A study of the magneto-optical Kerr spectra of bulk and ultrathin Fe3O4

Citation for published version (APA):

DOI:
10.1063/1.362112

Document status and date:
Published: 01/01/1996

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:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 16. Sep. 2023
A study of the magneto-optical Kerr spectra of bulk and ultrathin Fe$_3$O$_4$

P. J. van der Zaaag, a) W. F. J. Fontijn, P. Gaspard, b) and R. M. Wolf
Philips Research Laboratories, Professor Holstlaan 4, 5656 AA Eindhoven, The Netherlands

V. A. M. Brabers, R. J. M. van de Veerdonk, and P. A. A. van der Heijden
Department of Physics, Eindhoven University of Technology (EUT), 5600 MB Eindhoven, The Netherlands

An analysis of the complete dielectric tensor of bulk magnetite, Fe$_3$O$_4$, and of FeO$_x$ substituted with a variable degree of Mg$_{2+}$ or Al$_{3+}$ allowed the assignment of the main magneto-optical (MO) transitions in Fe$_3$O$_4$ between 0.5 and 4.0 eV. This assignment is consistent with our reinterpretation of the MgFe$_2$O$_4$ and Li$_{0.3}$Fe$_2$.5O$_4$ MO-Kerr spectra. An analysis of the stoichiometry of a thin Fe$_3$O$_4$ layer is made, based on the Kerr spectrum, which is compared to an analysis based on the Verwey transition. The Kerr spectrum is also used to compare wavelengths for MO-Kerr effect studies of wedge-shaped samples. © 1996 American Institute of Physics. [S0021-8979(96)22508-7]

I. INTRODUCTION

The interpretation of the magneto-optical (MO) Kerr spectrum of spinel ferrites, and notably magnetite, has been a subject of debate.1-3 Some authors have explained the part of the spectrum around 2.0 eV in terms of 3d crystal field transitions of Fe$^{3+}$ ions on the tetrahedral (A-) sites.1 Others have assigned the major peaks in the MO-Kerr spectrum of Fe$_3$O$_4$ to 3d$^n$→3d$^{n-1}$4s orbital promotion processes.2 The problem with these interpretations, however, is that they are based on forbidden transitions, whereas Fe$_3$O$_4$ has relatively strong MO transitions and absorption peaks with an oscillator strength of about 10$^{-3}$ below 4.0 eV. Hence, Feil proposed that the main MO-active transitions between 0.5 and 4.0 eV are intervalence charge transfer (IVCT) transitions (Fe$^{2+}$ + Fe$^{3+}$→Fe$^{3+}$ + Fe$^{2+}$).3 As the Fe$^{2+}$→Fe$^{3+}$ pair involved does not possess inversion symmetry, the parity selection rule is relaxed. Consequently, IVCT transitions should have much higher oscillator strengths than the transitions previously proposed.

We will show that IVCT transitions indeed explain the MO-Kerr spectrum of Fe$_3$O$_4$ between 0.5 and 4.0 eV. Key to the unraveling of the complicated Fe$_3$O$_4$ MO-Kerr spectrum were: first, the fitting of all four relevant elements of the dielectric tensor $\epsilon_{xx}$, $\epsilon_{yy}$, $\epsilon_{zz}$, and $\epsilon_{xy}$, simultaneously with one set of transitions. Secondly, the systematic substitution with nonmagnetic ions, Mg$^{2+}$ and Al$^{3+}$, which allows the determination of trends in the Kerr spectra with a reduction in [Fe$^{2+}$] and [Fe$^{3+}$] content (round brackets denote ions on A-sites, square brackets ions on B-sites). Of these substitutions, the Mg$^{2+}$ substitution is of special significance as it reduces the intense Fe$^{2+}$-dependent IVCT transitions, allowing the detection of other, overlapping transitions such as the intersublattice charge transfer (ISCT) transitions (Fe$^{3+}$ + Fe$^{1+}$→Fe$^{2+}$ + Fe$^{2+}$). Finally, the usefulness of this understanding of the MO spectra of Fe$_3$O$_4$ in the field of thin oxide films will be discussed.

a)Author to whom correspondence should be addressed. Electronic-mail: ZAAO@RFL.PHILIPS.NL
b)Permanent address: UFR de Physique, Université Joseph Fourier-Grenoble I, 38041 St. Martin d’Heres, France.

