  ( $\pi - \pi$  channel); two transitions  $t_{1u}(\pi)$ ,  $t_{2u}(\pi) \rightarrow e_g$  ( $\pi - \sigma$  channel); one transition  $t_{1u}(\sigma) \rightarrow t_{2g}$  ( $\sigma - \pi$  channel); and one transition  $t_{1u}(\sigma) \rightarrow e_g$  ( $\sigma - \sigma$  channel).

It should be noted that the dipole-forbidden  $t_{1g}(\pi) \rightarrow t_{2g}$  transition seemingly determines the onset energy of all the p–d CT bands.

For our analysis to be more quantitative, we make two rather obvious model approximations. First of all, we assume that, as is usually the case for cation–anion octahedra in 3d oxides [5,40,46,47,50,51], the non-bonding  $t_{1g}(\pi)$  oxygen orbital has the highest energy and forms the first electron removal oxygen state. Furthermore, to be sure, we assume that the energy spectrum of the non-bonding oxygen states for  $[Fe^{3+}O_6]^{9-}$  centers coincides with that calculated in [50] for  $[Fe^{3+}O_6]^{9-}$  in orthoferrite LaFeO<sub>3</sub>; in other words, we have (in eV):

$$\begin{aligned} \Delta(t_{1g}(\pi) - t_{2u}(\pi)) &\approx 0.8; \ \Delta(t_{1g}(\pi) - t_{1u}(\pi)) &\approx 1.8; \\ \Delta(t_{1g}(\pi) - t_{1u}(\sigma)) &\approx 3.0. \end{aligned}$$

Secondly, we choose for the Racah parameters B = 0.09 eV and C = 0.32 eV, the numerical values typical for the Fe<sup>3+</sup> ion [5].

The energies of the intra-center CT transitions for octahedral FeO<sub>6</sub> and tetrahedral FeO<sub>4</sub> clusters in  $Y_3Fe_5O_{12}$  were calculated using the spin-polarized  $X_{\alpha}$  discrete variational (SP- $X_{\alpha}$  DV) method [32,37]. These results are presented in Table 1 together with the results of fitting the experimental optical data [5,52,53], taking into account only the contribution of the intra-center CT transitions with a Lorentzian line shape.

**Table 1.** Parameters (energies, oscillator strength, line width) of the dipole allowed intra-center CT transitions in octahedral ( ${}^{6}A_{1g} \rightarrow {}^{6}T_{1u}$ , number = 1–6) and tetrahedral ( ${}^{6}A_{1g} \rightarrow {}^{6}T_{2}$ , number = 7–13) clusters in Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>. E<sub>comp</sub> and E<sub>fit</sub> are the computed and fitted CT transition energies, respectively. Adapted from references [32,37].

No.	Transition	E <sub>comp</sub> (eV)	E <sub>fit</sub> (eV)	f (×10 <sup>-3</sup> )	Γ (eV)
1	$t_{2u} \rightarrow t_{2g}$	3.1	2.8	4	0.2
2	$t_{1u}(\pi) \rightarrow t_{2g}$	3.9	3.6	30	0.3
3	$t_{2u} \rightarrow e_g$	4.4	4.3	60	0.3
4	$t_{1u}(\sigma) \rightarrow t_{2g}$	5.1	4.8	40	0.3
5	$t_{1u}(\pi) \rightarrow e_g$	5.3	5.2	200	0.3
6	$t_{1u}(\sigma) \rightarrow e_g$	6.4	6.1	200	0.3
7	$1t_1 \rightarrow 2e^-$	3.4	3.4	30	0.4
8	$6t_2 \rightarrow 2e$	4.3	4.6	20	0.3
9	$1t_1 \rightarrow 7t_2$	4.5	4.7	40	0.3
10	$5t_2 \rightarrow 2e$	5.0	4.9	30	0.3
11	$6t_2 \rightarrow 7t_2$	5.4	5.1	20	0.3
12	$1e \rightarrow 7t_2$	5.6	5.6	10	0.3
13	$5t_2 \rightarrow 7t_2$	6.0	6.0	20	0.3

In addition to several dipole-allowed CT transitions, the CT band also includes various forbidden transitions. First of all, these are dipole-forbidden p–d transitions between states with the same parity of the  $2pt_{1g}$ - $3dt_{2g}$  type, and satellites of allowed transitions having the same electronic configuration but different terms for the final states. For instance, in the FeO<sub>6</sub> octahedron, these are the  ${}^{6}A_{1g} \rightarrow {}^{6}\Gamma_{u}$  transitions ( $\Gamma = A_1, A_2, E, T_1$ ) forbidden by the quasimoment selection rule, and the  ${}^{6}A_{1g} \rightarrow {}^{4}\Gamma_{u}$  spin-forbidden transitions (if  $\Gamma \neq T_{1u}$ , then it is quasimoment forbidden, too). The forbiddenness of these transitions is lifted by the electron-lattice interaction, low-symmetry crystal field, spin–orbital interaction, or exchange interaction with neighboring clusters. A detailed analysis of the energy spectrum of the CT band requires taking into account the d–d, p–d and p–p correlation effects.

#### 3.3. Inter-Center d-d CT Transitions

Strictly speaking, reliable identification of the intra-center p–d CT transitions is possible only in highly dilute or impurity systems, such as YAlO<sub>3</sub>:Fe or Ca<sub>3</sub>Fe<sub>x</sub>Ga<sub>2-x</sub>Ge<sub>3</sub>O<sub>12</sub>, whereas in concentrated systems (YFeO<sub>3</sub>, Ca<sub>3</sub>Fe<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>, Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>, etc.), these transitions compete with inter-center d–d CT transitions [41–43,45,47,48].

The inter-center d–d CT transitions between two MeO<sub>n</sub> clusters centered at neighboring sites 1 and 2 define inter-center d–d CT excitons in 3d oxides [41–43,45,47,48]. These excitons may be addressed as quanta of the disproportionation reaction

$$Me_1O_n^v + Me_2O_n^v \to Me_1O_n^{v-1} + Me_2O_n^{v+1}$$
, (5)

with the creation of electron  $MeO_n^{v-1}$  and hole  $MeO_n^{v+1}$  centers. Depending on the initial and final single particle states, all the inter-center d-d CT transitions may be classified as  $e_g - e_g$ ,  $e_g - t_{2g}$ ,  $t_{2g} - e_g$  and  $t_{2g} - t_{2g}$  ones. For the 3*d* oxides with cations obeying the Hund rule, these can be divided to so-called high-spin (HS) transitions  $S_1S_2S \rightarrow S_1 \pm \frac{1}{2}S_2 \mp \frac{1}{2}S$ and low-spin (LS) transitions  $S_1S_2S \rightarrow S_1 - \frac{1}{2}S_2 - \frac{1}{2}S$ , respectively.

An inter-center d-d CT transition in iron oxides with Fe<sup>3+</sup>O<sub>6</sub> octahedra

$$[\text{FeO}_6]^{9-} + [\text{FeO}_6]^{9-} \to [\text{FeO}_6]^{10-} + [\text{FeO}_6]^{8-}$$
 (6)

implies the creation of electron  $[FeO_6]^{10-}$  and hole  $[FeO_6]^{8-}$  centers with electron configurations formally related to  $Fe^{2+}$  and  $Fe^{4+}$  ions, respectively. The low-energy inter-center d-d CT transitions from the initial  $Fe^{3+}O_6(t_{2g}^3e_g^2)$ :<sup>6</sup> $A_{1g}$  states can be directly assigned to  $e_g \rightarrow e_g$ ,  $e_g \rightarrow t_{2g}$ ,  $t_{2g} \rightarrow e_g$  and  $t_{2g} \rightarrow t_{2g}$  channels with final configurations and terms [40]

$$e_{g} \rightarrow e_{g} : t_{2g}^{3} e_{g}^{1}; {}^{5}E_{g} - t_{2g}^{3} e_{g}^{3}; {}^{5}E_{g},$$

$$e_{g} \rightarrow t_{2g} : t_{2g}^{3} e_{g}^{1}; {}^{5}E_{g} - t_{2g}^{4} e_{g}^{2}; {}^{5}T_{2g},$$

$$t_{2g} \rightarrow e_{g} : t_{2g}^{2} e_{g}^{2}; {}^{5}T_{2g} - t_{2g}^{3} e_{g}^{3}; {}^{5}E_{g},$$

$$t_{2g} \rightarrow t_{2g} : t_{2g}^{2} e_{g}^{2}; {}^{5}T_{2g} - t_{2g}^{4} e_{g}^{2}; {}^{5}T_{2g}.$$
(7)

In the framework of high-spin configurations, the  $e_g \rightarrow t_{2g}$  CT transition has the lowest energy  $\Delta = \Delta_{e_g - t_{2g}}$ ; while the  $e_g \rightarrow e_g$ ,  $t_{2g} \rightarrow t_{2g}$  and  $t_{2g} \rightarrow e_g$  transitions have the energies  $\Delta + 10Dq(3d^6)$ ,  $\Delta + 10Dq(3d^4)$  and  $\Delta + 10Dq(3d^6) + 10Dq(3d^4)$ , respectively. The transfer energy in the Fe<sup>3+</sup>-based ferrites for the  $e_g \rightarrow t_{2g}$  CT transition

$$\Delta_{e_g t_{2g}}^{\rm Fe-Fe} = A + 28 B - 10 Dq$$

can be compared with a similar quantity for the  $e_g \rightarrow e_g$  CT transition in Mn<sup>3+</sup>-based manganite LaMnO<sub>3</sub>:

$$\Delta_{e_g e_g}^{\mathrm{Mn}-\mathrm{Mn}} = A - 8 B + \Delta_{JT},$$

where  $\Delta_{JT}$  is the Jahn–Teller splitting of the  $e_g$  levels in manganite. Given  $B \approx 0.1$  eV,  $Dq \approx 0.1$  eV,  $\Delta_{JT} \approx 0.7$  eV,  $\Delta_{e_g e_g}^{\text{Fe}-\text{Fe}} \approx 2.0$  eV (see, e.g., [54]), we get  $A \approx 2.0$  eV,  $\Delta_{e_g t_{2g}}^{\text{Fe}-\text{Fe}} \approx 4.0$  eV. In other words, the onset of the *d*–*d* CT transitions in Fe<sup>3+</sup>-based ferrites is strongly (~2 eV) blue-shifted as compared to the Mn<sup>3+</sup>-based manganite LaMnO<sub>3</sub>.

Another important difference between ferrites and manganites lies in the opposite orbital character of initial and final states for the d-d CT transitions. Indeed, the low-energy  $d^4d^4 \rightarrow d^3d^5$  CT transition in manganites implies an orbitally degenerate Jahn–Teller initial state  ${}^5E_g{}^5E_g$  [55] and an orbitally non-degenerate final state  ${}^4A_{2g}{}^6A_{1g}$ ; and the low-energy  $d^5d^5 \rightarrow d^4d^6$  CT transitions in ferrites imply an orbitally non-degenerate initial state  ${}^6A_{1g}{}^6A_{1g}$  and an orbitally degenerate Jahn–Teller final state, such as  ${}^5E_g{}^5E_g$  for  $e_g \rightarrow e_g$  or  ${}^5E_g{}^5T_{2g}$  for  $e_g \rightarrow t_{2g}$  CT transitions. An unconventional final state with an orbital degeneracy on both sites or Jahn–Teller excited states may be responsible for the complex multi-peak lineshape of the inter-center d-d CT band in ferrites.

