On the origin of the magneto-optical effects in Li, Mg, Ni, and Co ferrite

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A reexamination of the magneto-optical (MO) spectra of Li0.5Fe2.5O4, MgFe2O4, NiFe2O4, and CoFe2O4 is presented. Thus far the MO spectra of these compounds have been explained by either orbital promotion processes, oxygen to iron charge transfer transitions or crystal field transitions and, in the case of CoFe2O4, a single intervalence charge transfer (IVCT) transition. For Li0.5Fe2.5O4 and MgFe2O4, the major transitions in the MO–Kerr spectra between 0.5 and 5.0 eV are assigned to intersublattice charge transfer (ISCT) transitions. The MO–Kerr spectrum of NiFe2O4 is more complex as in this case both Fe3+ and Ni2+ contribute to the spectrum. In NiFe2O4 an additional IVCT transition is observed at 2.9 eV. The complex MO spectrum of CoFe2O4 could be resolved using the dielectric tensors of Co2+Al3+Fe3-xO4 (x = 0, 0.1, 0.6, and 1) and rigorously fitting both the diagonal and the off-diagonal elements of the dielectric tensor with one set of transitions which was consistent for all degrees of Al3+ substitution. Thus, in these ferrites a consistent assignment of all the major transitions in the 2.0 to 5.0 eV energy range to either IVCT or ISCT transitions is made. © 1998 American Institute of Physics.

I. INTRODUCTION

The identification and assignment of magneto-optical (MO) active transitions in spinel ferrites have been a subject of debate for many years. The identification of transitions is complex as in these compounds many bands overlap. In addition, the electronic structure of transition metal oxides such as ferrites is complex1,2 which has resulted in a variety of interpretations of the observed transitions. Recently, we have unraveled the MO–Kerr spectrum of Fe3O4 between 0.7 and 4.0 eV by rigorous fitting of all four elements of the dielectric tensor of Fe3O4 simultaneously, using the equations of the elements of the dielectric tensor which describe the basic line shapes of transitions in the microscopic theory (Lorentz-type lineshape). In addition, the complete dielectric tensors of Fe3O4 and of partially Mg2+ or Al3+ substituted Fe3O4 were fitted with only one set of parameters for all samples. The influence on the intensity of transitions of the gradual substitution of Fe3+ and/or Fe3+ provided evidence that the major transitions in Fe3O4 can be assigned to intervalence charge transfer and intersublattice charge transfer transitions (IVCT and ISCT, respectively).3 IVCT transitions are transitions in which an electron, through optical excitation, is transferred to a neighboring cation. IVCT transitions between Fe3+ ions on different crystallographic sites are traditionally called ISCT transitions.3 For reasons of clarity we will continue to refer to these transitions as ISCT transitions. (In our discussions parenthesis denote tetrahedral A sites and square brackets octahedral B sites.)

Thus far multiple interpretations have been reported for the ferrites Li0.5Fe2.5O4, MgFe2O4, NiFe2O4, and CoFe2O4. We will discuss them in chronological order. Krinchik et al. reported the off-diagonal element of the dielectric tensor of Li0.5Fe2.5O4 between 2 and 5 eV.5 These authors reported also the off-diagonal elements of NiFe2O4, CoFe2O4, CoCrFeO4 between 1 and 5.4 eV and the equatorial Kerr effect of (Fe)[NiCr]O4.5,6 In addition to the transitions already identified in Li0.5Fe2.5O4 and MgFe2O4 an additional broad band near 3 eV was identified in NiFe2O4. This band was assigned to the CF transition 3A2g(F)→3T1g(P) of octahedrally coordinated Ni2+. However, in this interpretation the disappearance of this transition in (Fe)[NiCr]O4 cannot be accounted for. From the observed influence of Al3+ and Cr3+ substitution on the equatorial Kerr spectra of NiFe2O4 and CoFe2O4, Krinchik et al. conclude that the major transitions in Li0.5Fe2.5O4 and MgFe2O4 are ISCT transitions.

