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Citation for published version (APA):

DOI:
10.1103/PhysRevB.56.5432

Document status and date:
Published: 01/01/1998

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Optical and magneto-optical polar Kerr spectra of Fe$_3$O$_4$ and Mg$^{2+}$- or Al$^{3+}$-substituted Fe$_3$O$_4$

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Received 5 November 1996; revised manuscript received 21 March 1997

The diagonal elements of the dielectric tensor, between 0.5 and 5.0 eV, and the magneto-optical polar Kerr spectra, between 0.7 and 4.0 eV, have been determined for a synthetic crystal of magnetite, Fe$_3$O$_4$, and a systematic investigation of these properties for Mg$^{2+}$ and Al$^{3+}$ substitutions has been carried out. From these spectra the off-diagonal elements of the dielectric tensor was calculated between 0.7 and 4.0 eV. Through fitting simultaneously both the diagonal and the off-diagonal elements of this tensor with one set of parameters and consistently for all partially substituted ferrite samples, we were able to resolve the magneto-optical spectrum of Fe$_3$O$_4$ between 0.7 and 4.0 eV. The observed trends in the major transitions upon substitution provide the experimental evidence for intervalence charge transfer and interstitial charge transfer transitions in Fe$_3$O$_4$.[S0163-1829(97)03833-2]

I. INTRODUCTION

Magnetite crystallizes in the inverse spinel structure, with cation distribution (Fe$^{3+})$[Fe$^{3+}$Fe$^{2+}]$O$_4$. In this structural formula the parentheses denote tetrahedral (A) sites and the square brackets denote the octahedral (B) sites. For most purposes, Fe$_3$O$_4$ can be considered to be the prototype of an inverse spinel ferrite. Most of the properties of ferrites have been thoroughly studied and are well documented.1,2 However, the electronic structure of Fe$_3$O$_4$, as well as that of other transition-metal (TM) oxides such as NiO, is still a subject of debate.3-9 In transition-metal oxides the valence bands of oxygen 2$p$ character are separated from the transition-metal ion’s empty 4$s$ band by an energy gap of several (4–6) eV.3,5 The TM 3$d$ electrons are considered to interact strongly with the surrounding oxygen anions to form more or less localized states. These states are spread out over a wide energy range, because of the strong Coulomb repulsion between $d$ electrons. This repulsion splits the $d^n$ configuration into various multiplets, which are further split by the crystal field. As a consequence 3$d$-derived bands appear usually both within and above the O 2$p$ TM 4$s$ gap. For the particular case of Fe$_3$O$_4$ the actual conductivity gap, i.e., the valence band to conduction band gap, is assumed to be of 3$d$→3$d$ nature,8 but clearly a variety of other neutral excitations exists. Understandably, this rather complex electronic structure of TM oxides has led for Fe$_3$O$_4$ and related ferrites to a confusing variety of interpretations of the optical and magneto-optical (MO) Kerr spectra, due to different assignments of the observed transitions.

Various studies on the magneto-optical properties of mag-netite and substituted spinel ferrites in the visible and near infrared part of the spectrum have been reported in the past. Simiša and co-workers reported the polar Kerr rotation and ellipticity of Fe$_3$O$_4$ as well as the influence of a systematic substitution of Fe$^{3+}$ by Mn$^{2+}$ in the 0.5–3.0 eV energy range.10,11 In their study the peak at 0.9 eV in the Kerr rotation spectrum of Fe$_3$O$_4$ was ascribed to the presence of charge carriers (i.e., Fe$^{2+}$) and was assumed to be related to charge transfer between [Fe$^{2+}$] and [Fe$^{3+}$]. The spectrum around 2.0 eV was explained in terms of 3$d$ crystal-field transitions of iron ions on tetrahedral sites. Zhang and co-workers also reported the polar Kerr spectra and the off-diagonal element of the dielectric tensor of Fe$_3$O$_4$ between 0.5 and 4.3 eV,12 and in addition that of Li$_{0.5}$Fe$_{2.5}$O$_4$ and MgFe$_2$O$_4$ between 0.5 and 5.0 eV.13 All major peaks in the Kerr spectrum of Fe$_3$O$_4$ were assigned to 3$d^m$→3$d^{n-1}$ 4$s$ orbital promotion processes. Also Višňovský et al. reported polar Kerr spectra of Li$_{0.5}$Fe$_{2.5}$O$_4$ and MgFe$_2$O$_4$, and derived the complete dielectric tensor of the latter compound between 2.0 and 6.0 eV.14 Bands at 3.4, 3.6, 4.3, and 4.7 eV were identified as 2$p$→3$d$ charge-transfer transitions between O$^{2-}$ and Fe$^{3+}$. Finally, Peeters and Martens reported the polar Kerr rotation of CoFe$_2$O$_4$ between 0.6 and 5.5 eV,15 Bands below 3.0 eV were assigned to crystal-field transitions of Co$^{2+}$, and around 2.0 eV a charge-transfer transition between [Co$^{2+}$] and [Fe$^{3+}$] was identified. Thus, despite considerable experimental efforts, no coherent picture concerning the microscopic origin of the MO active transitions in Fe$_3$O$_4$ and related substituted spinel ferrites is available. For the sake of completeness, we should mention a possible Drude term or, in other words, the intraband transitions (see,
for instance, the analysis of Ga by Erskine and Stern\textsuperscript{16}. In Fe\textsubscript{3}O\textsubscript{4} these transitions occur around 0.2 eV,\textsuperscript{17} and therefore do not play a role in the energy range investigated here.