#### 3.4. Interplay of the CT Transitions in Ferrites

The most complete and detailed analysis of the optical spectra for a wide range of ferrites has been carried out in relatively recent papers [39,40]. The authors analyzed optical ellipsometry data in the spectral range of 0.6–5.8 eV for two groups of the iron oxides with more or less distorted FeO<sub>6</sub> octahedral and FeO<sub>4</sub> tetrahedral clusters. One of the two groups of materials includes orthoferrites RFeO<sub>3</sub>, bismuthate BiFeO<sub>3</sub>, Y<sub>0.95</sub>Bi<sub>0.05</sub>FeO<sub>3</sub>, hematite  $\alpha$ –Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2–x</sub>Ga<sub>x</sub>O<sub>3</sub> and borate Fe<sub>3</sub>BO<sub>6</sub> in which iron Fe<sup>3+</sup> ions occupy only octahedral centro- or non-centrosymmetric positions, and distortions range from 1 to 20%.

The second group includes lithium ferrite LiFe<sub>5</sub>O<sub>8</sub>, barium hexaferrite BaFe<sub>12</sub>O<sub>19</sub>, iron garnets  $R_3Fe_5O_{12}$  and calcium ferrite  $Ca_2Fe_2O_5$ , in which  $Fe^{3+}$  ions occupy both octahedral and tetrahedral positions with a rising tetra/ortho ratio. Experimental data were discussed within the cluster model, which implies an interplay of intra- (*p*–*d*) and inter-center (*d*–*d*) CT transitions.

Some previously reported optical data on ferrites were in most cases obtained with the use of conventional reflection and absorption methods. The technique of optical ellipsometry [39,40] provides significant advantages over conventional reflection and transmittance methods in that it is self-normalizing and does not require reference measurements. The optical complex dielectric function  $\varepsilon = \varepsilon' - i\varepsilon''$  is obtained directly without a Kramers–Krönig transformation. The dielectric function  $\varepsilon$  was obtained in the range from 0.6 to 5.8 eV at room temperature. The comparative analysis of the spectral behavior of  $\varepsilon'$  and  $\varepsilon''$  is believed to provide a more reliable assignment of spectral features. The spectra were analyzed using the set of the Lorentz functions.

To begin our discussion of the CT transitions in ferrites, we refer to the spectroscopic data for garnets  $Y_3Fe_xGa_{5-x}O_{12}$  (x = 5, 3.9, 0.29, 0.09) [56]. They demonstrate that the optical response in the spectral range up to 30000 cm<sup>-1</sup> (~3.7 eV) is governed by the intra-center transitions for both octahedral and tetrahedral Fe<sup>3+</sup> centers. It means that the onset energy for different *d*–*d* CT transitions in ferrites is expected to be >3.7 eV, which is in agreement with our model estimates discussed in Section 3.3.

To uncover the role played by the octahedral Fe<sup>3+</sup> centers, we turn to the optical response of the orthoferrites RFeO<sub>3</sub>. These compounds contain the only type of centrosymmetric, slightly (~1%) distorted, FeO<sub>6</sub> octahedra. Despite the long story of optical and magneto-optical studies (see, e.g., [5,57]), the microscopic origin of the main spectral features in orthoferrites remains questionable, and the transition assignments made earlier in [5] need a comprehensive revisit. The  $\varepsilon', \varepsilon''$  spectra of ErFeO<sub>3</sub> for three main polariations shown in Figure 2 are typical for orthoferrites, RFeO<sub>3</sub> [5,57,58]. The low-energy intense band around 3 eV may be assigned to a strong dipole-allowed intra-center  $t_{2u}(\pi) \rightarrow t_{2g}$  CT transition, as was proposed in [5]. This is a characteristic feature of the octahedral Fe<sup>3+</sup> centers in oxides. However, such an assignment also implies the existence of a weak band due to a low-energy, dipole-forbidden, intra-center  $t_{1g}(\pi) \rightarrow t_{2g}$  CT transition, red-shifted by about 0.8 eV, as expected from estimates [50]. Indeed, a band around 2.5 eV can be found in the optical and magneto-optical spectra of different orthoferrites [5]. This band is clearly visible in the hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) spectrum near 2.4 eV [39,40], where the  $t_{1g}(\pi) \rightarrow t_{2g}$  transition becomes allowed due to a breaking of the centro-symmetry for Fe<sup>3+</sup> centers.

The nearest high-energy neighborhood of the 3 eV band is expected to be composed of  $t_{1u}(\pi) \rightarrow t_{2g}$  CT transitions of comparable intensity and estimated energy about 4 eV. All the dipole-allowed intra-center p-d CT transitions to the  $e_g$  state are blue-shifted by  $10Dq(3d^5)$  as compared to their  $\gamma \rightarrow t_{2g}$  counterparts with the onset energy of the order of 4 eV. Interestingly, for the dipole-allowed  $\gamma_u \rightarrow t_{2g}$  transitions, the maximum intensity is expected for the low-energy  $t_{2u}(\pi) \to t_{2g}$  transition, whereas for  $\gamma_u \to e_g$  transitions, the maximum intensity is expected for the high-energy (~6–7 eV)  $t_{1u}(\sigma) \rightarrow e_g$  transition. The analysis of the experimental spectra for orthoferrites demonstrates the failure of the intra-center p-d CT transitions to explain the broad intensive band centered near 4.5 eV together with a narrow low-energy satellite peaked near 3.9 eV. Both features are typical for orthoferrites [5,57] and may be assigned to a  $e_g \rightarrow t_{2g}$  low-energy inter-center CT transition  ${}^{6}A_{1g}{}^{6}A_{1g} \rightarrow {}^{5}E_{g}{}^{5}T_{2g}$  to an unconventional final state with an orbital degeneracy on both sites. These Jahn–Teller excited states are responsible for the complex line-shape of the  $e_g \rightarrow t_{2g}$  CT band, which is composed of a narrow exciton-like feature and a broad intense band separated by  $\sim$ 0.5 eV, which is believed to be a measure of the Jahn–Teller splitting in the excited state. Thus, we see that all the spectral features observed in the optical spectra of orthoferrites for energies below 5 eV can be directly assigned to the low-energy intra-center *p*–*d* and inter-center *d*–*d* CT transitions.



**Figure 2.** (Color online) The dielectric function spectra in ErFeO<sub>3</sub> orthoferrite for three main polarizations. The Lorentzian fitting is marked by dotted curves and filling. Adapted from [39,40].

It is worth noting that the dielectric function in orthoferrites is nearly isotropic due to very weak ( $\sim$ 1%) rhombic distortions of FeO<sub>6</sub> octahedra and nearly equivalent different Fe–O–Fe bonds. Nevertheless, a fine structure of the main CT bands is clearly revealed in magneto-optical spectra of orthoferrites, which was earlier assigned to the dipole-forbidden *d*–*d* crystal field transitions [5,57]. In our opinion, their relation to the low-symmetry distortions in the *p*–*d* CT band seems to be more reasonable.

The effect of a strong change in bulk crystalline symmetry and local trigonal noncentrosymmetric distortions of FeO<sub>6</sub> octahedra is well illustrated by the optical response of hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [39,40]. First of all, there is a noticeable rise in intensity and a splitting for dipole-forbidden  $t_{1g}(\pi) \rightarrow t_{2g}$  transition at 2.4 eV, which is clearly visible in the spectrum of the gallium-substituted sample. Second, one should note a clear splitting in the order of 0.3–0.4 eV of the 3 eV band due to a sizable trigonal distortion of the FeO<sub>6</sub> octahedra. In both cases, the band splitting effect reflects the singlet–doublet splitting of the initial orbital triplets,  $t_{1g}(\pi)$  and  $t_{2u}(\pi)$ , respectively, due to the low-symmetry trigonal crystal field. Interestingly, the integral intensity of the  $t_{2u}(\pi) \rightarrow t_{2g}$  band at 3 eV is visibly enhanced in hematite as compared to similar bands in orthoferrites, which may result from the more covalent Fe–O bonding in hematite.

#### 4. Effective Hamiltonian for Fe Clusters in Ferrites

As the principal interactions determining the CT transitions' contributions to the optics and magneto-optics of ferrites, we note the low-symmetry crystal field (*LSCF*), Zeeman interaction  $V_Z$ , spin–orbit interaction  $V_{SO}$ , exchange interaction  $V_{ex}$  and exchange relativistic interactions  $V_{so}^{ex}$ . The CT configurations have two unfilled shells—the  $3d^6 (t_{2g}^4 e_g^2 \text{ or } t_{2g}^3 e_g^3)$  shell and the  $\gamma_{2p}$  shell ( $\tilde{\gamma}_{2p}^1$ -hole), which distinguishes them considerably from the ground state configuration having only one unfilled shell  $3d^5 (t_{2g}^3 e_g^3)$ , and leads to the

specificity of the manifestation of various interactions, especially anisotropic ones. Below, we consider the aforementioned interactions in the cluster approach.

#### 4.1. Low-Symmetry Crystal Field

Using the the cubic-group irreducible tensor operator technique, in particular, the Wigner–Eckart theorem [29], we can write the matrix of the effective Hamiltonian of the low-symmetry crystal field,  $\hat{H}_{LSCF}$ , in general as follows:

$$\left\langle \kappa S M_{s} \Gamma M | \hat{H}_{LSCF} | \kappa' S' M_{s}' \Gamma' M' \right\rangle = \sum_{\gamma \nu} \sum_{\Gamma \Gamma'} B_{\nu}^{\gamma \star} (\kappa \Gamma \kappa' \Gamma') (-1)^{\Gamma - M} \left\langle \begin{array}{cc} \Gamma & \gamma & \Gamma' \\ -M & \nu & M' \end{array} \right\rangle \delta_{SS'} \delta_{M_{s} M_{s}'} , \quad (8)$$

where  $\gamma = E, T_2, \langle ... \rangle$  is the 3 $\Gamma$  symbol [29],  $\kappa, \kappa'$  are certain CT configurations and  $B_{\nu}^{\gamma}(\Gamma\Gamma')$  are crystal field parameters.

For a certain  $T_1(T_2)$  term, the  $\hat{H}_{LSCF}$  can be written as an effective operator:

$$V_{LSCF} = \sum_{ij} B_{ij}^{CF} \left[ \widetilde{L_i L_j} - \frac{1}{3} L(L+1) \,\delta_{ij} \right].$$
(9)

where  $B_{ij}^{CF}$  is the symmetric traceless matrix of the *LSCF* parameters;  $\widetilde{L_iL_j} = (L_iL_j + L_jL_i)/2$ ; **L** is the effective orbital moment of the  $T_1$ -,  $T_2$ -term (L = 1). However, in general, the *LSCF* can lead to the mixing of different cubic terms,  ${}^{2S+1}\Gamma$ ,  ${}^{2S+1}\Gamma'$  ( $E, T_2 \in \Gamma \times \Gamma'$ ), of identical or different CT configurations with the same spin multiplicity. All these effects may be of importance, since  $H_{LSCF}$  reaches a magnitude up to ~0.1 eV under the low-symmetry distortions of the [FeO<sub>6</sub>]<sup>9-</sup> complex of order 10<sup>-2</sup>.