Subsequently, Višnovsky et al. reported the diagonal and off-diagonal elements of the dielectric tensor of MgFe2O4 and reflectivity and polar Kerr spectra of Li0.5Fe2.5O4 between 2 and 5.5 eV. These authors assigned the transitions identified to oxygen (2p) to iron (3d) charge transfer transitions.7 From the work of Bocquet et al., however, it follows that this is an unlikely interpretation as the oxygen to iron charge transfer transitions are centered around 6 eV (Ref. 2) in agreement with previous reports.4,8 In 1983 Zhang et al. reported the diagonal (0.5–12 eV) and off-diagonal (0.5–5 eV) elements of the dielectric tensor of Li0.5Fe2.5O4 and MgFe2O4. The identified bands were assigned to 3dν→3dν′→′3s orbital promotion transitions.8 However, these transitions are parity and partly spin forbidden and can, therefore, not account for the relatively large oscillator strength (10−3) of the transitions observed in these ferrites. Finally, the MO–Kerr spectrum of CoFe2O4 has been extensively studied by Martens and co-workers.9,10 Two narrow diamagnetic transitions at 0.8 and 2.0 eV were identified and assigned to CF transitions [4A2→→4T1(F) and 4A2→→4T1(P)] of tetrahedrally coordinated Co2+. A broad paramagnetic band also at 2.0 eV was assigned to a [Co2+]→[Fe3+] IVCT transition. The broad diamagnetic band in the region above 3 eV remained unresolved.

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Here we report a study of the MO spectra of Li$_{0.5}$Fe$_{2.5}$O$_4$, MgFe$_2$O$_4$, NiFe$_2$O$_4$, and CoFe$_2$O$_4$ and identify the major transitions. For this purpose, we have taken the elements of the dielectric tensor of these compounds from literature and applied the same method used to resolve the MO spectrum of Fe$_3$O$_4$. 3

II. RESULTS AND DISCUSSION

First, we examine MgFe$_2$O$_4$. We applied the method used to resolve the spectrum of Fe$_3$O$_4$ to the diagonal and off-diagonal element of the dielectric tensor of MgFe$_2$O$_4$ obtained from Refs. 8 and 7, respectively. The off-diagonal element and the fits are presented in Fig. 1(a). The set of transitions identified in MgFe$_2$O$_4$ is listed in Table I. To assign these transitions, we compare them to the transitions found in Fe$_3$O$_4$. 3 The MO spectrum of Fe$_3$O$_4$ consists of two sets of transitions: IVCT transitions involving Fe$^{2+}$ and Fe$^{3+}$ and the ISCT involving two Fe$^{3+}$ ions located on different crystallographic sites. Since the Fe$^{2+}$ ions present in Fe$_3$O$_4$ are replaced by the nonmagnetic Mg$^{2+}$, the ISCT transitions should be the only remaining major transitions. Substitution of one ion with another may distort the lattice resulting in a shift in energy of the ISCT transitions. However, replacing Fe$^{2+}$ with Mg$^{2+}$ only has a small effect on the lattice since the lattice parameter of MgFe$_2$O$_4$ matches closely the lattice parameter of Fe$_3$O$_4$. We conclude from our fit [Fig. 1(a)] that the MO–Kerr spectra of MgFe$_2$O$_4$ can be explained in a manner consistent with our interpretation of Fe$_3$O$_4$, based on ISCT transitions, as suggested previously. 11

For Li$_{0.5}$Fe$_{2.5}$O$_4$ the elements of the dielectric tensor were obtained from Refs. 8 and 9. The set of transitions identified from our fits is listed in Table I. The same three major bands as in MgFe$_2$O$_4$ could be identified. The fact that the intensities in Li$_{0.5}$Fe$_{2.5}$O$_4$ are substantially higher than in MgFe$_2$O$_4$ is to be expected as this compound contains a larger amount of [Fe$^{3+}$]$_2$, which is one of the participating ions in the transition. 5 Thus also the MO–Kerr spectra of Li$_{0.5}$Fe$_{2.5}$O$_4$ can be explained in a manner consistent with Fe$_3$O$_4$ based on ISCT transitions.

Only the off-diagonal element of the dielectric tensor of NiFe$_2$O$_4$ was available. 5 The off-diagonal element and fit are presented in Fig. 1(b). The results of the fit are given in Table I. Again we observe the same set of ISCT transitions as in the previous samples. In addition, we observe an additional strong, relatively broad transition at 2.9 eV. This transition cannot be assigned to a CF transition. First of all, CF transitions of ions on octahedral sites are parity forbidden for any ion. Second, transitions of Ni$^{2+}$ on tetrahedral sites cannot occur, as the NiFe$_2$O$_4$ sample used, is reported to be completely inverse, as expected for NiFe$_2$O$_4$. 12 Third, CF transitions of Fe$^{3+}$ on tetrahedral sites do not occur, as the term of a free Fe$^{3+}$ ion is nondegenerate (L = 0). Further-

![Image](66x534 to 283x739)

**FIG. 1.** (a) The measurement Ref. 7 and the fits of the real and imaginary part of the off-diagonal element of the dielectric tensor, $\epsilon_{xy}$, of MgFe$_2$O$_4$. (b) The measurement Ref. 5 and the fits of the real and imaginary part of the off-diagonal element of the dielectric tensor, $\epsilon_{xy}$, of NiFe$_2$O$_4$. 