The problem with the interpretations given so far is that Fe\textsubscript{3}O\textsubscript{4} exhibits a relatively strong MO-Kerr effect in the visible region and absorption peaks with an oscillator strength, \( f \), of about \( 10^{-3} \)\textsuperscript{7}. The interpretations given above are based on transitions which are either spin or parity forbidden, and in some cases even both. For instance, crystal-field transitions involving Fe\textsuperscript{3+} are spin forbidden, while in addition crystal-field transitions on octahedral sites are parity forbidden. On the tetrahedral site, crystal-field transitions are not strictly parity forbidden due to the lack of inversion symmetry in the crystal field at that site. As a result the oscillator strength of crystal-field transitions is expected to be about \( 10^{-4} - 10^{-5} \).\textsuperscript{18} In a similar way orbital promotion processes \( d \rightarrow s \) via an electric dipole transition are forbidden since \( \Delta l = 2 \). Moreover, \( d \rightarrow s \) transitions involving iron ions on a centrosymmetric, octahedral site are parity forbidden. Only due to distortion of the octahedral symmetry may the parity selection rule be weakened.\textsuperscript{13} Therefore, the most recent theoretical work on the Kerr spectrum of Fe\textsubscript{3}O\textsubscript{4} by Feil suggests that the main transitions in the region between 0.5 and 3 eV are intervalence charge transfer (IVCT) transitions,\textsuperscript{7} while transitions involving iron ions on a perpendicularly magnetized sample. The Kerr rotation \( \theta_k \) is related to the change in the phase in the polarization state of the light reflected from the surface and the Kerr ellipticity \( \epsilon_k \) to the change in amplitude. To a first approximation the Kerr effect depends linearly on the magnetization.

The Kerr effect signal originates from a surface layer of which the thickness is approximately twice the penetration depth of the light, \( d_p \). This is defined as the depth for which the intensity of the light is reduced by a factor \( e^{-1} \): \( d_p = \lambda/(4\pi n) \) where \( \lambda \) is the wavelength.

The dielectric tensor for a crystal with cubic symmetry magnetized in the \( z \) direction (perpendicular to the surface) has in the convention used in this paper the form

\[
\varepsilon = \begin{pmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & 0 \\
-\varepsilon_{xy} & \varepsilon_{xx} & 0 \\
0 & 0 & \varepsilon_{zz}
\end{pmatrix},
\]

where \( \varepsilon_{xx} = \varepsilon'_{xx} + i\varepsilon''_{xx} \); \( \varepsilon_{xy} = \varepsilon'_{xy} + i\varepsilon''_{xy} \).

The relation of the elements of this tensor to the refractive index \( n \), the absorption coefficient \( k \), and the Kerr rotation \( \theta_k \) and ellipticity \( \epsilon_k \), is for the polar Kerr effect given by\textsuperscript{21}

\[
\varepsilon'_{xx} = n^2 - k^2; \quad \varepsilon''_{xx} = 2nk;
\]

\[
\varepsilon'_{xy} = A \theta_k - B \epsilon_k,
\]

\[
\varepsilon''_{xy} = -B \theta_k - A \epsilon_k,
\]

with \( A = (n^3 - 3nk^2 - n); \quad B = (-k^3 + 3nk^2 - k) \).

B. Microscopic theory: The dielectric tensor

At a microscopic level the diagonal element of the dielectric tensor is for single-ion electric-dipole transitions given by\textsuperscript{22}

\[
\varepsilon_{xx} = 1 + \sum_{e,d} \varepsilon_{xx, e, d}
= 1 + \frac{4\pi N e^2}{m}
\times \sum_{e,d} \sum_{i} f_{e,d} \left[ \frac{\omega_{e, i}^2 e_{e, i} - \omega^2 + \Gamma_{e, i}^2}{\omega_{e, i}^2 - \omega^2 + \Gamma_{e, i}^2} - 2i\omega \Gamma_{e, i} \right],
\]

where \( N \) is the number of active absorbing centers per unit volume, \( e \) the electronic charge, and \( m \) the electronic mass. Further, \( \omega_{e, i} \) and \( \Gamma_{e, i} \) are the resonance frequency and half-width at half-maximum of the optical transitions between the ground state \( |g) \) and excited states \( |e, i) \) with \( i \) indicating the orbital degeneracy. If \( \Gamma_{e, i}/\omega_{e, i} \ll 1 \) applies

II. THEORETICAL BACKGROUND

A. Macroscopic theory: The Kerr effect

The MO-Kerr effect is caused by electronic transitions in a magnetic material, of which the degeneracy of the orbital quantum number \( m_f \) is lifted, due to spin-orbit coupling. This gives rise to optical anisotropy; the off-diagonal element of the dielectric tensor will be nonzero.

The polar Kerr effect is the change in the polarization state of a light beam which is reflected at normal incidence on a perpendicularly magnetized sample. The Kerr rotation \( \theta_k \) is related to the change in the phase of the light reflected from the surface and the Kerr ellipticity \( \epsilon_k \) to the change in amplitude. To a first approximation the Kerr effect depends linearly on the magnetization.

The Kerr effect signal originates from a surface layer of which the thickness is approximately twice the penetration depth of the light, \( d_p \). This is defined as the depth for which the intensity of the light is reduced by a factor \( e^{-1} \): \( d_p = \lambda/(4\pi n) \) where \( \lambda \) is the wavelength.

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\]

\[
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\]

\[
\varepsilon''_{xy} = -B \theta_k - A \epsilon_k,
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\]

where \( N \) is the number of active absorbing centers per unit volume, \( e \) the electronic charge, and \( m \) the electronic mass. Further, \( \omega_{e, i} \) and \( \Gamma_{e, i} \) are the resonance frequency and half-width at half-maximum of the optical transitions between the ground state \( |g) \) and excited states \( |e, i) \) with \( i \) indicating the orbital degeneracy. If \( \Gamma_{e, i}/\omega_{e, i} \ll 1 \) applies
the maximum of $\epsilon''_{xx}$ occurs at $\omega = \omega_{e(u)}$ and the oscillator strength, $f_{e(u)}$, is given to a good approximation by

$$f_{e(u)} = \frac{m}{2 \pi N e^2 L} \omega_{e(u)} \epsilon_{e(u)}(\epsilon''_{xx,e(u)})_{\text{max}},$$  \hspace{1cm} (4)$$