#### 4.2. Conventional Spin–Orbital Interaction

The conventional "intra-center" spin–orbital interaction  $V_{SO} = \sum_i a(r_i) \mathbf{l}_i \cdot \mathbf{s}_i$  for a certain  $T_1(T_2)$  term can be written as follows:

$$V_{so} = \lambda \mathbf{L} \cdot \mathbf{S} , \qquad (10)$$

where  $\lambda$  is the effective spin–orbit coupling constant, tabulated for the CT states of the  $[\text{FeO}_6]^{9-}$  and  $[\text{FeO}_4]^{5-}$  clusters in [32,37]. The contributions to  $\lambda$  are due to both the ligand (oxygen) 2p-subsystem and the iron subsystem, the latter contribution being dominant.  $V_{SO}$  leads to the terms splitting and mixing, the latter being especially significant in the case of identical configurations or those differing from each other in the state of the 3*d*-shell, only. However, in general, the  $V_{SO}$  can lead to the mixing of different cubic terms  ${}^{2S+1}\Gamma$ ,  ${}^{2S'+1}\Gamma'$  ( $|S-S'| \leq 1 \leq S+S'$ ;  $T_1 \in \Gamma \times \Gamma'$ ).

#### 4.3. Zeeman Interaction

The Zeeman interaction  $V_Z = \sum_i \mu_B(\mathbf{l}_i + 2\mathbf{s}_i) \cdot \mathbf{H}$  can be written for a certain  $T_1(T_2)$  term as an effective operator:

$$V_Z = \mu_B(g_L \mathbf{L} + g_S \mathbf{S}) \cdot \mathbf{H}, \qquad (11)$$

where  $g_S$  and  $g_L$  are, respectively, the spin *g*-factor ( $g_S \approx 2$ ) and the effective orbital *g*-factor, whose values are listed in [32,37]. Note that  $g_L$  can disagree with the classical orbital value  $g_L = 1$  not only in magnitude, but even in sign. In particular, the CT state of the  $t_{2u}^5 (t_{2g}^4 e_g^2 {}^5 T_2)$  configuration dominating the magneto-optics of ferrites at the long wavelength tail has the value  $g_L = -\frac{3}{4}$ . It is worth noting that at variance with the spin-orbital coupling, the contributions to  $g_L$  due to the oxygen  $\tilde{\gamma}_{2p}$ -hole and the 3d electrons have comparable values.

#### 4.4. Exchange Interaction

The Heisenberg exchange interaction of the  $[FeO_6]^{9-}$  *m*-cluster in the CT state with the neighboring *n*-cluster in the ground  ${}^6A_{1g}$  state can be written in a simplified form as follows:

$$V_{ex} = -2 \sum_{m>n} J_{mn}(\mathbf{S}_m \cdot \mathbf{S}_n), \qquad (12)$$

where  $J_{mn}$  is the exchange integral, although in general it should be replaced by the orbital operator, e.g., for a certain  ${}^{6}T_{1u}$  term for the *m*-cluster:

$$\hat{J}_{mn} = J_{mn}^{0} + \sum_{i=\alpha\beta} J_{mn}^{\alpha\beta} (\widetilde{\hat{L}_{\alpha}\hat{L}_{\beta}} - \frac{2}{3}\delta_{\alpha\beta}).$$
(13)

In general, the cluster spin momentum operators in (12) should be replaced by the first rank spin operators, which can change the spin multiplicity. The  $V_{ex}$  gives rise to the orbital and spin splitting and mixing of the *CT* configuration terms. The exchange parameters in  $V_{ex}$  are determined not only by the ordinary cation–anion–cation superexchange,  $Fe^{3+}-O^{2-}-Fe^{3+}$ , but also by the considerably stronger direct cation–anion exchange,  $Fe^{3+}-O^{2-}$ , reaching the magnitude in the order ~0.1 eV. Strictly speaking, at variance with the antiferromagnetic exchange interaction between the ground states, the exchange in the CT state can lead to both antiferro- and ferromagnetic spin coupling. Interestingly, the matrix of the orbital operator  $\hat{J}_{mn}$  in (13) has a structure similar to  $V_{LSCF}$  (8) with the main orbitally isotropic  $\gamma = A_{1g}$  term included. In other words, a nontrivial orbital part of  $\hat{V}_{ex}$  can be considered as a spin-dependent contribution to the low-symmetry crystal field.

It should be noted that, in addition to the spin-dependent part, the exchange interaction also contains a spin-independent contribution, which has a similar orbital structure.

#### 4.5. Exchange-Relativistic Interactions

The combined effect of a conventional intra-center spin–orbital coupling and orbitally non-diagonal exchange coupling for an excited orbitally degenerated state of the Fe cluster within the second-order perturbation theory can give rise to a novel type of exchange-relativistic interaction, modified spin–orbital coupling  $\hat{V}_{SO}^{ex}$ , which can be written as a sum of isotropic, anisotropic antisymmetric and anisotropic symmetric intra-center and inter-center terms [31,32,37,59]:

$$\hat{V}_{SO}^{ex} = \sum_{m,n} \lambda_{mn}^{(0)} (\mathbf{L}_m \cdot \mathbf{S}_n) + \sum_{m,n} (\boldsymbol{\lambda}_{mn} \cdot [\mathbf{L}_m \times \mathbf{S}_n]) + \sum_{m,n} (\mathbf{L}_m \stackrel{\leftrightarrow}{\boldsymbol{\lambda}}_{mn} \mathbf{S}_n).$$
(14)

It is worth noting that  $\lambda_{mn}$  has the symmetry of the Dzyaloshinskii vector [11,21,60,61], and the last term has the symmetry of the two-ion quasi-dipole spin anisotropy. Generally speaking, all the three terms can be of a comparable magnitude.

The contribution to the intra-center (m = n) bilinear interaction is determined by the spin-independent purely orbital exchange, and the inter-center ( $m \neq n$ ) term, or "spin-other-orbit" coupling  $\hat{V}_{SoO}$ , is determined by the spin-dependent exchange interaction. However, the spin-dependent exchange leads to the occurrence of additional nonlinear spin-quadratic terms, the contributions of which can be taken into account by the formal replacement of the linear spin operator  $S_n$  in (14) for the nonlinear operator  $S_{nn}$ :

$$\hat{S}_{q}(mn) = \hat{S}_{q}(n) + \gamma \left[ \hat{V}^{2} \left( S(m) \right) \times S^{1}(n) \right]_{q}^{1} = \hat{S}_{q}(n) + \gamma \sum_{q_{1}, q_{2}} \left[ \begin{array}{cc} 2 & 1 & 1 \\ q_{1} & q_{2} & q \end{array} \right] \hat{V}_{q_{1}}^{2} \left( S(m) \right) S_{q_{2}}(n) ,$$
(15)

where [:::] is the Clebsch–Gordan coefficient [62] and  $V_q^2(S)$  is the rank 2 spin irreducible tensor operator. In particular,

$$\hat{V}_0^2(S) = 2 \left[ \frac{(2S-2)!}{(2S+3)!} \right]^{1/2} \left( 3\hat{S}_z^2 - S(S+1) \right).$$
(16)

The coefficient  $\gamma$  in (15) can be calculated for specific terms. The isotropic part of  $V_{SoO}$  can be presented, in the general case, as follows:

$$V_{SoO}^{iso} = \sum_{mn} \lambda(mn) (\mathbf{L}(m) \cdot \mathbf{S}(n)) + \sum_{m \neq n} \lambda'(mn) \left( \mathbf{L}(m) \cdot \mathbf{S}(m) \right) \left( \mathbf{S}(m) \cdot \mathbf{S}(n) \right).$$
(17)

Similarly to the Dzyaloshinskii vector, to estimate the parameters of the spin-otherorbit coupling, we can use the simple relation [63]

$$\lambda(m) \approx \lambda(mn) \approx \frac{\lambda' J'}{\Delta E_{S\Gamma}},$$
(18)

where  $\lambda'$  and J' are the spin-orbital constant for the  $T_1$  and  $T_2$ -states and the nondiagonal exchange parameter, respectively;  $\Delta E_{S\Gamma}$  is a certain excitation energy. Parameters such as  $\lambda(m)$ ,  $\lambda(mn)$  can have values considerably larger than typical values of the Dzyaloshinskii vector [11,21,61], due both to smaller values of  $\Delta E_{S\Gamma}$  and the direct 2p–3d exchange, which as stated above, is stronger than the 3d–2p–3d superexchange determining  $\mathbf{d}(mn)$ . Effective orbital magnetic fields acting on the  $T_1$  and  $T_2$  orbital states, e.g., for Fe<sup>3+</sup>ions in ferrites due to  $V_{SO}^{ex}$ , can reach magnitudes larger than 10 T ( $\lambda' \geq 10^2 \text{ cm}^{-1}$ ,  $J' \geq 10^2 \text{ cm}^{-1}$ ,  $\Delta E_{S\Gamma} \sim 10^4 \text{ cm}^{-1}$ ).

The approach presented here can be immediately extended to tetrahedral clusters  $[FeO_4]^{5-}$ .

# 5. Anisotropic Polarizability of the Octahedral [FeO<sub>6</sub>]<sup>9–</sup>-Cluster

Almost all ferrites are low anisotropic optical media in a wide spectral range:  $\Delta \epsilon / \epsilon_0 \leq 10^{-2}$ ,  $\epsilon_0$  and  $\Delta \epsilon$ , which are, respectively, the isotropic and anisotropic parts of the permittivity tensor  $\hat{\epsilon}$ . The latter can be written as the sum of the symmetric and antisymmetric parts:

$$\Delta \epsilon = \Delta \epsilon_{ii}^s + \Delta \epsilon_{ii}^a \,, \tag{19}$$

characterizing the linear birefringence/dichroism and the circular birefringence/dichroism, respectively. The latter can be described by axial gyration vector **g** [64] which is dual to  $\Delta \epsilon_{ii}^{a}$ :

$$g_i = \frac{1}{2} e_{ijk} \Delta \epsilon^a_{jk} , \qquad (20)$$

where  $e_{ijk}$  is the Levi–Civita tensor.

Within a linear approximation, the Fe cluster's contribution to the anisotropic permitivity tensor can be expressed in terms of the cluster anisotropic polarizability tensor  $\hat{\alpha}$ as follows:

$$\Delta \hat{\epsilon} = 4\pi N L \hat{\alpha} , \qquad (21)$$

where *N* is the number of clusters per unit volume;  $L = \frac{n_0^2 + 2}{9}$  is the Lorentz-Lorenz factor. Hence, for the gyration vector we have

$$\mathbf{g} = 4\pi N L \boldsymbol{\alpha} \,, \tag{22}$$

with  $\alpha$  being the "microgyration vector," related to the antisymmetric part of the cluster polarizability tensor by an expression analogous to (20).