II. RESULTS AND DISCUSSION

To arrive at a consistent transition assignment for Fe$_3$O$_4$, we determined the complete dielectric tensor for synthetic crystals of Fe$_3$O$_4$, and Mg$^{2+}$- and Al$^{3+}$-substituted Fe$_3$O$_4$, prepared by a floating zone technique.4 The diagonal element of the dielectric tensor was determined by ellipsometry between 0.5 and 5.0 eV.5 The polar MO-Kerr spectrum was measured between 0.7 and 4.0 eV.6,7 From these spectra the off-diagonal element was calculated between 0.7 and 4.0 eV. Thus, for each sample the complete dielectric tensor was obtained, amounting to four spectra: $\epsilon_{xx}$, $\epsilon_{yy}$, $\epsilon_{xy}$, and $\epsilon''_{xy}$. As these spectra consist of many overlapping bands, partly of opposing sign,8 inspection of the spectra does not yield proper transition identification. To achieve this, rigorous fitting, using equations describing the basic line shapes of transitions in the microscopic theory of the dielectric tensor,6 is needed. The complete dielectric tensor of Fe$_3$O$_4$ and of the Mg$^{2+}$- or Al$^{3+}$-substituted Fe$_3$O$_4$ were least-square fitted with one set of transitions for all samples. The criterion for a good fit was that the difference between the measured spectrum and the fit was on average less than 1% of the tensor element.7

Trends in MO-peak intensity and energy shift could be established due to the variable degree of substitution. Furthermore, as Mg$^{2+}$ and Al$^{3+}$ both preferentially occupy only the octahedral site, we are able to establish the nature of the MO-active transitions. The key results are summarized in Fig. 1, which depicts $\epsilon'_{xy}$, $\epsilon''_{xx}$, $\epsilon''_{xy}$, and $\epsilon''_{yx}$ max vs $\epsilon''_{yy}$ for Fe$^{2+}$ and Fe$^{3+}$ content. The nonlinear dependence on [Fe$^{2+}$] points to a pair interaction for all these transitions.9 Given their behavior on substitution of [Fe$^{3+}$] with Al$^{3+}$ the transitions at 0.56 and 1.94 eV involve also this ion, while the transitions at 3.11 and 3.93 eV involve (Fe$^{3+}$). Consequently, four of the main transitions are assigned to intervalence charge transfer transitions (0.56 eV: $\epsilon''_{xy}$−$\epsilon''_{xx}$−$\epsilon''_{yy}$ 1.94 eV: $\epsilon''_{xy}$ 3.11 eV: $\epsilon''_{xy}$ 3.93 eV: $\epsilon''_{xy}$). For the three major transitions remaining we propose a new assignment. These transitions are assigned to intersublattice charge transfer transitions (2.61 eV: $\epsilon''_{xy}$−$\epsilon''_{yy}$ 2.94 eV: $\epsilon''_{xy}$ 3.94 eV: $\epsilon''_{xy}$). Since the relative peak positions, the relative strengths and the linewidths of these transitions
are consistent with the results reported for YIG.\textsuperscript{8} From this transition assignment for Fe\textsubscript{3}O\textsubscript{4} the transition assignment for related ferrites such as MgFe\textsubscript{2}O\textsubscript{4} and Li\textsubscript{0.5}Fe\textsubscript{2.5}O\textsubscript{4} can be derived. This assignment should be the same as that of Fe\textsubscript{3}O\textsubscript{4} without the IVCT transitions as these involve Fe\textsuperscript{2+}, although one should allow for some shift in transition energy and differences in intensity. We used the dielectric tensor of MgFe\textsubscript{2}O\textsubscript{4} and Li\textsubscript{0.5}Fe\textsubscript{2.5}O\textsubscript{4} can be interpreted in a consistent manner with the proposed transition assignment for Fe\textsubscript{3}O\textsubscript{4}. The polar Kerr spectra between 0.7 and 4.0 eV were measured of thin layers of Fe\textsubscript{3}O\textsubscript{4} deposited by oxidic molecular beam epitaxy (MBE)\textsuperscript{11} on MgAl\textsubscript{2}O\textsubscript{4} (100) with thicknesses of 40, 115 (see Fig. 2), and 360 nm. The polar Kerr spectra of these layers are distorted by interference. From the dielectric tensor of Fe\textsubscript{3}O\textsubscript{4} we were able to calculate the theoretical polar Kerr spectra of these layers (dashed line in Fig. 2), thereby isolating the interference effects from true changes in the dielectric tensor. In the measured spectra (solid line) an energy shift and a reduced intensity for the IVCT transitions is observed. Based on the transition assignment for Fe\textsubscript{3}O\textsubscript{4} we could identify oxidation of part of the layer as the cause of these changes. Subsequent model calculations (leading to the dotted line in Fig. 2) enabled us to localize and quantify this oxidation to the upper 2–4 nm of the layer\textsuperscript{12,13}.

Since the Verwey transition is often taken as an indication for the stoichiometric quality of thin layers of Fe\textsubscript{3}O\textsubscript{4}. The polar Kerr spectra of these layers are found. Since the Verwey transition is often taken as an indication for the stoichiometric quality of thin layers of Fe\textsubscript{3}O\textsubscript{4}.14,15 We also determined the Verwey temperature, $T_\text{V}$, of the 40, 115, and 360 nm thick layers on MgAl\textsubscript{2}O\textsubscript{4}; see Fig. 3. $T_\text{V}$ was identified through changes in resistivity, $\rho$, with temperature, $T$. We take as a measure for $T_\text{V}$ the temperature at which the derivative of the $\rho/T$ vs $T^{-1}$ is maximum.\textsuperscript{16} For the 360 nm thick layer this leads to $T_\text{V} = 122 \pm 1$ K, equal to the bulk value. For the 115 nm layer $T_\text{V}$ is $109 \pm 1$ K. For the 40 nm thick layer a barely discernable $T_\text{V}$ at $107 \pm 1$ K is found. In addition to the shift to lower transition temperature for thinner films, also a broadening of the transition and changes in the high temperature $\rho$ are found.