where $L$ is the Lorentz local field correction, $L = [(n^2 + 2)^2/9]$, which must be applied since for Fe$_3$O$_4$ the condition that $|\epsilon''_{xx} - 1| \leq 1$ does not hold.\textsuperscript{23} For electric dipole transitions the off-diagonal element is given by\textsuperscript{22}

$$\epsilon_{xy} = \sum_{\alpha,\beta} \tilde{\epsilon}_{xy,e(u)}$$

$$= \frac{2 \pi N e^2}{m} \sum_{\alpha,\beta} \left[ \frac{\bar{f}_{-e(u)} - \bar{f}_{+e(u)}}{\omega^2 - \omega^2_{e(u)} - \Gamma^2_{e(u)} - 2i \omega \Gamma_{e(u)}} \right]$$

$$\times \frac{\omega - i \Gamma_{e(u)}}{\omega_{e(u)}},$$  \hspace{1cm} (5)$$

where $f_{\pm e(u)}$ are the oscillator strengths for transitions caused by right and left circularly polarized light (RCP and LCP, respectively).

The optical anisotropy in materials which exhibit a Kerr effect arises from spin-orbit coupling. Due to the spin-orbit coupling the electron system is able to distinguish between spin-up and spin-down transitions, which result in two distinct types of line shapes. For instance, the spin-allowed charge transfer bands. In this case the following equation describes the transition:

$$f = 1.085 \times 10^{-5} \nu \omega^2 (1 - \alpha^2) R_{xy}^2$$  \hspace{1cm} (8)$$

where $\nu$ is the wave number at which the transition occurs. Combining Eq. (8) and Eq. (4), and neglecting effects on $R_{xy}$ and $\nu$, yields

$$(\epsilon_{xy})_{\max} \approx N \alpha^2 (1 - \alpha^2)$$  \hspace{1cm} (9)$$

with $N$ the number of absorbing species per unit volume. We thus find that $(\epsilon_{xy})_{\max}$ depends in a nonlinear way on the degree of delocalization, $\alpha$. For a given IVCT a change in the lattice which diminishes the equivalence of sites or increases the distance between the cations will increase the localization of the electron, increasing the transition energy and lowering oscillator strength. Examples are increased polarization of the intermediate oxygen and localized distortions due to vacancies or substitutions. We refer to the literature for more general discussions on IVCT transitions.\textsuperscript{23,26} as well as more quantitative ones.\textsuperscript{27,28}

Finally, it should be noted that the so-called intersublattice charge transfer transitions described by Scott and co-workers\textsuperscript{18,24} are IVCT transitions between Fe$^{3+}$ ions on different crystallographic sites.\textsuperscript{23} For reasons of clarity we will still refer to these transitions as ISCT transitions in this paper.

C. Intervalence charge transfer

Intervalence charge transfer (IVCT) transitions are transitions in which an electron, through optical excitation, is transferred to a neighboring cation. Mixed valence compounds, i.e., compounds containing an element in two different oxidation states, such as Fe in Fe$_3$O$_4$, often show unusually intense absorption in the visible region that can be attributed to IVCT transitions.\textsuperscript{25,26} Overlapping Fe(3$d$) orbitals, across the shared edges of adjacent Fe-O polyhedra, result in weak Fe-Fe bonds. The IVCT bands are the result of electronic transitions between the Fe-Fe bonding and antibonding orbitals. In Fe$_3$O$_4$, the electron transfer between Fe$^{2+}$ and Fe$^{3+}$ may be mediated by O$^{2-}$ ions, in particular when $e_g$ orbitals are involved. In such a case, the transfer occurs more readily for smaller electrostatic polarization of the O$^{2-}$ ions.\textsuperscript{25,27} Between Fe $t_{2g}$ orbitals direct electron transfer is possible as a result of the overlap between these orbitals.

The intensity and transition energy of an IVCT are sensitive to changes in the lattice. Factors to be considered are the equivalence of sites, the distance between the sites $x$ and $y$, $R_{xy}$, and the degree of delocalization of the electron involved, $\alpha$. Using the standard optical matrix element one can derive the following expression for the oscillator strength, $f$, of IVCT transitions:\textsuperscript{7,27}

$$f = 1.085 \times 10^{-5} \nu \omega^2 (1 - \alpha^2) R_{xy}^2$$  \hspace{1cm} (8)$$

with $\nu$ the wave number at which the transition occurs. Combining Eq. (8) and Eq. (4), and neglecting effects on $R_{xy}$ and $\nu$, yields

$$(\epsilon_{xy})_{\max} \approx N \alpha^2 (1 - \alpha^2)$$  \hspace{1cm} (9)$$

with $N$ the number of absorbing species per unit volume. We thus find that $(\epsilon_{xy})_{\max}$ depends in a nonlinear way on the degree of delocalization, $\alpha$. For a given IVCT a change in the lattice which diminishes the equivalence of sites or increases the distance between the cations will increase the localization of the electron, increasing the transition energy and lowering oscillator strength. Examples are increased polarization of the intermediate oxygen and localized distortions due to vacancies or substitutions. We refer to the literature for more general discussions on IVCT transitions\textsuperscript{23,26} as well as more quantitative ones\textsuperscript{7,27,28}.

Finally, it should be noted that the so-called intersublattice charge transfer transitions described by Scott and co-workers\textsuperscript{18,24} are IVCT transitions between Fe$^{3+}$ ions on different crystallographic sites.\textsuperscript{23} For reasons of clarity we will still refer to these transitions as ISCT transitions in this paper.