#### 5.1. Simple Microscopic Theory

The microscopic analysis of the optical anisotropy is usually carried out on the basis of the Kramers–Heisenberg formula [65] for the electronic polarizability; in the case of the microgyration vector, it takes on following form:

$$\boldsymbol{\alpha} = \frac{1}{\hbar} \sum_{ij} \rho_i \left[ \mathbf{d}_{ij} \times \mathbf{d}_{ji} \right] \cdot F_1(\omega, \omega_{ij}) \,. \tag{23}$$

For the symmetric part of  $\hat{\alpha}$ , the Kramers–Heisenberg formula reduces to

$$\alpha_{kl}^{sym} = \frac{1}{\hbar} \sum_{ij} \rho_i \langle i | d_k | j \rangle \langle j | d_l | i \rangle \cdot F_2(\omega, \omega_{ij}).$$
<sup>(24)</sup>

In these formulae,  $\mathbf{d}_{ij}$  is the matrix element of the electric dipole moment  $\mathbf{d}$  ( $d_{k,l}$  being its Cartesian projections) between the initial state  $|i\rangle$  and the final state  $|j\rangle$  for the CT transition;  $\rho_i$  is the statistical weight of the  $|i\rangle$  state.  $F_k$  (k = 1, 2) is the Lorentz dispersion factor

$$F_k(\omega, \omega_{ij}) = \frac{(\omega + i\Gamma_{ij})[1 - (-1)^k] + \omega_{ij}[1 + (-1)^k]}{(\omega + i\Gamma_{ij})^2 - \omega_{ij}^2} .$$
(25)

 $\omega_{ij}$  denotes the CT transition frequency, and  $\Gamma_{ij}$  is the line width.

Instead of the Cartesian tensor, one can introduce the irreducible polarizability tensor [32,37]:

$$\alpha_q^k = \frac{1}{\hbar} \sum_{ij} \sum_{q_1q_2} \rho_i \begin{bmatrix} 1 & 1 & k \\ q_1 & q_2 & q \end{bmatrix} \langle i | d_{q_1} | j \rangle \langle j | d_{q_2} | i \rangle \cdot F_k(\omega, \omega_{ij}), \qquad (26)$$

where [:::] is the Clebsch–Gordan coefficient [62], and  $d_q$  is the irreducible tensor component of the dipole moment **d**  $(d_{\pm 1} = \mp \frac{1}{\sqrt{2}}(d_x \pm id_y), d_0 = d_z)$ .

An important advantage of the irreducible tensor form is the natural separation of isotropic and anisotropic contributions:  $\alpha_0^0$  describes the isotropic refraction/absorption;  $\alpha_q^1$  and  $\alpha_q^2$  describe the circular and linear birefringence/dichroism, respectively.

For octahedral [FeO<sub>6</sub>]<sup>9–</sup> (tetrahedral [FeO<sub>4</sub>]<sup>5–</sup>) clusters with an orbitally non-degenerate ground state  ${}^{6}A_{1g}$  in ferrites, the contribution of the CT transitions  ${}^{6}A_{1g} \rightarrow {}^{6}T_{1u}$  ( ${}^{6}A_{1g} \rightarrow {}^{6}T_{2}$ ) to the anisotropic polarizability will be associated only with certain "perturbation" in excited  ${}^{6}T_{1u}$  ( ${}^{6}T_{2}$ ) CT states.

In the linear approximation, we single out two main contributions,  $\alpha_q^k(split)$  and  $\alpha_q^k(mix)$ , associated with the orbital splitting of excited <sup>6</sup>*T*-states and mixing/interactions of different <sup>6</sup>*T*-states, respectively, under the action of various perturbations,  $V_{LSCF}$ ,  $V_Z$ ,  $V_{SO}$  and  $V_{SO}^{ex}$  [32,37].

$$\alpha_{q}^{k}(split) = \frac{1}{\hbar^{2}} \sum_{i=6A_{1g}} \sum_{j=6T_{1u}} \sum_{\mu\mu'} \sum_{q_{1}q_{2}} \rho_{i} \begin{bmatrix} 1 & 1 & k \\ q_{1} & q_{2} & q \end{bmatrix} \times \langle i|d_{q_{1}}|j\mu\rangle \langle j\mu|\hat{V}|j\mu'\rangle \langle j\mu'|d_{q_{2}}|i\rangle \cdot \frac{\partial F_{k}(\omega, \omega_{ij}^{0})}{\partial \omega_{ij}^{(0)}}$$

$$(27)$$

$$\alpha_{q}^{k}(mix) = \frac{1}{\hbar} \sum_{i=6A_{1g}} \sum_{\substack{\left(j,j'=6T_{1u}\right)\\E_{j}>E_{j}'}} \sum_{q_{1}q_{2}} \rho_{i} \begin{bmatrix} 1 & 1 & k\\q_{1} & q_{2} & q \end{bmatrix} \times \langle i|d_{q_{1}}|j\rangle \cdot \frac{\langle j|V|j'\rangle}{E_{j}-E_{j'}} \cdot \langle j'|d_{q_{2}}|i\rangle \cdot F_{k}(\omega, \omega_{ij})$$

$$(28)$$

A simple illustration of the nature of circular and linear birefringence due to a splitting mechanism is presented in Figure 3.



**Figure 3.** An illustration of the nature of circular and linear birefringence due to a splitting mechanism: (a) schematic for the dipole allowed CT transitions  ${}^{6}A_{1g} \rightarrow {}^{6}T_{1u}$  for the light with right and left circular polarization under external magnetic field and orbital *Zeeman* splitting; (b) schematic for the CT transitions  ${}^{6}A_{1g} \rightarrow {}^{6}T_{1u}$  for the light with a linear polarization in a low-symmetry (rhombic) crystal field and *Stark* splitting for excited  ${}^{6}T_{1u}$  state. Note that we are dealing with final current (a) and currentless (b) states, respectively.

Note that in ferrites with an orbitally non-degenerate ground  ${}^{6}A_{1g}$  state of Fe clusters, both linear and circular birefringence will be associated with orbital splitting/mixing in excited states. Obviously, the Fe cluster's contribution to the linear birefringeance/dichroism will be related to the low-symmetry crystal field  $V_{LSCF}$  in excited  ${}^{6}T_{1u}$  states, and its contribution to circular birefringence/dichroism will be determined by the orbital Zeeman interaction or complex spin–orbital interactions, such as  $V_{SO}$  and  $V_{SO}^{ex}$ . Large exchange spin fields of up to  $10^3$  T and large spin Zeeman splittings do not make direct contributions to circular magneto-optics in ferrites.

Due to a competition of the splitting and mixing mechanisms, the spectral dependence of the polarizability cannot be considered to be a sum of separate individual  ${}^{6}A1g \rightarrow {}^{6}T$  CT transitions.

#### 5.2. Symmetry Considerations

Accounting for local point symmetry, crystal and magnetic symmetry in many cases provides important qualitative and even quantitative information about various anisotropic effects—in particular, the roles of certain microscopic mechanisms.

#### 5.2.1. Linear Birefringeance in Orthoferrites

Simple symmetry considerations within the framework of the so-called "deformation" model made it possible to explain the dependence of linear birefringence on the type of R-ion in orthoferrites, RFeO<sub>3</sub> [1].

The real FeO<sub>6</sub> cluster in orthoferrites can be represented as a homogeneously deformed ideal octahedron. To find the degree of distortion, we introduce a symmetric strain tensor  $\varepsilon_{ii}$  according to the standard rules. In the local system of cubic axes of the octahedron,

$$\varepsilon_{ij} = \frac{1}{4l^2} \sum_{n=1}^{6} (R_i(n)u_j(n) + R_j(n)u_i(n)),$$
(29)

where  $\mathbf{R}(n)$  is the radius-vector of the Fe-O<sub>n</sub> bond,  $\mathbf{u}(n)$  is the O<sub>n</sub>-ligand displacement vector or

$$\hat{\varepsilon} = \begin{pmatrix} 1 - \frac{l_1}{l} & \frac{1}{2}(\frac{\pi}{2} - \theta_{12}) & \frac{1}{2}(\frac{\pi}{2} - \theta_{13}) \\ \frac{1}{2}(\frac{\pi}{2} - \theta_{21}) & 1 - \frac{l_2}{l} & \frac{1}{2}(\frac{\pi}{2} - \theta_{23}) \\ \frac{1}{2}(\frac{\pi}{2} - \theta_{31}) & \frac{1}{2}(\frac{\pi}{2} - \theta_{32}) & 1 - \frac{l_3}{l} \end{pmatrix},$$
(30)

where *l* is the Fe–O separation in an ideal octahedron,  $l_i$  are the Fe–O<sub>i</sub> inter-atomic distances  $\frac{1}{3}(l_1 + l_2 + l_3) = l$  and  $\theta_{ij}$  are the bond angles of O<sub>i</sub>–Fe–O<sub>j</sub> in a real complex. Local *x*, *y*, *z* axes in octahedron are defined as follows: the *z*-axis is directed along the Fe–O<sub>I</sub> bond, the *x*-axis is along the Fe–O<sub>I</sub>, the shortest Fe–O bond. In general, the deformations of octahedra in orthoferrites are small and do not exceed 0.02.

Diagonal components of the traceless strain tensor (30) (tensile/compressive deformations) can be termed as *E*-type deformations, since  $\varepsilon_{zz}$  and  $\frac{1}{\sqrt{3}}(\varepsilon_{xx} - \varepsilon_{yy})$  transform according to the irreducible representation (irrep) *E* of the cubic group O<sub>h</sub>, and off-diagonal components (shear deformations) can be termed as *T*<sub>2</sub>-type deformations, since  $\varepsilon_{yz}$ ,  $\varepsilon_{xz}$  and  $\varepsilon_{xy}$  transform according to the irrep *T*<sub>2</sub> of the cubic group O<sub>h</sub>.

In the linear approximation, the symmetric anisotropic polarizability of the octahedron FeO<sub>6</sub> can be related to its deformation as follows [1]:

$$\alpha_{ij} = \begin{cases} p_E \varepsilon_{ij}, & i = j \\ p_{T_2} \varepsilon_{ij}, & i \neq j, \end{cases}$$
(31)

where  $\varepsilon_{ij}$  is the FeO<sub>6</sub> octahedron deformation tensor ( $Tr \hat{\varepsilon} = 0$ );  $p_{E, T_2}$  are the photo-elastic constants, relating the polarizability to  $E, T_2$ -deformations, respectively. The relation (31) is valid in the local coordinate system of the FeO<sub>6</sub> octahedron. In the *abc*-axes system, it can be rewritten as

$$\alpha_{ij} = p_E \varepsilon_{ij}^{\scriptscriptstyle L} + p_{T_2} \varepsilon_{ij}^{\scriptscriptstyle 1_2} , \qquad (32)$$

where  $\varepsilon_{ij}^E$  and  $\varepsilon_{ij}^{T_2}$  are the components of the tensors of the *E*- and *T*<sub>2</sub>-deformations of the octahedron in the *abc*- system, respectively.