Oxidation of the total layer might lead to the observed reduction in $T_\text{V}$.\textsuperscript{14} However, the Kerr measurements point to an oxidized surface layer. The changes observed are, therefore, better explained by the influence of the substrate on the conductance of the film. As the perpendicular lattice parameter at room temperature of the 115 nm thick Fe\textsubscript{3}O\textsubscript{4} layer is $8.398 \pm 0.004$ Å, which is within the experimental accuracy equal to the bulk lattice parameter, epitaxial strain is ruled out as the prime cause for the reduced $T_\text{V}$ in this case. However, the difference in thermal expansion coefficients between substrate and the Fe\textsubscript{3}O\textsubscript{4} film could give rise to the observed increased reduction of $T_\text{V}$ for thinner layers. Hence,

The data obtained for the transition assignment of Fe\textsubscript{3}O\textsubscript{4} and the assignment itself can be applied to the investigation of the stoichiometric quality of thin layers of Fe\textsubscript{3}O\textsubscript{4}. The increased intensity is in part due to the perturbation of the octahedral symmetry as a result of the small ion radius of Li\textsuperscript{+}. The latter is also responsible for the increase in transition energy. The same shift in transition energy is observed for Al\textsuperscript{3+} substitution of Fe\textsubscript{3}O\textsubscript{4}.\textsuperscript{7} Thus, also the MO-Kerr spectra of MgFe\textsubscript{2}O\textsubscript{4} and Li\textsubscript{0.5}Fe\textsubscript{2.5}O\textsubscript{4} can be interpreted in a consistent manner with the proposed transition assignment given for Fe\textsubscript{3}O\textsubscript{4}.
as strain due to differences in thermal expansion coefficient influences $T_V$. This parameter may not be suited to assess the stoichiometric quality of epitaxial thin Fe$_3$O$_4$ layers. In addition, it does not provide depth dependent information as the Kerr spectrum does.

Finally, we wish to point out the importance of spectral variations in MO-Kerr effect (MOKE) experiments to determine the magnetic anisotropy in ferrite layers grown on a certain substrate. As an example we give the Kerr ellipticity and rotation at a wavelength $\lambda = 514$ nm versus the Fe$_3$O$_4$ thickness, $t_{Fe_3O_4}$, for a wedge of Fe$_3$O$_4$ grown on MgO (100) covered with a 2 nm MgO/3 nm NiO capping layer. MgO was chosen as substrate as previous work has shown that growth on this substrate results in proper Fe$_3$O$_4$. Figure 4 shows that $\lambda = 633$ nm (HeNe laser) and $\lambda = 514$ nm (the green line of an Ar$^+$ laser) allow the polar MOKE detection of hysteresis loops down to 9 and 2.5 nm, respectively. We should remark that reliable hysteresis loops for anisotropy analysis are only obtained at somewhat larger thicknesses than those listed above, e.g., 12 nm for $\lambda = 633$ nm and 8.5 nm for 514 nm. The fact that 514 nm allows the detection at lower thickness is caused by several effects. We have found that intercalation shifts the MO-Kerr spectrum of thin Fe$_3$O$_4$ layers to the blue; a capping layer may enhance this effect. Furthermore, the Fe$_3$O$_4$ absorption is larger at shorter wavelengths. From Fig. 4 we conclude that for studies of wedged-shaped samples judicious selection of the wavelength is important.

III. CONCLUSIONS

We have found through systematic substitution with Mg$^{2+}$ and Al$^{3+}$ that the main transitions in the magneto-optical (MO)-Kerr spectrum of Fe$_3$O$_4$ can be assigned to intervalence charge transfer transitions at 0.56, 1.94, 3.11, and 3.93 eV and intersublattice charge transfer transitions at 2.61, 3.46, and 3.94 eV. Also the MO-Kerr spectra of MgFe$_2$O$_4$ and Li$_{0.5}$Fe$_{2.5}$O$_4$ can be assigned consistently. Two applications of this understanding of the MO-Kerr spectrum of Fe$_3$O$_4$ have been shown in the field of thin oxide films: first in a stoichiometry analysis of an Fe$_3$O$_4$ layer, second, in the wavelength selection in MO-Kerr effect studies of such layers.

7 W. F. J. Fontijn, P. J. van der Zaag, M. A. C. Devillers, V. A. M. Brabers, and R. Metselaar (to be published).
14 Interestingly, preliminary magnetization and resistivity data as a function of Fe$_3$O$_4$ layer thickness suggest a "dead" layer of a similar thickness of about 3 nm.
17 Note that in inhomogeneously strained systems the normal definition of $T_V$ loses meaning due to the broadening of the Verwey transition.