III. EXPERIMENTAL PROCEDURES

The polar Kerr spectra from 0.7 to 4.0 eV (1700–310 nm), were measured for a series of single-crystalline spinel ferrite samples ([110] oriented) with varying degrees of Mg$^{2+}$ or Al$^{3+}$ substitution. A list of the samples studied is given in Table I. To prepare these samples, stoichiometric (M$_{x}$Fe$_{3-x}$O$_{4+0.05}$) polycrystalline rods
TABLE I. Survey of the single-crystalline spinel ferrite samples studied and the figures in which their spectra are presented.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Indication in figures and text</th>
<th>Figures</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fe_2O_3$</td>
<td>Fe$_3$O$_4$</td>
<td>1,2,4,5,7,8,11</td>
</tr>
<tr>
<td>$Mg_xFe_{2-x}Fe_{2+x}O_4$</td>
<td>$0.1 , \text{Mg}$</td>
<td>11</td>
</tr>
<tr>
<td>$Fe_{0.2}Fe_{1.8}O_4$</td>
<td>$0.2 , \text{Mg}$</td>
<td>2,5,8,11</td>
</tr>
<tr>
<td>$Fe_{0.5}Fe_{1.5}O_4$</td>
<td>$0.4 , \text{Mg}$</td>
<td>11</td>
</tr>
<tr>
<td>$Fe_{0.8}Fe_{1.2}O_4$</td>
<td>$0.8 , \text{Mg}$</td>
<td>2,5,8,11</td>
</tr>
<tr>
<td>$Fe_{1.0}Fe_{0.0}Fe_{2.0}O_4$</td>
<td>$0.005 , \text{Al}$</td>
<td>3,6,9,11</td>
</tr>
<tr>
<td>$Fe_{1.0}Fe_{0.0}Fe_{2.0}O_4$</td>
<td>$0.02 , \text{Al}$</td>
<td>3,6,9,11</td>
</tr>
<tr>
<td>$Fe_{1.0}Fe_{0.0}Fe_{2.0}O_4$</td>
<td>$0.2 , \text{Al}$</td>
<td>3,6,9,11</td>
</tr>
<tr>
<td>$Fe_{1.0}Fe_{0.0}Fe_{2.0}O_4$</td>
<td>$0.4 , \text{Al}$</td>
<td>3,6,9,11</td>
</tr>
</tbody>
</table>

were prepared by ceramic techniques and subsequently regrown with a floating zone technique in nitrogen atmosphere ($P_{O_2}=0.1 \, \text{Pa}$). The obtained crystals were annealed at equilibrium oxygen pressure in the temperature range between 1200 and 1300 °C and cooled slowly in 3 h to room temperature in an adjusted atmosphere to prevent oxidation. In addition, the Mg-substituted crystals were wrapped into Pt foils and further annealed in evacuated and sealed silica tubes for 4 h at 600 °C, followed by slow cooling with 12 °C/h to room temperature. This procedure yields high-quality stoichiometric single crystals and due to the slow cooling rate more than 95% of the Mg$^{2+}$ and Al$^{3+}$ substituents will be located at octahedral sites as well as 100% of the Fe$^{3+}$. Thus, these ferrites have a well-defined cation distribution whereas ferrites prepared through other methods may have a more random, nonequilibrium cation distribution whereas ferrites prepared through other methods may have a more random, nonequilibrium cation distribution. A detailed description of the preparation techniques employed can be found elsewhere. For the magneto-optical measurements platelets were cut from the crystals and Syton polished to mirror finish.

For the Kerr measurements the following setup was used: Light from a 450 W Xe arc lamp (Osmac XBO) is focused with a set of mirrors on the entrance slit of a monochromator (SPEX 1702). The beam from the monochromator passes a filter, a Glan-Thompson polarizer, a photoelastic modulator (Hinds CF5), and a lens which focuses the light on the sample, situated between the poles of a 1400 kA/m water-cooled electromagnet. After reflection from the sample, the light passes through a lens, a chopper, and an analyzer before reaching the detector. This is either a Ge photodiode (Rofin 7460) for the 0.7–1.4 eV range or a photomultiplier (Hamamatsu R943-02) for the 1.4–4.0 eV range. The detector signal was preamplified (current to voltage) and fed into three lock-in amplifiers (EG&G 5209, 5205, and 5207) to measure the light intensity, rotation and ellipticity. The setup was controlled by a Hewlett Packard computer (HP-300). This setup is similar to the one described by Martens et al. A detailed description of the employed measuring technique using a photoelastic modulator (PEM) has been given by Sato.

Kerr rotation and ellipticity, $\theta_k$ and $\varepsilon_k$, were measured at ambient temperature, with a saturating magnetic field applied perpendicularly to the sample surface (1400 kA/m). By averaging measurements in opposite field directions any offset in Kerr amplitude due to the setup is eliminated. More details on the Kerr spectrometer and measurement procedure can be found elsewhere. The diagonal element of the dielectric tensor between 0.5 and 5.0 eV was obtained through spectroscopic ellipsometry as described previously.

IV. EXPERIMENTAL RESULTS

A. Absorption spectra

In Figs. 1–3 the diagonal element of the dielectric tensor of Fe$_3$O$_4$ and several Mg$^{2+}$- or Al$^{3+}$-substituted samples are shown. These spectra were obtained from spectroscopic ellipsometry measurements and were subsequently used in the calculation of the off-diagonal element of the dielectric tensor from the Kerr measurements by means of Eq. (2). Apart from the influence of substitution of [Fe$^{3+}$] by Al$^{3+}$ on $\varepsilon_{xx}$, which shows a nearly linear decrease in intensity with Al$^{3+}$ concentration over the entire spectral range investigated, no clear trends are apparent in these spectra. This is due to the fact that $\varepsilon_{xx}$ is composed of a large number of overlapping optical transitions, each possibly having a different dependence on, as well as energy shift with, the substituent concentration. Therefore, inspection of the $\varepsilon_{xx}$ spectrum is insufficient to establish peak positions or trends in peak position or intensity. The complete dielectric tensor should be determined and all elements of this tensor should be fitted simultaneously with one set of parameters.