Proceeding to the permittivity tensor  $\hat{e}$  and summing over all Fe-ions sites, we arrive at nonzero diagonal components of  $\hat{e}$ :

$$\varepsilon_{ii} = P_E \varepsilon_{ii}^E + P_{T_2} \varepsilon_{ii}^{T_2} , \qquad (33)$$

where  $P_{E,T_2} = 4\pi N \left(\frac{n_0^2 + 2}{3}\right)^2 p_{E,T_2}$ ; *N* is the number of Fe<sup>3+</sup> ions per 1 cm<sup>3</sup>. The components of  $\hat{\epsilon}^E$ ,  $\hat{\epsilon}^{T_2}$  tensors serve as the *structure factors* and may be calculated taking into account the known components of the tensor of FeO<sub>6</sub> octahedron local deformations and the Eulerian angles relating the local axes to the *abc* ones.

Thus, we have a two-parameter Formula (33) for the birefringence of orthoferrites as a function of rhombic distortions of their crystal structure [1]. The photo-elastic constants  $P_E$ ,  $P_{T_2}$  can be found from the comparison of experimental data [66,67] with the theoretical structure dependence of the *ab* plane birefringence:

$$\Delta n_{ab} = n_a - n_b = \frac{1}{2n_0} \Big[ P_E(\varepsilon_{xx}^E - \varepsilon_{yy}^E) + P_{T_2}(\varepsilon_{xx}^{T_2} - \varepsilon_{yy}^{T_2}) \Big]$$
(34)

treated as a dependence on the type of the orthoferrite. The Figure 4 shows both experimental and calculated  $\Delta n_{ab}$  given  $P_E = 6.2 n_0$ ,  $P_{T_2} = 4.0 n_0$  (values obtained from the least-squares fitting). Very nice agreement of the two-parameter Formula (34) with the experiment testifies to the validity of the deformation model of the birefringence.

Using the determined parameter  $P_{E,T_2}$  values, we are able to describe all the peculiarities of the orthoferrite birefringence [1]. In particular, Figure 4 shows the theoretical predictions for the orientation angles  $\pm \theta$  of optical axes, measured from the *c*-axis for the *ac* and *bc* planes and from the *a*-axis for the *ab* plane, together with scarce experimental data on Eu, Tb, Dy, Y, Yb orthoferrites [67,68]. Quite good agreement with the available experimental data is another confirmation of the validity of the deformation model of birefringence of orthoferrites. In general, for all its simplicity, the deformation model reflects quite correctly the main peculiarities of the natural birefringence of orthoferrites.



**Figure 4.** Left panel: Linear birefringeance  $\Delta n_{ab}$  for orthoferrites RFeO<sub>3</sub> in *ab* plane. Solid circles are predictions of the deformation model; hollow circles are experimental data ( $\lambda = 0.633 \mu m$ ) [66]. Right panel: The orientation angles ( $\pm \theta$ ) of optical axes in respective planes of orthoferrites predicted by the deformation model. The solid black circles are scarce experimental data for *bc* plane ( $\lambda = 0.68 \mu m$ ) [67,68]. Adapted from [1].

#### 5.2.2. Circular Birefringeance/Dichroism in Ferrites

First of all, note that the gyration vector and the magnetic moment (or the ferromagnetic vector  $\mathbf{m}$ ) have the same transformation properties. For *ferrimagnetic* iron garnets,

$$\mathbf{g} = \hat{A}_a \mathbf{m}_a + \hat{A}_d \mathbf{m}_d + \hat{C} \mathbf{H},\tag{35}$$

where  $\mathbf{m}_a$  and  $\mathbf{m}_d$  are magnetic moments, or ferromagnetic vectors, of octahedral and tetrahedral sublattices, respectively.

In weak ferromagnets such as  $RFeO_3$ , and in a number of other magnetic compounds with non-equivalent magnetic sublattices, certain components of the ferromagnetic vector **m** and the antiferromagnetic vector **l** in a two-sublattice model transform identically, which enables one to write **g** in the linear approximation through **m**, **l**, and the external magnetic field **H**, as

$$\mathbf{g} = \hat{A} \,\mathbf{m} + \hat{B} \,\mathbf{l} + \hat{C} \,\mathbf{H}, \quad (m^2 + l^2 = 1)$$
 (36)

(the ferromagnetic (FM), antiferromagnetic (AFM) and field contributions, respectively).

The form of each of  $\hat{A}$ ,  $\hat{B}$ ,  $\hat{C}$  tensors is determined by the crystal symmetry. For example, in orthorhombic weak ferromagnetic orthoferrites, RFeO<sub>3</sub>:

$$\hat{A} = \begin{pmatrix} a_{xx} & 0 & 0 \\ 0 & a_{yy} & 0 \\ 0 & 0 & a_{zz} \end{pmatrix}, \quad \hat{B} = \hat{B}^{s} + \hat{B}^{a} = \begin{pmatrix} 0 & 0 & b_{xz} \\ 0 & 0 & 0 \\ b_{zx} & 0 & 0 \end{pmatrix},$$

$$a_{xx} \neq a_{yy} \neq a_{zz}$$
,  $b_{zx} \neq b_{xz}$ .

In rhombohedral weak ferromagnets ( $\alpha$ -*Fe*<sub>2</sub>*O*<sub>3</sub>, *FeBO*<sub>3</sub>, *FeF*<sub>3</sub>, etc.):

$$\hat{A} \;=\; \left( egin{array}{ccc} a_{\perp} & 0 & 0 \ 0 & a_{\perp} & 0 \ 0 & 0 & a_{\parallel} \end{array} 
ight), \quad \hat{B} \;=\; \hat{B}^a \;=\; \left( egin{array}{ccc} 0 & b_{xy} & 0 \ b_{yx} & 0 & 0 \ 0 & 0 & 0 \end{array} 
ight),$$

i.e.,  $b_{yx} = -b_{xy}$ , and the  $\hat{B}$  tensor, in contrast with orthoferrites, is antisymmetric. The symmetry properties of the  $\hat{A}$  and  $\hat{C}$  tensors are identical.

The special role of the antiferromagnetic contribution to the gyration vector for weak ferromagnets is due to the fact that for them, as a rule,  $m \ll l$ ; for example,  $m/l \approx 0.01$  in YFeO<sub>3</sub> and  $m/l \approx 0.001$  in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, respectively [11,21,69]. However, the components

of the gyration vector **g** in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and YFeO<sub>3</sub> are comparable in magnitude with those for the yttrium iron garnet, Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> [5,70], although the magnetization of the latter is approximately by two orders larger than in the hematite and by one order larger than in orthoferrites. It seems impossible to explain this phenomenon other than in terms of the *AFM* contribution. Hence, it appears that there must be microscopic mechanisms causing the antisymmetric relations of the gyration vector to spins:

$$\mathbf{g} = \sum_{mn} \left[ \mathbf{B}(mn) \times \langle \mathbf{S}(n) \rangle \right], \tag{37}$$

where the vector **B**(*mn*) is determined by the antisymmetric part of  $\hat{B}$ .

# 6. Charge Transfer Transitions and Magneto-Optical Effects (MOE) in Ferrites

#### 6.1. Working Microscopic Models for Circular MOE

The main contributions to the micro-gyration vector for  $[FeO_6]^{9-}$  and  $[FeO_4]^{5-}$  clusters and the circular MOE for ferrites are determined by the splitting and mixing mechanisms [32]. In the first order of perturbation theory, only the interactions  $V_{SO}$ ,  $V_Z$ ,  $V_{SO}^{ex}$  play a part, as these are odd in the orbital moment and enable the orbital splitting and mixing of excited CT states of the  ${}^{6}T_{1u}$  type. Note that the spin part of  $V_Z$ , just as the isotropic Heisenberg spin exchange of the  $[FeO_6]^{9-}$  cluster with its magnetic surroundings, characterized by the spin exchange field  $H_{ex}$ , does not contribute in the linear approximation to the circular MOE.  $V_{SO}$  and the orbital part of  $V_Z$  yield the FM and field contributions to the gyration vector; their combined action for the "octahedral" CT transitions due to the splitting of the excited  ${}^{6}T_{1u}$  states is given by

$$\mathbf{g}_{a}^{split} = 2 \sum_{j=6T_{1u}} \frac{\pi e^{2} L N}{\hbar m_{e} \omega_{0j}} \left( \lambda^{j} \langle \mathbf{S} \rangle + \mu_{B} g_{L}^{j} \mathbf{H} \right) f_{j} \frac{\partial F_{1}(\omega, \omega_{0j})}{\partial \omega_{0j}} \,. \tag{38}$$

where  $\langle \mathbf{S} \rangle$  is the thermodynamic spin average;  $f_j$  is the oscillator strength for  ${}^{6}A_{1g} - {}^{6}T_{1u}$ CT transition;  $\lambda^{j}$  and  $g_{L}^{j}$  are the effective spin–orbital constant and orbital *g*-factor for a certain  ${}^{6}T_{1u}$  term (see Tables 1 and 2 in reference [32]).

The contribution of the mixing mechanism, that is, of the interaction of different  ${}^{6}T_{1u}$  CT terms of the octahedral [FeO<sub>6</sub>]<sup>9–</sup> ( ${}^{6}T_2$  CT terms of the tetrahedral [FeO<sub>4</sub>]<sup>5–</sup>) cluster, can be written as follows [32]):

$$\mathbf{g}_{a}^{mix} = 4 \sum_{\substack{(j,k=6T_{1u})\\E_{0j}>E_{0k}}} \frac{\pi e^{2}LN}{m_{e}} \Big(\lambda^{jk} \langle \mathbf{S} \rangle + \mu_{B} g_{L}^{jk} \mathbf{H} \Big) \left(\frac{f_{j} f_{k}}{\omega_{0j} \omega_{0k}}\right)^{1/2} \times sign\Big( \langle {}^{6}A_{1g} \| d \| j \rangle \langle {}^{6}A_{1g} \| d \| k \rangle \Big) \cdot \frac{F_{1}(\omega, \omega_{0j}) - F_{1}(\omega, \omega_{0k})}{E_{0j} - E_{0k}},$$
(39)

where  $\langle {}^{6}A_{1g} || d || j \rangle$  is the dipole moment submatrix element. The parameters of the type of effective orbital *g*-factors  $g_{L}^{jk}$  and spin–orbit coupling constants  $\lambda^{jk}$ 

$$g_L^{jk} = \frac{\langle \kappa_j \, {}^6T_{1u} \| \sum_n \mathbf{l}_n \| \kappa_k \, {}^6T_{1u} \rangle}{\langle 1 \| \, \hat{l} \, \| 1 \rangle} \, ; \, g_L \equiv g_L^{jj} \equiv g_L^j \, ; \tag{40}$$

$$\lambda^{jk} = \frac{\langle \kappa_j \,^{6}T_{1u} \| \, \hat{Q}^{11} \, \| \kappa_k \,^{6}T_{1u} \rangle}{\langle 1 \| \, \hat{l} \, \| 1 \rangle \langle \frac{5}{2} \| \hat{s} \| \frac{5}{2} \rangle} ; \ \lambda \equiv \lambda^{jj} \equiv \lambda^j , \tag{41}$$

are determined by the submatrix elements of the sum  $\sum_{n} \mathbf{l}_{n}$  of one-particle orbital moment operators acting on all atomic orbitals in the molecular orbitals, and by the submatrix element of the double irreducible spin–orbit tensor operator  $\hat{Q}^{11}$  [71]. Numerical val-

ues of  $g_L^{jk}$  and  $\lambda^{jk}$  for the *CT* states of the [FeO<sub>6</sub>]<sup>9–</sup> and [FeO<sub>4</sub>]<sup>5–</sup> clusters are given in Tables 1 and 2 in [32]. In (40) and (41), both the splitting (j = k) and mixing  $(j \neq k)$ are taken into account.  $\kappa_j$  is the set of intermediate quantum numbers necessary for distinguishing different  ${}^{6}T_{1u}$  terms.  $f_j$  is the oscillator strength of the  ${}^{6}A_{1g} \rightarrow \kappa_j {}^{6}T_{1u}$  CT transition, and  $E_{0j}$  is its energy.