**TABLE I.** The main MO-active transitions in MgFe$_2$O$_4$, Li$_{0.5}$Fe$_{2.5}$O$_4$, NiFe$_2$O$_4$, and CoFe$_2$O$_4$, between 0.5 and 5.0 eV. Listed are transition energy, $\omega$ (eV), linewidth, $\Gamma$ (eV), intensity, $(\epsilon_{xy})_{max}$, and assignments. Typical error bars for $\omega$, $\Gamma$, and $(\epsilon_{xy})_{max}$ are $\pm 0.02$ eV; $\pm 0.03$ eV; and $\pm 0.002$, respectively. (Note that the parenthesis denote tetrahedral coordination and square brackets octahedral coordination.)

<table>
<thead>
<tr>
<th>Sample</th>
<th>CF (Co$^{3+}$) $\omega$</th>
<th>CF (Co$^{2+}$) $\omega$</th>
<th>IVCT [M$^{2+}$] $\epsilon g$</th>
<th>ISCT [Fe$^{3+}$]$_{\Lambda}$ $\epsilon g$</th>
<th>ISCT [Fe$^{2+}$]$_{\Lambda}$ $\epsilon g$</th>
<th>ISCT [Fe$^{3+}$]$_{\Sigma}$ $\epsilon g$</th>
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<tr>
<td>MgFe$_2$O$_4$</td>
<td>2.64</td>
<td>3.47</td>
<td>3.95</td>
<td>3.00</td>
<td>3.13</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>$\omega$</td>
<td>$\Gamma$</td>
<td>$(\epsilon_{xy})_{max}$ shape</td>
<td>dia</td>
<td>dia</td>
<td>dia</td>
</tr>
<tr>
<td></td>
<td>2.60</td>
<td>3.55</td>
<td>4.00</td>
<td>3.05</td>
<td>3.20</td>
<td>3.05</td>
</tr>
<tr>
<td>Li$<em>{0.5}$Fe$</em>{2.5}$O$_4$</td>
<td>2.86</td>
<td>2.57</td>
<td>3.17</td>
<td>0.53</td>
<td>0.22</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>$\omega$</td>
<td>$\Gamma$</td>
<td>$(\epsilon_{xy})_{max}$ shape</td>
<td>dia</td>
<td>dia</td>
<td>dia</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>0.83</td>
<td>1.82</td>
<td>2.21</td>
<td>0.53</td>
<td>0.22</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.18</td>
<td>-0.056</td>
<td>0.007</td>
<td>0.011</td>
<td>0.017</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>0.10</td>
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<td>0.25</td>
<td>0.29</td>
<td>0.80</td>
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<tr>
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more, this additional transition cannot be due to an oxygen 2p to metal 3d charge transfer transition. Such a transition should occur at an energy of 6 eV (Ref. 1) and it would be both broader and more intense than the observed band. Therefore, we assign this transition to an IVCT transition between [Ni$^{2+}$] and [Fe$^{3+}$].$^{13}$ This is consistent with the strength and width of similar transitions in Fe$_2$O$_3$. Furthermore, the energy of an IVCT transition between two different cations is expected to be substantially higher than that between two identical cations which in Fe$_2$O$_3$ occurs at 0.55 eV.$^3$

Evidence that the transition at 2.9 eV is indeed due to an IVCT transition between [Ni$^{2+}$] and [Fe$^{3+}$] comes from the equatorial Kerr spectrum of (Fe)$_x$(NiCr)$_{1-x}$O$_2$, between 1 and 5.4 eV.$^6$ No transitions whatsoever are found in this spectrum, ruling out the transition at 2.9 eV in NiFe$_2$O$_4$ is due to a CF transition of Ni$^{2+}$. The absence of this transition is, however, in line with an IVCT involving [Fe$^{3+}$]. This also supports our assignment of the remaining transitions in NiFe$_2$O$_4$ to ISCT transitions. Another indication that all transitions in NiFe$_2$O$_4$ are similar transitions involving [Fe$^{3+}$] is the influence of Al$^{3+}$ substitution on the MO spectrum of NiAl$_x$Fe$_{2-x}$O$_4$(0 < x $\leq$ 1.2) which remains completely inverse up to x = 1.$^{14}$ The entire spectrum remains unchanged up to x = 0.3, then the intensity of the entire spectrum decreases homogeneously.