B. MO spectra

In Figs. 4–6 the Kerr spectra of Fe$_3$O$_4$ and of several of the Mg$^{2+}$- or Al$^{3+}$-substituted ferrites are presented. Both the measured polar Kerr spectrum (Fig. 4) and the derived off-diagonal element of the dielectric tensor (Fig. 7) of pure Fe$_3$O$_4$ are in fair agreement with those reported in the literature. The best way to study magneto-optical transitions is to examine the off-diagonal element of the dielectric tensor, where diamagnetic and paramagnetic transitions can be identified at their exact frequency and linked to their microscopic origin. Therefore, we will focus on the dielectric
tensor in the remainder of this paper. From Fig. 7 three major bands in the off-diagonal tensor element of pure magnetite are found: around 0.56 eV a paramagnetic band (only tail visible), around 1.94 eV a paramagnetic band, and around 3.0–4.0 eV a diamagnetic band. This last, broad shape is found to be composed of transitions at 3.11, 3.45, and 3.94 eV, as will be explained below.

Figure 8 shows the influence of Mg$^{2+}$ substitution on the off-diagonal element of the dielectric tensor. Mg$^{2+}$ mainly occupies B sites replacing [Fe$^{3+}$]. From Fig. 8 one can see that the transitions at 0.56 and 1.94 eV exhibit a nonlinear dependence on the Mg$^{2+}$ content. The influence of substitution of Fe$^{3+}$ with Mg$^{2+}$ on the spectra in the 3.0–4.0 eV range is complex and requires a more detailed analysis given in the next section. Comparison of the position of the extrema for Fe$_3$O$_4$ and Mg$_{0.2}$Fe$_{2.8}$O$_4$ shows no shifts. This is consistent with the small effect Mg$^{2+}$ substitution has on the lattice, since the lattice parameter of MgFe$_2$O$_4$ is only 0.3% smaller than that of Fe$_3$O$_4$, i.e., 8.370–8.380 Å versus 8.396 Å.$^{19,31}$

FIG. 2. The diagonal element of the dielectric tensor of (Fe$^{3+}$)(Mg$^{2+}$Fe$^{3+}$)$_{1-x}$O$_4$ for $x=0.0$, 0.2, and 0.8; (a) real part, $\varepsilon'_x$; (b) imaginary part, $\varepsilon''_x$.

FIG. 3. The diagonal element of the dielectric tensor of (Fe$^{3+}$)(Al$^{3+}$Fe$^{3+}$)$_{1-x}$O$_4$ for $x=0.02$, 0.2, and 0.4; (a) real part, $\varepsilon'_x$; (b) imaginary part, $\varepsilon''_x$.

FIG. 4. The Kerr rotation $\theta_k$ and Kerr ellipticity $\varepsilon_k$ of Fe$_3$O$_4$. 

$^{19,31}$
In Fig. 9 the influence of Al$^{3+}$ substitution on the real and imaginary part of the off-diagonal element of the dielectric tensor is shown. In general, Al$^{3+}$ mainly occupies B sites, as in a normal spinel, where it replaces Fe$^{3+}$ and decreases the lattice parameter linearly down to 8.269 Å for AlFe$_2$O$_4$, consistent with Vegard’s law. Due to its small ion radius, Al$^{3+}$ will, more than Mg$^{2+}$, perturb the octahedral symmetry and polarize O$_2$. The substitution of one octahedrally coordinated Fe$^{3+}$ ion with Al$^{3+}$ influences the electrostatic polarization and relative position of six oxygen anions. These oxygen anions are directly coupled to a total of six other B sites and six A sites. Thus, the substitution disturbs directly the trigonal symmetry of six tetrahedral clusters formed by three B sites and one A site with an oxygen anion at the center. Since each A site is part of four such clusters, another 18 tetrahedral clusters could be influenced. This would mean that for another 36 B sites the trigonal symmetry is lost. As a result, replacing 0.5% of the [Fe$^{3+}$] would influence 10% of the octahedral sites. This is thought to be the cause of the pronounced effect on the MO spectrum of only a small amount of Al$^{3+}$ (Fig. 9). Already a 0.005 Al$^{3+}$ content (not shown) results in a shift of the total spectrum to higher energies, as well as an enhancement of the transitions around 0.56 and 3.0–4.0 eV. In Fig. 9(a) the extremum near 3 eV clearly shows a linear shift in energy and a decrease in $\varepsilon'_{xy}$ upon Al$^{3+}$ substitution.

So far, the observed effects of substitutions of Fe with the nonmagnetic Mg$^{2+}$ and Al$^{3+}$ on the off-diagonal element of the dielectric tensor: the comparatively small effect on the peak positions of Mg$^{2+}$ substitution versus the comparatively large effect of Al$^{3+}$ substitution and the pronounced effect of only a small amount of Al$^{3+}$, are not inconsistent with the proposition that IVCT transitions are at the basis of the MO spectrum of Fe$_3$O$_4$. 

FIG. 5. The Kerr rotation $\theta_k$ (a) and Kerr ellipticity $\varepsilon_k$ (b), of Mg-substituted Fe$_3$O$_4$: (Fe$^{3+}$)[Mg$^{2+}$Fe$^{3+}_{1-x}$]Fe$^{3+}$O$_4$ for $x=0.0$, 0.2, and 0.8.

FIG. 6. The Kerr rotation $\theta_k$ (a) and Kerr ellipticity $\varepsilon_k$ (b), of Al-substituted Fe$_3$O$_4$: (Fe$^{3+}$)[Al$^{3+}$Fe$^{3+}_{1-x}$]O$_4$ for $x=0.02$, 0.2, and 0.4.
V. DATA-ANALYSIS AND DISCUSSION