Thus,  $V_{SO}$  and  $V_Z$  to the 1st order of the perturbation theory give rise to *isotropic*  $\hat{A}$ ,  $\hat{C}$  tensors (36). The frequency dependencies of the real and imaginary parts of the splitting contribution to **g** for a *CT* transition have, respectively, the "dissipative" and "dispersive" forms.

The splitting contribution of the exchange-relativistic interaction  $V_{SO}^{ex}$  (14) for the isolated  ${}^{6}T_{1u}$  term to the gyration vector can be represented as follows [31,32,37,59]:

$$\mathbf{g} = \frac{2\pi L e^2 f_{AT}}{m\hbar\omega_0} \left( \stackrel{\leftrightarrow}{\lambda} \langle \hat{\mathbf{S}} \rangle + \sum_n \stackrel{\leftrightarrow}{\lambda}_n \langle \hat{\mathbf{S}}_n \rangle \right) \frac{\partial F(\omega, \omega_0)}{\partial\omega_0} , \qquad (42)$$

where first and second terms in brackets correspond to intra-center and inter-center, or spin-other-orbit exchange-relativistic contributions, respectively; and  $\stackrel{\leftrightarrow}{\lambda}$  and  $\stackrel{\leftrightarrow}{\lambda}_n$  are the effective tensors of the respective interactions. In other words, these terms correspond to contributions with m = n and  $m \neq n$  in  $V_{SO}^{ex}$  (14). The summation over n in (42) extends to the nearest neighbors of the considered center;  $f_{AT}$  is the oscillator strength of the  ${}^6A_{1g} - {}^6T_{1u}$  transition. In general, in accordance with (14), the tensors  $\stackrel{\leftrightarrow}{\lambda}$  and  $\stackrel{\leftrightarrow}{\lambda}_n$ of the intra- and inter-center exchange-relativistic contributions in (42) contain isotropic, antisymmetric and symmetric anisotropic components.

In addition to the "gyro-electric" contribution to the gyration vector that we have considered, we should note the existence of a small "gyro-magnetic" contribution related to the magnetic susceptibility, which determines the frequency-independent contribution to the Faraday rotation [72]:

$$\Delta \Theta_F = \frac{2\pi n_0}{c} \gamma \, m, \tag{43}$$

where  $\gamma$  is gyro-magnetic ratio and *m* is the magnetic moment. It is interesting that the yttrium iron garnet in the wavelength range  $\lambda > 5 \,\mu\text{m}$  is a gyro-magnetic medium, since the gyro-magnetic contribution to the Faraday rotation is predominant ( $\Theta_F \approx 60 \,\text{deg/cm}$  at T = 300 K), although in the wavelength range  $\lambda < 4 \,\mu\text{m}$ , it can be considered as an ordinary gyro-electric medium due to a sharp increase in the gyro-electric contribution in  $\Theta_F$  [72].

# 6.2. Fe<sup>3+</sup> Diluted Nonmagnetic Compounds

The most suitable objects for the application and justification of the cluster theory for ferrites are the Fe<sup>3+</sup> diluted nonmagnetic compounds, such as YAlO<sub>3</sub> and Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>, which have crystal structures similar to those of orthoferrite YFeO<sub>3</sub> and iron garnet Ca<sub>3</sub>Fe<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>, respectively. In such dilute systems, band models are inapplicable for describing Fe 3d states, so that the cluster model has virtually no competitors for describing the optical and magneto-optical responses of dilute systems in the O 2p-Fe 3d charge transfer range, especially since it becomes possible to restrict ourselves to taking into account only intra-center p–d transfer.

The Faraday effect was measured in single-crystalline samples of diluted garnet  $Ca_3Ga_{2-x}Fe_xGe_3O_{12}$  (x = 0.15) [31], where the  $Fe^{3+}$  ions occupy only the octahedral positions, and the  $[FeO_6]^{9-}$  octahedrons are assumed to be essentially non-interacting. Making use of the splitting (38) and mixing (39) contributions to the gyration vector with the data for effective orbital *g*-factors and spin–orbital parameters from Table 1 in reference [32] and assuming that energies of all "octahedral" CT transitions in this garnet are blue-shifted by 1.4 eV in comparison with corresponding energies in "orthoferrite" complexes (see Table 1), the authors calculated both ferromagnetic and field contributions to the Faraday rotation

$$\Theta_F = \frac{\omega}{2n_0c}g = A_Fm + C_FH, \qquad (44)$$

over the entire CT band. As a result, good agreement was obtained with the experimental values of the ferromagnetic and field contributions to  $\Theta_F$ , measured in the spectral range 1.4–3.1 eV (see Figure 2 in [31]).

Unfortunately, there are few examples in the literature of a systematic study of the concentration dependence of optical and magneto-optical effects in diluted systems.

#### 6.3. The Yttrium Iron Garnet

The absence of the magneto-optically active rare-earth sublattice in yttrium iron garnet  $Y_3Fe_5O_{12}$  permits the evaluation of the "undistorted" iron sublattices contribution. In addition, experimental studies of YIG magneto-optics are abundant [5,56,73,74]. The authors [32] undertook the model computation of the FM and field contributions (36) to the gyration vector of YIG, taking into account the CT transitions both in octahedral  $[FeO_6]^{9-1}$ and tetrahedral  $[FeO_4]^{5-}$  clusters. Figure 5 shows the results of the theoretical simulation of the spectral dependencies of the real and imaginary parts of the gyration vector z-component,  $Re g_z$  and  $Im g_z$ , in YIG (solid lines), with dipoles allowed and a number of dipole forbidden CT transitions (marked by long and short line segments at the bottom of Figure 5), taken into account. The parameters of the main CT transitions used in the model simulation are presented in Table 1. Besides satisfactory agreement with the experimental data in a wide spectral range, 2.5–5.5 eV, the computed  $Reg_z$  value on the long wavelength tail of the *CT* transitions band ( $\lambda = 0.63 \mu$ m) yielded the Faraday rotation in YIG  $\Theta_F$  = 860 deg/cm, practically coinciding with the experimental value 830 deg/cm [75,76]. The computed values of the partial Faraday rotation's contributions due to octahedral CT transitions (6500 deg/cm) and tetrahedral ones (-5640 deg/cm) satisfactorily agree with the experimental values 8670 and -7840 deg/cm, respectively [75,76]. As expected for a longitudinal ferrimagnet, we see the effect of significant mutual compensation for the contributions of the octa- and tetra-sublattices.



**Figure 5.** Spectral dependence of the real and imaginary parts of the *z*-component of the gyration vector in YIG: experimental data are shown by dotted curves; model fitting is shown by solid curves. Adapted from [32].

In the octahedral CT transitions' contribution to  $Re g_z$  and in that of the tetrahedral transitions, the main role belongs to the mixing mechanism, in agreement with the predominance of paramagnetic-shaped lines in magneto-optical spectra of YIG noted in [77].

The authors of [32] have also computed the field contribution (36) to the YIG gyration vector **g**, with theoretical values of the orbital Landé factors  $g_L^{jk}$  (see Tables 1 and 2 in [32]), taking into account the main electric-dipole-allowed CT transitions only. Rough as it is, the approximation of allowed CT transitions nevertheless gives the  $\Theta_F/H$  values of  $-10^{\circ} \cdot \text{cm}^{-1} \cdot \text{T}^{-1}$  ( $\lambda = 0.7 \,\mu\text{m}$ ) and  $-2.4^{\circ} \cdot \text{cm}^{-1} \cdot \text{T}^{-1}$  ( $\lambda = 1.1 \,\mu\text{m}$ )—near the

corresponding experimental data ( $-12.4^{\circ} \cdot \text{cm}^{-1} \cdot \text{T}^{-1}$  [78] and  $-2.5^{\circ} \cdot \text{cm}^{-1} \cdot \text{T}^{-1}$  [79], respectively). The lack of experimental data precluded a comparison at shorter wavelengths.

The electronic structure, and magnetic, optical and magneto-optical properties of yttrium iron garnet were investigated recently [4] by using "first principles" GGA+U calculations with Hubbard energy correction for the treatment of the strong electron correlation. The authors boldly made too strong of a statement: "The calculated Kerr spectrum which included on-site Coulomb interaction of Fe 3d electrons described well the experimental results," which clearly does not follow from the data presented in Figure 6 from their article, especially since the calculated dielectric function shows a dramatic discrepancy with the experiment.



**Figure 6.** Spectral dependence of the real part of the z-component of the gyration vector in EuFeO<sub>3</sub>: experimental data are shown by the dotted curve; model fitting is shown by the solid curve. Adapted from [34].

#### 6.4. Bi-Substituted Iron Garnets

Although pure yttrium iron garnet has several advantages in terms of magneto-optical response, it has not been widely applied in integrated devices due to its limited Faraday rotation. However, decompensation of the contributions of the octa- and tetra-sublattices, in particular, due to the replacement of R-ions in  $R_3Fe_5O_{12}$  garnets by  $Bi^{3+}$  or  $Pb^{3+}$  ions, makes it possible to increase the Faraday rotation of iron garnets by one or two orders of magnitude in the visible and near-infrared region (see, e.g., [52]).

Wittekoek et al. [52] proposed in a purely qualitative manner that the origin of the large Faraday rotation in Bi,Pb-substituted iron garnets is the hybridization of Bi,Pb 6p orbitals, which possess anomalously large spin–orbit coupling ( $\zeta_{6p} \approx 2 \text{ eV}$ ), with the O 2p and Fe 3d orbitals. Later, this idea was supported and developed within cluster molecular orbital theory [36,38,53]. The enhancement of spin–orbit coupling in Fe 3d orbitals was assumed to be much smaller than that in O 2p orbitals, because Fe sites are located more distant than O sites from Bi sites.