The complete dielectric tensors of CoFe$_2$O$_4$ and CoAl$_x$Fe$_{2-x}$O$_4$ (x = 0.1, 0.6, 1) were taken from Martens et al.$^9,10$ All four elements of the dielectric tensors of CoFe$_2$O$_4$ and CoAl$_x$Fe$_{2-x}$O$_4$ were fitted simultaneously with only one set of parameters for all spectra, thus allowing trends in intensity upon Al$^{3+}$ substitution to be observed. The results of the fits for CoFe$_2$O$_4$ are shown in Table I. Our assignment of the first three transitions is identical to the assignment made previously.$^9$ The first two are assigned to the CF transitions $\Delta A_2 \rightarrow T(1)$ and $\Delta A_2 \rightarrow T(1)$ (Co$^{3+}$) on A sites. These are the only two CF transitions which are allowed from the singlet $\Delta A_2$ ground state of (Co$^{3+}$) (note that CF transitions from octahedrally coordinated [Co$^{3+}$] are parity forbidden). The third is assigned to a [Co$^{2+}$]→[Fe$^{3+}$] IVCT transition. The remaining two transitions are two of the three ISCT transitions observed in each of the three previous investigated compounds. The third ISCT near 2.6 eV, present in all other spinel ferrites discussed so far, is obscured in CoFe$_2$O$_4$ due to the intense band at 2.2 eV. To the evidence presented for the assignment of the CF transitions proposed by Martens et al.$^9$ one can add the observed changes in intensity as reported for CoAl$_x$Fe$_{2-x}$O$_4$.$^{14}$ CoAl$_x$Fe$_{2-x}$O$_4$ changes from inverse to normal spinel between x = 0 to x = 1.2, i.e., Co$^{2+}$ migrates to the tetrahedral site. The intensity of the transition at 1.9 eV increases for x = 0.0 to 0.8 then decreases for x > 0.8. The intensity of the transition at 2.2 eV slightly increases for x = 0.3 then decreases. This enhancement effect on IVCT transitions of a small amount of Al$^{3+}$, resulting from perturbation of the octahedral symmetry, was observed also in Fe$_2$O$_3$ containing a small amount of Al$^{3+}$. The bands between 3 and 5 eV decrease steadily for 0 < x $\leq$ 1.2. The dependencies of the intensities of the IVCT transition (2.2 eV) and the ISCT transitions on the degree of Al$^{3+}$ substitution tend, as expected, towards zero for CoAlFeO$_4$ in our fits. As discussed by Martens et al. the gradual decrease in intensity for the CF transitions of (Co$^{2+}$), however, is not straightforward. Their claim is that the sharp drop in Curie temperature for the series causes this. The fact that the energy of the IVCT transition is considerably larger than that of the first IVCT in Fe$_2$O$_4$ can be attributed to the fact that the IVCT is in this case between cations with different nuclei. The fact that the energy of this IVCT is smaller compared to the energy of the observed IVCT in NiFe$_2$O$_4$ is also not unexpected, if we take into account the relative energy position of the 3d bands.$^1$

### III. CONCLUSIONS

The common feature of all spinel ferrites of the general type M$_x$Fe$_{2-x}$O$_4$ with Fe$^{3+}$ ions on both tetrahedral and octahedral sites is a set of ISCT transitions at 2.6, 3.5, and 4.0 eV. This is evident from Table I for those spinel ferrites, where M is the nonmagnetic Mg$^{2+}$ and Li$^+$ as well as for those where M is the magnetic Ni$^{2+}$ and Co$^{2+}$. (This even applies to γ-Fe$_2$O$_3$, where M is in fact a vacancy.$^{14}$) Whether these transitions dominate the spectrum depends on the presence of other contributing transitions. For M=Mg, Li, or other nonmagnetic ion (or vacancies), the set of ISCT transitions is the main feature. In Fe$_2$O$_4$ several IVCT transitions between [Fe$^{2+}$] and Fe$^{3+}$ are main contributors.$^3$ In NiFe$_2$O$_4$ an IVCT between [Ni$^{2+}$] and [Fe$^{3+}$] at 2.9 eV is a main contributor. In CoFe$_2$O$_4$ CF transitions of tetrahedrally coordinated Co$^{2+}$ and an IVCT transition between Co$^{2+}$ and Fe$^{3+}$ contribute significantly below 2.5 eV. These assignments are consistent with our interpretation of the MO spectra of Fe$_2$O$_4$.


$^{13}$Recently, a similar assignment for this peak was reached independently by M. Lenglet, F. Hochu, and J. Dühr (private communication).