A. Analysis of the spectra

To arrive at a correct transition assignment for Fe\(_3\)O\(_4\), the exact peak positions in the substituted ferrites should also be determined. As we have seen above, peak positions in substituted ferrites may be shifted, in particular for Al\(^3+\)-substituted ferrites. In order to find the correct transition energies all spectra of the elements of the dielectric tensor were fitted by means of Eqs. (3) or (6) and (7). To evaluate the fits the three following criteria were used. First, the difference between the measured spectrum and the fit should be on average less than 1% of the tensor element. Secondly, one set of peaks should describe all four spectra, \(\varepsilon'_{xx}\), \(\varepsilon'_{xx}\), \(\varepsilon'_{yy}\), and \(\varepsilon'_{xy}\) of a given ferrite. This fitting of all four elements of the dielectric tensor simultaneously is a more refined step in the analysis of the magneto-optical Kerr spectra of ferrites. Moreover, it is an essential step since due to the differences in line shape between the real and imaginary parts of the tensor elements overlapping bands can be resolved. Finally, the set of peaks should not depend on the Mg\(^{2+}\) or Al\(^{3+}\) substitution, as these ions are both nonmagnetic and the substitution is only partial. In Fig. 10 we show, by way of example, the fit to the imaginary part of \(\varepsilon'_{xx}\) the diagonal element, \(\varepsilon'_{xx}\), and \(\varepsilon'_{xy}\), of the dielectric tensor. The error in the fit is defined as the average difference between the fit and the dielectric tensor element in the energy range \(\pm 0.1\) eV from the transition energy. The importance of the third criterion can be illustrated by first considering the Fe\(_3\)O\(_4\) spectra by themselves and only then taking the influence of Mg\(^{2+}\) substitution into account. All four Fe\(_3\)O\(_4\) spectra can be described with a similar quality fit by a more limited set of transitions compared to the set reported in Table II. However, such a limited set of peaks fails to describe the spectra of Mg\(^{2+}\)-substituted ferrites. There are two reasons for this. First, a few strong transitions in the 3.0–4.0 eV range obscure other, weaker transitions. In Mg\(^{2+}\)-substituted ferrites strong Fe\(^{2+}\)-dependent transitions are suppressed, allowing the detection of weaker Fe\(^{3+}\)-dependent peaks. Second, a complicating factor is that around 4.0 eV two relatively strong transitions with identical line shapes but opposing signs are present.

Thus by means of the Mg\(^{2+}\) substitution the Fe\(_3\)O\(_4\) spectrum could be unravelled. In addition, we could determine which transitions are dependent on Fe\(^{2+}\) content, and which are not. This leads to the more complete set of transitions given in Table II, which describes all spectra throughout the range of Mg\(^{2+}\) and Al\(^{3+}\) substitution.

B. Peak assignment and discussion

The key results that enable us to assign of the main transitions are given in Fig. 11. In Fig. 11(a) the maximum \(\varepsilon'_{xy}\) value is given, relative to the value for Fe\(_3\)O\(_4\), versus [Fe\(^{2+}\)] content of the Mg\(^{2+}\)-substituted ferrite, for the transitions at 0.56, 1.94, 3.11, and 3.93 eV. Similarly Fig. 11(b) gives the relative maximum \(\varepsilon''_{xy}\) value versus [Fe\(^{3+}\)] content of the Al\(^{3+}\)-substituted ferrite for the same transitions. Substitution with Mg\(^{2+}\) [Fig. 11(a)] as well as substitution with Al\(^{3+}\) [Fig. 11(b)] causes a marked decrease in \(\varepsilon''_{xy}\) for the transi-
tion at 0.56 eV. Hence, for this transition both $[\text{Fe}^{2+}]$ and $[\text{Fe}^{3+}]$ are involved. Therefore, the transition at 0.56 eV is assigned to intervalence charge transfer (IVCT): $[d^3] + [d^6] \rightarrow [d^6] + [d^5]$ at $B$ sites. More specifically, it is the lowest IVCT $t_{2g} \rightarrow t_{2g}$ (see Fig. 12) in accordance with the proposition of Feil.

Assignment of the band at 1.94 eV is more complex because several transitions, including weak crystal-field transitions, overlap here. The main transition, however, is IVCT: $t_{2g} \rightarrow e_g$ between $[\text{Fe}^{2+}]$ and $[\text{Fe}^{3+}]$. This is the next IVCT (see Fig. 12). As can be seen in Fig. 11(a), substitution with $\text{Mg}^{2+}$ again exerts a clear influence. In addition, Fig. 11(b) shows that $\text{Al}^{3+}$ substitution has the same effect as on the transition at 0.56 eV. Hence, for this transition again both $[\text{Fe}^{2+}]$ and $[\text{Fe}^{3+}]$ are involved.

The transition at 3.11 eV is assigned to IVCT transition: $t_{2g} \rightarrow e$, i.e., from $[\text{Fe}^{2+}]$ to $[\text{Fe}^{3+}]$. Note the notation for $A$-site and $B$-site ions which are between parentheses and square brackets, respectively. Again we observe a dependence on $\text{Mg}^{2+}$ substitution [Fig. 11(a)]. However, in this case $\text{Al}^{3+}$ substitution [Fig. 11(b)] has no significant effect on the intensity of the transition after the initial change on substitution of $\text{Fe}^{3+}$ with 0.02 $\text{Al}^{3+}$. Finally, the transition at 3.93 eV is assigned to the IVCT transition $t_{2g} \rightarrow t_2$, which exhibits similar behavior upon $\text{Mg}^{2+}$ and $\text{Al}^{3+}$ substitution as the transition at 3.11 eV does (Fig. 11).

Next, we consider the line shapes of these transitions, reported in Table II. For the transition at 0.56 eV, $[\text{Fe}^{2+}]t_{2g} \rightarrow [\text{Fe}^{3+}]t_{2g}$, both the ground state and the excited state are split. In addition there is a distinct difference in occupation of the $t_{2g}$ ground state levels (see Fig. 12). Furthermore, the band-structure calculations by Feil show that the $t_{2g}$ band in $\text{Fe}_3\text{O}_4$ is relatively broad. This will mask the effect of the split excited state and as a result the shape of the transition will be determined by the difference in ground-state populations, i.e., the difference in oscillator strength for $\Delta m_j = 1$ (RCP) and $\Delta m_j = -1$ (LCP). Hence, the observed paramagnetic line shape is expected. In the case of the transition at 1.94 eV, $[\text{Fe}^{2+}]t_{2g} \rightarrow [\text{Fe}^{3+}]e$, only the partially occupied ground state is split and the aforementioned band-
structure calculation shows that the $e_g$ band is also relatively broad, hence a paramagnetic line shape is again observed for this transition. The band-structure calculations further show that the bands situated on the tetrahedral sublattice are distinctly narrower than the bands on the octahedral sublattice.