Taking account of the overlap of  $2p(O^{2-})$  and  $6p(Bi^{3+})$  electronic shells and the *virtual* transition of the oxygen 2p electron to the bismuth empty 6p shell, the wave function of the outer 2p electrons of the neighboring oxygen ion thereby acquires an admixture of Bi 6p-states [36,38]:

$$\varphi_{2p\,m} \longrightarrow \psi_{2p\,m} = \varphi_{2p\,m} - \sum_{m'} \langle 6p\,m' \,|\, 2p\,m \rangle^* \,\varphi_{6p\,m'} , \qquad (45)$$

where  $\varphi_{2pm}$  and  $\varphi_{6pm}$  are atomic wave functions.

The Bi 6p-O 2p hybridization results in the modification of the spin–orbit interaction on the oxygen ion:

$$V_{SO} = V_{SO}(2p) + \Delta V_{SO}^{iso}(2p) + \Delta V_{SO}^{an}(2p), \qquad (46)$$

where  $V_{SO}(2p) = \zeta_{2p} (\mathbf{l} \cdot \mathbf{s})$  is the conventional spin–orbital interaction with  $\zeta_{2p} \approx 0.02$  eV,  $\Delta V_{SO}^{iso}(2p)$  and  $\Delta V_{SO}^{an}(2p)$  are effective isotropic and anisotropic terms due to the Bi 6p-O 2p hybridization:

$$\Delta V_{SO}^{iso}(2p) = \Delta \zeta_{2p} (\mathbf{l} \cdot \mathbf{s}), \tag{47}$$

where the effective spin–orbital parameter is estimated in [38] to be  $\Delta \zeta_{2p} \leq 0.1$  eV per Bi<sup>3+</sup>-ion; that is several times larger than conventional parameter  $\zeta_{2p}$ :

$$\Delta V_{SO}^{an}\left(2p\right) = \lambda_{ij}\,\hat{l}_i\,\hat{s}_j\,,\tag{48}$$

where the effective spin–orbit interaction tensor  $\lambda_{ij}$  depends on the geometry of the Bi–O bond [36,38]

$$\lambda_{ij} \propto \zeta_{6p} \left( R_i R_j - \frac{1}{3} \delta_{ij} \right), \tag{49}$$

where **R** is a unit vector along the Bi–O bond.

Thus, the effect of the bismuth ions on the circular MOE in iron garnets is essentially related to the oxygen O2p-states in  $[FeO_6]^{9-}$  and  $[FeO_4]^{5-}$  clusters. The Bi<sup>3+</sup> ions, leading to an increase in the effective spin–orbital coupling constant for oxygen ions, have a significant effect on the circular magneto-optics of iron garnets, through a change in the effective spin–orbital coupling parameters

$$\lambda = \lambda(3d) + \lambda(2p)$$

for the excited  ${}^{6}T$ -states with the p–d charge transfer.

The simple theory we are considering allows us to make a number of predictions. First, the effect of the Bi 6p-O 2p hybridization may be particularly significant for the CT transitions, whose final state spin–orbit coupling constant  $\lambda$  contains the ligand contribution  $\lambda(2p)$  only, e.g., the transitions  $t_{2u} - e_g$  and  $t_{1u}(\pi) - e_g$  in the [FeO<sub>6</sub>]<sup>9–</sup> clusters (predicted energies 4.4 and 5.3 eV, respectively). Since  $\zeta_{2p} \ll \zeta_{3d} \approx 0.1$  eV, the contribution of such transitions to the *FM* part of the gyration vector (36) in unsubstituted garnets is practically zero. The Bi substitution makes these transitions observable. On the contrary, the CT transitions whose final state  $V_{SO}$  constant  $\lambda$  includes only the 3d contribution, e.g., transition  $t_{1u}(\sigma) - e_g$  in the [FeO<sub>6</sub>]<sup>9–</sup> clusters (predicted energy 6.4 eV), are not appreciably influenced by the Bi<sup>3+</sup>-ions. Thus, the spectral dependence of the gyration vector in YIG and Bi-substituted compounds can differ greatly. Second, the Bi 6p-O2p hybridization induces the anisotropy of the  $\hat{A}$  tensor in the FM contribution to the gyration vector (36), which differs for the octa- and tetra-positions of the Fe clusters. Third, in our model, bismuth ions do not directly affect the value of the field contribution  $\hat{C} \mathbf{H}$  (36) to the gyration vector.

At variance with the cluster model, the "first-principles" band calculations indicate a slightly different, albeit contradictory, picture of Bi 6p-O 2p-Fe 3d hybridization. Thus, analyzing the electronic structure of  $Bi_3Fe_5O_{12}$  (BIG) calculated by the fully relativistic first-principles method based on the full-potential linear-combination-of-atomic-orbitals (LCAO) approach within the local-spin-density-approximation (LSDA), Oikawa et al. [2] found that the enhancement of the spin-orbit coupling due to the hybridization of Bi 6p is considerably larger in the Fe 3d conduction bands than in the O 2p and Fe 3d valence bands. The origin of this enhancement is that the Fe 3d conduction bands energetically overlap with Bi6p bands. Their results indicate the significance of spin–orbit coupling in Fe 3d conduction bands in relation to the large magneto-optical effect observed in BIG. However, the results of recent GGA+U calculation by Li et al. [15] show that, quite to the contrary, Bi 6p orbitals in BIG hybridize significantly with Fe 3d orbitals in the lower conduction bands, leading to large  $V_{SO}$ -induced band splitting in the bands. Consequently, the transitions between the upper valence bands and lower conduction bands are greatly enhanced when Y is replaced by Bi. Such contradictions turn out to be typical for various "ab initio" DFT-based calculations.

# 6.5. Exchange-Relativistic Interaction and Unconventional Magneto-Optics of Weak Ferromagnetic Orthoferrites

Interestingly, circular magneto-optical effects in weak ferromagnets are anomalously large and comparable with the effects in ferrite garnets, despite two-three orders of magnitude smaller magnetization [5,67,70,80–83]. In 1989, the anomaly has been assigned to a novel type of magnetooptical mechanism related to exchange-relativistic interactions, in particular, with so-called spin-other-orbit coupling [59]. We have shown that an anti-symmetric exchange-relativistic spin-other-orbit coupling gives rise to an unconventional "antiferromagnetic" contribution to the circular magneto-optics for weak ferromagnets, which can surpass the conventional "ferromagnetic" term [31–35,37,59] (see, also [81]). The ferromagnetic and antiferromagnetic terms with identical transformation properties are competing contributors to the gyration vector in weak ferromagnets; see Exp. (36). It should be noted that within the two-sublattice model for orthoferrites, we neglect weak antiferromagnetic A- and C-modes (see, e.g., [1,11,21,61]).

For the first time, the antiferromagnetic contribution to circular MOE was experimentally identified and evaluated in orthoferrite YFeO<sub>3</sub> [59]. An analysis of the field dependence of the Faraday rotation  $\Theta_F(\mathbf{H}_{ext})$  made it possible to determine all the contributions to the gyration vector ( $\lambda = 0.6328 \,\mu$ m):

$$A_{zz}m_{z} = (0.95 \pm 0.55) \times 10^{-3}; B_{zx}|l_{x}| = (3.15 \pm 0.55)) \times 10^{-3};$$
  

$$A_{xx}m_{x} = (0.2 \pm 0.7) \times 10^{-3}; B_{xz}|l_{z}| = (-2.1 \pm 1.0)) \times 10^{-3};$$
  

$$C_{zz} \approx C_{xx} = (-1.1 \pm 2.8) \times 10^{-6} \, kOe^{-1},$$
(50)

where  $|l_x| \approx |l_z| \approx 1$ . Interestingly, rather large measurement errors allow for certain to determine only the fact of a large if not a dominant antisymmetric antiferromagnetic contribution related to antisymmetric spin-other-orbit coupling. Strictly speaking, the mutual orientations of the ferro- (**m**) and antiferromagnetic (**l**) vectors depend on the sign of the Dzyaloshinskii vector [11,21,61]. Interestingly, rather arbitrarily chosen relative orientations of these vectors in reference [59] with positive signs of  $m_z$  and  $l_x$  exactly match the theoretical predictions about the sign of the Dzyaloshinskii vector [11,21,61].

The existence of spontaneous spin-reorientational phase transitions  $\Gamma_4(F_z G_x) \rightarrow$  $\Gamma_2(F_xG_z)$  in several rare-earth orthoferrites does provide large opportunities to study anisotropy of circular magneto-optics [5,33–35,37,67,80]. Gan'shina et al. [34] measured the equatorial Kerr effect in  $EuFeO_3$ ,  $TmFeO_3$  and  $HoFeO_3$ , and found the gyration vector anisotropy in a wide spectral range 1.5–4.5 eV. The magneto-optical spectra, both real and imaginary parts of the gyration vector, were nicely fitted within a microscopic model theory based on the dominating contribution of the O2p-Fe3d charge transfer transitions and spin-other-orbit coupling in  $[FeO_6]^{9-}$  octahedra. An example of modeling the spectrum of the real part of the gyration vector in orthoferrite  $EuFeO_3$  is shown in Figure 6. Let us again pay attention to the comparable values of circular MOEs in orthoferrites and ferrite garnets at more than an order of magnitude lower magnetic moments in weak ferromagnets of the YFeO<sub>3</sub> type and longitudinal ferrimagnets of the YIG type. The authors [34] have demonstrated a leading contribution of the antisymmetric spin-other-orbit coupling and estimated effective orbital magnetic fields in excited  ${}^{6}T_{1u}$  states of the [FeO<sub>6</sub>]<sup>9-</sup> octahedra,  $H_L \sim 100 T$ . These anomalously large fields can be naturally explained to be results of strong exchange interactions of the charge transfer  ${}^{6}T_{1u}$  states with nearby octahedra that are determined by a direct p-d exchange.

While the existence of the antiferromagnetic contribution to the gyration vector is typical of a large number of multi-sublattice magnetic materials, the antisymmetry of the tensor  $\stackrel{\leftrightarrow}{B}$  is a specific feature of weak ferromagnets alone. In the case of rhombohedral weak ferromagnets, such as FeBO<sub>3</sub>, FeF<sub>3</sub> or  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the tensor  $\stackrel{\leftrightarrow}{B}$ , governing the antiferromagnetic contribution to the Faraday effect, is entirely due to the antisymmetric contribution, in view of the requirements imposed by the crystal symmetry. In crystals of this kind the

appearance of the antiferromagnetic contribution to the gyration vector is entirely due to allowance for the antisymmetric spin-other-orbit coupling.