As a result we observe a diamagnetic line shape for the transitions at 3.11 and 3.93 eV, $[\text{Fe}^{2+}]_{t_{2g}} \rightarrow (\text{Fe}^{2+})_{e_g}$ and $[\text{Fe}^{2+}]_{t_{2g}} \rightarrow (\text{Fe}^{2+})_{t_2}$, respectively, since the difference in energy between the transitions with selection rules $\Delta m_l = 1$ and $\Delta m_l = -1$ will determine the line shape.

Regarding the relative strength of the IVCT transitions, we observe (Table II) that transitions between two $t$ orbitals are stronger than transitions between a $t$ and an $e$ orbital and that the transitions between cations on the octahedral sublattice are stronger than the transitions between the two sublattices. Both effects are to be expected. First, $t_{2g} \rightarrow t_{2g}$ orbitals have a large overlap, as these orbitals point towards each other in between the oxygen anions. The $t_{2g} \rightarrow e_g$ orbitals have a much smaller overlap as the $e_g$ is directed towards the oxygen anion. Secondly, as electron spin reorientation upon excitation is an improbable process, transitions between antiferromagnetically coupled ions are weaker than between ferromagnetically coupled ions. A theoretical analysis has, however, shown that IVCT transitions between antiferromagnetically coupled ions are still possible, albeit at reduced intensity.

The data in Fig. 11(a) show that the MO transitions depend in a nonlinear manner on the $[\text{Fe}^{2+}]$ concentration. Within the margin of error no straight line can be drawn through the datapoints. This can be seen by comparing these points with the straight dotted line in Fig. 11(a) representing a linear dependence. According to some authors this already

![TABLE II. The main transitions occurring in Fe₃O₄ between 0.5 and 5.0 eV. Listed are peak position $\omega_0$, width $\Gamma_0$, intensity $(\varepsilon_{xy})_{\text{max}}$, as well as peak assignment. For details see text.](image)

<table>
<thead>
<tr>
<th>$\omega_0$ (eV)</th>
<th>$\Gamma_0$ (eV)</th>
<th>$(\varepsilon_{xy})_{\text{max}}$</th>
<th>Type</th>
<th>Transition</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongly dependent on Fe²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.56</td>
<td>0.21</td>
<td>-0.085</td>
<td>IVCT</td>
<td>$[\text{Fe}^{2+}]<em>{t</em>{2g}} \rightarrow [\text{Fe}^{2+}]<em>{t</em>{2g}}$</td>
<td>−para</td>
</tr>
<tr>
<td>1.94</td>
<td>0.45</td>
<td>0.044</td>
<td>IVCT</td>
<td>$[\text{Fe}^{2+}]<em>{t</em>{2g}} \rightarrow [\text{Fe}^{2+}]<em>{t</em>{2g}}$</td>
<td>+para</td>
</tr>
<tr>
<td>3.11</td>
<td>0.61</td>
<td>0.031</td>
<td>IVCT</td>
<td>$[\text{Fe}^{2+}]<em>{t</em>{2g}} \rightarrow (\text{Fe}^{2+})_{e_g}$</td>
<td>+dia</td>
</tr>
<tr>
<td>3.93</td>
<td>0.37</td>
<td>-0.039</td>
<td>IVCT</td>
<td>$[\text{Fe}^{2+}]<em>{t</em>{2g}} \rightarrow (\text{Fe}^{2+})_{t_2}$</td>
<td>−dia</td>
</tr>
<tr>
<td>Weakly dependent on Fe²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.61</td>
<td>0.20</td>
<td>-0.004</td>
<td>ISCT</td>
<td>$(\text{Fe}^{2+})<em>{t_2} \rightarrow [\text{Fe}^{2+}]</em>{t_{2g}}$</td>
<td>−dia</td>
</tr>
<tr>
<td>3.46</td>
<td>0.42</td>
<td>0.014</td>
<td>ISCT</td>
<td>$[\text{Fe}^{2+}]<em>{e_g} \rightarrow (\text{Fe}^{2+})</em>{t_2}$</td>
<td>+dia</td>
</tr>
<tr>
<td>3.94</td>
<td>0.51</td>
<td>0.065</td>
<td>ISCT</td>
<td>$(\text{Fe}^{2+})<em>{t_2} \rightarrow [\text{Fe}^{2+}]</em>{t_{2g}}$</td>
<td>+dia</td>
</tr>
<tr>
<td>4.51</td>
<td>0.40</td>
<td></td>
<td></td>
<td>$(\text{O}<em>2p \rightarrow [\text{Fe}^{2+}]</em>{t_{2g}})$</td>
<td></td>
</tr>
</tbody>
</table>

As a result we observe a diamagnetic line shape for the transitions at 3.11 and 3.93 eV, $[\text{Fe}^{2+}]_{t_{2g}} \rightarrow (\text{Fe}^{2+})_{e_g}$ and $[\text{Fe}^{2+}]_{t_{2g}} \rightarrow (\text{Fe}^{2+})_{t_2}$, respectively, since the difference in energy between the transitions with selection rules $\Delta m_l = 1$ and $\Delta m_l = -1$ will determine the line shape.

![FIG. 11. Relative maximum $\varepsilon_{xy}$ value for the IVCT transitions; (a) versus $[\text{Fe}^{2+}]$ content (Mg substitution), (b) versus $[\text{Fe}^{3+}]$ content (Al substitution).](image)

![FIG. 12. Schematic representation of the electronic structure of the Fe ions in Fe₃O₄.](image)
indicates that a pair interaction is responsible for this transition.\textsuperscript{7,42} The argument is that normally the oscillator strength of a transition is independent of the concentration of the absorbing species. This results in a linear dependence of the intensity of a transition on the concentration in the case of a single-ion transition (Lambert-Beer law).\textsuperscript{18,23,24} If the absorption process involves pairs of ions, as in the case of an IVCT or ISCT transition, the Lambert-Beer law no longer applies and a nonlinear dependence on the concentration may be observed.\textsuperscript{7,42} In ferrites this simple situation may be complicated by disturbances of the lattice upon substitution. However, in the case of substitution with Mg\textsuperscript{2+} the lattice parameter changes less than 0.3\% in the case of complete substitution of Fe\textsuperscript{2+}.\textsuperscript{1} As a result the lattice is hardly disturbed. In contrast, the delocalization $\alpha$ is expected to be influenced by Mg substitution as the electron is now pinned on the Mg\textsuperscript{2+} site. Hence, referring to Eq. (9), a nonlinear dependence of $(e_{\text{max}})$ on Mg\textsuperscript{2+} substitution can be expected for IVCT transitions.

The transitions that are only weakly dependent on Fe\textsuperscript{2+} content are reported in the second part of Table II. The transitions in the 2.5–4.0 eV range have the same relative position, linewidth, and relative intensity as the ISCT transitions reported by Scott\textsuperscript{18} for yttrium iron garnet (YIG). Hence, we attribute these transitions to intersublattice charge transfer transitions. Since in this case for the ground state the split $t$ orbitals are fully occupied while the ground-state $e$ orbitals are not split, we expect the observed diamagnetic line shape for all ISCT transitions. The transition at 4.51 eV was assigned by Scott to the first O $2p$→Fe $3d$ charge-transfer transition. We have been unable to draw any conclusion concerning this assignment, as no MO data were available above 4.0 eV.

As a final check on the consistency of the peak assignment given in Table II, the relative energy differences of the excited states can be calculated. From the foregoing it follows that the difference between the energies of the first two IVCT transitions (1.38 eV) must be equal to the difference between the first and the last ISCT transition (1.33 eV) as both these differences reflect the crystal-field splitting between $t_{2g}$ and $e_{g}$. The values thus obtained are in fair agreement with the crystal-field splitting between $t_{2g}$ and $e_{g}$ calculated by Feil (1.5 eV) (Ref. 7) and derived by Camphausen, Coey, and Chakraverty (1.3 eV).\textsuperscript{3} Furthermore, the difference between the energies of the last two IVCT transitions (0.82 eV) should equal the difference between the middle ISCT transition and the ISCT transition: $[\text{Fe}^{3+}e_{g}→(\text{Fe}^{2+})e]$. This last transition should then be situated around 2.64 eV and can therefore, unfortunately, not be separated from the $(\text{Fe}^{3+})t_{2g}→(\text{Fe}^{2+})t_{2g}$ transition at 2.61 eV which has the same line shape. In addition, in YIG the latter transition is reported to be about twice as intense as the former.\textsuperscript{15} The crystal-field splitting between $t_{2g}$ and $e_{g}$ calculated by Feil to be 1 eV (Ref. 7) and derived by Camphausen, Coey, and Chakraverty to be 0.8 eV.\textsuperscript{3}

\section*{VI. CONCLUSIONS}

We have measured both the optical and the magneto-optical polar Kerr spectrum of pure Fe$_3$O$_4$ and of Mg\textsuperscript{2+}-substituted and Al\textsuperscript{3+}-substituted Fe$_3$O$_4$ at 293 K. This has enabled us to determine the complete dielectric tensor of these compounds between 0.7 and 4.0 eV. Key to the subsequent unravelling of the complicated Fe$_3$O$_4$ spectra were the following: First the fitting of all four $(e_{xx}, e_{yy}, e'_{xy},$ and $e''_{xy})$ parts of the dielectric tensor simultaneously with one set of transitions. As a result overlapping bands can be resolved due to the differences in line shape between the real and imaginary parts of the tensor elements. Second, the systematic substitution with nonmagnetic ions, of which the Mg\textsuperscript{2+} substitution was essential to separate the intense, Fe\textsuperscript{3+}-dependent IVCT transitions from the ISCT transitions.

The observed dependence on both [Mg\textsuperscript{2+}] and [Al\textsuperscript{3+}] of certain MO transitions have provided us with experimental evidence that IVCT transitions are at the basis of the Fe$_3$O$_4$ MO-Kerr spectrum. The assignment of the main MO active transitions in Fe$_3$O$_4$ to IVCT transitions is consistent with the observed line shapes, relative strengths, and relative transition energies. Furthermore, ISCT transitions consistent with YIG could be identified. The IVCT transitions occur at 0.56, 1.94, 3.11, and 3.94 eV. From these transitions we find, in agreement with the assignment of the ISCT transitions, that in Fe$_3$O$_4$ the $t_{2g}→e_{g}$ excited state energy or crystal-field splitting of octahedral Fe\textsuperscript{3+} is 1.38 eV and that the $t_{2g}→e$ energy splitting of tetrahedral Fe\textsuperscript{3+} is 0.82 eV.

\section*{ACKNOWLEDGMENTS}

It is a pleasure to acknowledge H. Feil for the stimulating discussions and J. C. Jans for initial spectroscopic ellipsometry measurements. Furthermore, we would like to thank L. F. Feiner and P. F. Bongers for critically reading the manuscript.
30 See, for instance, P. J. van der Zaag, A. Noordermeer, M. T. Johnson, and P. F. Bongers, Phys. Rev. Lett. 68, 3112 (1992), and references therein; V. A. M. Brabers, ibid. 68, 3113 (1992), and references therein.
37 L. de Bont and V. A. M. Brabers (unpublished).
40 Note that the $\varepsilon_{xx}$ spectra have been determined between 0.5 and 5.0 eV. Consequently, although the 0.56 eV transition is beyond the range where MO measurements have been made the peak position is well established from the optical data. Furthermore, the 0.56 eV peak position is consistent with previous experiments (Refs. 7, 10, and 13). Moreover, this transition is relatively strong, which allows an unambiguous determination of line shape and transition energy.