However, the data on the anisotropy of the Faraday effect in TmFeO<sub>3</sub> [80] and the values of the Faraday effect in SmFeO<sub>3</sub> (**m** || *a*-axis) and a number of other orthoferrites with **m** || *c*-axis [67] bear evidence of the existence of an appreciable symmetric *AFM*  $\hat{B}^{s1}$  contribution to the gyration vector of orthoferrites. Indeed, the Faraday effect in the  $\Gamma_4$  phase (**m** || *c*) and in the  $\Gamma_2$  phase (**m** || *a*) are determined, respectively, by the *z*- and *x*-component of **g**:

$$g_z = A m_z + B_{zx} l_x; \quad g_x = A m_x + B_{xz} l_z$$
 (51)

(under the justified assumption that  $\hat{A}$  be isotropic). Since  $\mathbf{m} \perp \mathbf{l}$  and  $m_x \approx m_z = m$ , while letting  $l_x = 1$  with the view of the definitude, we obtain:

$$g_z = A m + B_{zx}^a + B_{zx}^s; \quad g_x = A m + B_{zx}^a - B_{zx}^s,$$
 (52)

so that the experimentally found ratio [67,80]  $Re g_z / Re g_x \approx 2.5 - 3$  (at  $\lambda \approx 1-2 \mu m$ ) indicates unambiguously the existence of an appreciable symmetric *AFM* term  $B_{zx}^s$ :

$$\frac{B_{zx}^s}{A\,m\,+\,B_{zx}^a}\,\sim\,0.5\,.$$

#### 6.6. The Temperature Dependence of the Circular Magneto-Optics of Ferrites

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The analysis of the temperature dependencies of *MOE* can yield an important information about the role of various mechanisms of the circular *MOE*. Experimental studies of the Faraday and Kerr effects in weak ferromagnets  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [81], FeBO<sub>3</sub> [82,83], YFeO<sub>3</sub> [70] have shown that their circular *MOE* and the magnetic moment, both total and that of each sublattice, have *different* temperature dependencies. In references [70,81,83], an attempt was made to connect this phenomenon with the so-called *pair* transitions.

However, we show here that all peculiarities of the temperature dependence of the Faraday and Kerr effects for weak ferromagnets can be naturally and consistently explained by taking into account the  $AFM \hat{B}l$  contribution to the gyration vector due to the exchange-relativistic interactions. In spite of the  $FM \hat{A}m$  contribution to g (36), the  $AFM \hat{B}^{sym}l$  contribution due to LSCF in  ${}^{6}T_{1u}CT$  states (36), and the contributions due to intra-center  $V_{so}^{ex}$  have the temperature dependence determined by the ordinary thermodynamic average of the spin  $\langle S(m) \rangle$ ; the AFM contribution owing to the "spin-other orbit" interaction is related to the average value of a complicated spin operator  $\hat{S}(mn)$  (15).

In the molecular field approximation, the thermodynamic average of the nonlinear operator  $S_{mn}$  in (15) can be written as follows [84]:

$$\langle \hat{S}_q(mn) \rangle = \langle \hat{S}_z(n) \rangle C_q^1(\mathbf{S}(n)) + \gamma \langle \hat{V}_0^2(S(m)) \rangle_T \langle \hat{S}_z(n) \rangle \sum_{q_1, q_2} \begin{bmatrix} 2 & 1 & 1 \\ q_1 & q_2 & q \end{bmatrix} C_{q_1}^2(\mathbf{S}(m)) C_{q_2}^1(\mathbf{S}(n)),$$
(53)

where  $C_{q_1}^2(\mathbf{S}(m))$  and  $C_{q_2}^1(\mathbf{S}(n))$  are spherical tensorial harmonics ( $C_q^k = \sqrt{\frac{4\pi}{2k+1}}Y_{kq}$ ) as the functions of classical spin direction:

$$\langle S_z \rangle = S B_S(x)$$

where  $B_S(x)$  is the Brillouin function

$$B_{S}(x) = \frac{2S+1}{2S} coth \frac{2S+1}{2S} x - \frac{1}{2S} coth \frac{1}{2S} x; \ x = \frac{3S}{S+1} \frac{\sigma}{\tau}$$

( $\sigma = S_z/S$  and  $\tau$  being the reduced magnetic moment and temperature, respectively);

$$\langle \hat{V}_0^2(S) \rangle_T = 2 \left[ \frac{(2S-2)!}{(2S+3)!} \right]^{1/2} \left( 3 \langle \hat{S}_z^2 \rangle - S(S+1) \right),$$
 (54)

where

$$\left(3\langle \hat{S}_z^2\rangle - S(S+1)\right) = \left(2S\left(S+1\right) - 3S\coth\frac{x}{2S} \cdot B_S(x)\right),\tag{55}$$

Thus, the temperature dependence of the gyration vector in the molecular field approximation is determined by the following two-parameter formula:

$$g(T) = a \langle S_z \rangle + a' \langle S_z \rangle \langle S_z^2 \rangle \approx A m + A' m^3,$$
(56)

with the frequency dependent coefficients *a*, *b*. Temperature dependencies of the thermodynamic factors  $\langle S_z \rangle$  and  $\langle S_z \rangle \langle S_z^2 \rangle$  are presented in Figure 7, where the inset shows examples of fitting experimental data on the temperature dependencies of the equatorial Kerr effect in hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (see Figure 6 in [70]) using the two-parameter Formula (56).



**Figure 7.** Temperature dependence of the normalized thermodynamic quantities determining the temperature dependence of the circular MOE. The inset shows an example of fitting the experimental data on the temperature dependencies of the equatorial Kerr effect in hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (see Figure 6 in [70]) using the two-parameter Formula (56). Dotted curve is the  $\langle S_z \rangle$  dependence.

In other words, the MOE in weak ferromagnets will be characterized by a clear nonlinear dependence on the magnetic moment of sublattices, the presence of which is a direct indication of the contribution of exchange-relativistic interactions of the spin-other-orbit type. As expected, the nonlinear contribution, both in magnitude and in sign, will depend substantially on the frequency [70,81–83].

It is worth noting that Exp. (53) provides a dependence of the exchange-relativistic contribution to the gyration vector on the mutual orientation of neighboring spins.

#### 6.7. The High-Energy Optics and Magneto-Optics of Ferrites

The availability of modern high-intensity synchrotron radiation has facilitated the refinement of conventional spectroscopy. This is especially true in the field of *MOE*, where the synchrotron radiation is a convenient tool of obtaining the spectra at high energies.

Kučera et al. [85] have obtained the reflectivity spectra of a number of iron and noniron garnets and yttrium orthoferrite in the vacuum ultraviolet 5 to 30 eV range using synchrotron radiation as the light source. Contrary to the visible and near UV regions, all the spectra obtained are strikingly similar in this spectral range. Two broad bands situated at about 10 and 17 eV have been found in both garnet and orthoferrite reflectivity and optic absorption spectra. The 10 eV band was assigned to the CT transition from the oxygen 2p valence band to the yttrium 4d or 5s conduction states. The band centered near 17 eV was attributed to the "orbital-promotion" inter-configurational Fe  $3d \rightarrow$  Fe 4p transition. Despite the large peak values, the contribution of these transitions to the MOE of ferrites in the visible region, being structureless, is significantly inferior to the contribution of O 2p–Fe 3d CT transitions.

#### 6.8. Rare-Earth Ions in Ferrites

The simplest expression for the contribution of the dipole-allowed 4f—5d transition to the rare-earth ion polarizability tensor can be obtained by neglecting the splitting of the  $4f^{n-1}5d$ - configuration [86]:

$$\alpha_{q}^{k} = (-1)^{1+k} 3\sqrt{2k+1} \frac{1}{\hbar} \left\{ \begin{array}{ccc} 3 & 3 & k \\ 1 & 1 & 2 \end{array} \right\} e^{2} r_{fd}^{2} F_{k}(\omega, \omega_{fd}) \langle \hat{U}_{q}^{k}(J) \rangle$$
(57)

where {:::} is the 6j-symbol [62],  $r_{fd} = \langle 4f | r | 5d \rangle$  is the radial integral, and  $\langle \hat{U}_q^k(J) \rangle$  is the thermodynamical average of the irreducible tensor  $\hat{U}_q^k(J)$  with submatrix element  $U_{SLI;SL'I'}^{(k)}$  [62].

The components of the tensor  $\alpha_q^1$ , which determine the contribution of the rare-earth ion to the circular magneto-optics, can be written as follows:

$$\boldsymbol{\alpha} = -\frac{1}{7\sqrt{2}}e^2 r_{fd}^2 F_1(\omega, \omega_{fd}) \frac{2-g_J}{g_J \mu_B} \mathbf{m}_R, \qquad (58)$$

where  $\mathbf{m}_R$  is the magnetic moment of the R-ion and  $g_J$  is the Lande factor. The symmetric anisotropic part of the polarizability tensor determines the effects of linear birefringence and dichroism. In Cartesian form, we get [86]

$$\alpha_{ij} = \frac{\sqrt{3}}{14} e^2 r_{fd}^2 F_2(\omega, \omega_{fd}) \alpha \langle 3 \hat{j}_i \hat{j}_j - J(J+1) \rangle, \tag{59}$$

where  $J_i J_j = \frac{1}{2} (\hat{J}_i \hat{J}_j + \hat{J}_j \hat{J}_i)$ ,  $\alpha$  is the Stevens parameter [87].

A detailed analysis of the role of the effects of a strong crystal field for the 5d electron was carried out in [86,88].

#### 7. Conclusions

The paper presents the theory of the optical and magneto-optical properties of strongly correlated iron oxides, primarily iron garnets and orthoferrites, based on the cluster model, including the leading contribution of the charge transfer transitions. At variance with the "first-principles" DFT-based band models, the cluster model is physically clear; it allows one to describe impure, dilute, and concentrated systems; provides a self-consistent description of the optical, magnetic, and magneto-optical characteristics of the Fe centers with a detailed account of local symmetry, low-symmetry crystal field effects, spin-orbital and Zeeman interactions and also the relatively new exchange-relativistic interaction, which plays a fundamental role in the circular magneto-optics of weak ferromagnets. The cluster approach provides a regular procedure for classifying and estimating the probabilities of allowed and forbidden electric-dipole CT transitions and their contributions to optical and magneto-optical anisotropy. The model makes it possible to describe all the specific features of the influence of Bi ions on the circular magneto-optics of ferrites by the Bi 6p-O2p hybridization and partial Bi-O "transfer" of the large Bi6p spin-orbit interaction. It predicts the "selective" nature of the influence of the Bi ions only for certain CT transitions, the appearance of an anisotropy of the ferromagnetic contribution and the absence of any influence on the field contribution to the gyration vector.

We presented numerous examples of comparisons of cluster theory with experimental data for orthoferrites, iron garnets and other ferrites. As one of the most important results of the theory, we considered the introduction of a new exchange-relativistic interaction and the elucidation of its role in the circular magneto-optics of ferrites. The contribution

of this interaction for the excited  ${}^{6}T_{1u}$  terms in  $[\text{FeO}_{6}]^{9-}$  clusters leads not only to the appearance of a puzzling "antiferromagnetic" contribution to the gyration vector of weak ferromagnets, such as orthoferrite RFeO<sub>3</sub> and hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, but also to the deviation of the temperature dependence of circular MOE from the simple proportionality to the magnetization **m**. The appearance of a nonlinear **m**-dependence is an indication of the contribution of the unusual "spin-other-orbit" interaction in excited  ${}^{6}T_{1u}$  states.

Undoubtedly, the considered version of the cluster theory requires more detailed development both in terms of improving the used MO-LCAO scheme and in terms of the possible application of the "hybrid" LDA + MLFT scheme [30]. In any case, the further development of the cluster model of magneto-optical effects in ferrites needs data from systematic experimental studies of the concentration, spectral and temperature dependencies of various optical and magneto-optical effects for the Fe centers in oxides.

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