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

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An analysis of the complete dielectric tensor of bulk magnetite, Fe₃O₄, and of Fe₃O₄ substituted with a variable degree of Mg²⁺ or Al³⁺ allowed the assignment of the main magneto-optical (MO) transitions in Fe₃O₄ between 0.5 and 4.0 eV. This assignment is consistent with our reinterpretation of the MgFe₂O₄ and Li_{0.5}Fe_{2.5}O₄ MO-Kerr spectra. An analysis of the stoichiometry of a thin Fe₃O₄ 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 Fe³⁺ ions on the tetrahedral (A-) sites.¹ Others have assigned the major peaks in the MO-Kerr spectrum of Fe₃O₄ to 3dⁿ → 3dⁿ⁻¹4s orbital promotion processes.² The problem with these interpretations, however, is that they are based on forbidden transitions, whereas Fe₃O₄ 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 (Fe²⁺ + Fe³⁺ → Fe³⁺ + Fe²⁺).³ As the Fe²⁺-Fe³⁺ 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 Fe₃O₄ between 0.5 and 4.0 eV. Key to the unraveling of the complicated Fe₃O₄ MO-Kerr spectrum were: first, the fitting of all four relevant elements of the dielectric tensor ϵ'_{xx} , ϵ''_{xx} , ϵ'_{xy} and ϵ''_{xy} simultaneously with one set of transitions. Secondly, the systematic substitution with nonmagnetic ions, Mg²⁺ and Al³⁺, which allows the determination of trends in the Kerr spectra with a reduction in [Fe²⁺] and [Fe³⁺] content (round brackets denote ions on A-sites, square brackets ions on B-sites). Of these substitutions, the Mg²⁺ substitution is of special significance as it reduces the intense Fe²⁺-dependent IVCT transitions, allowing the detection of other, overlapping transitions such as the intersublattice charge transfer (ISCT) transitions (Fe³⁺ + Fe³⁺ → Fe²⁺ + Fe⁴⁺). Finally, the usefulness of this understanding of the MO spectra of Fe₃O₄ in the field of thin oxidic films will be discussed.

II. RESULTS AND DISCUSSION

To arrive at a consistent transition assignment for Fe₃O₄, we determined the complete dielectric tensor for synthetic crystals of Fe₃O₄, and Mg²⁺- and Al³⁺-substituted Fe₃O₄, 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: ϵ'_{xx} , ϵ''_{xx} , ϵ'_{xy} , and ϵ''_{xy} . As these spectra consist of many overlapping bands, partly of opposing sign,^{2,7} 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 Fe₃O₄ and of the Mg²⁺- or Al³⁺-substituted Fe₃O₄ 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 Mg²⁺ and Al³⁺ 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 $\epsilon_{xy,max}$ vs [Fe²⁺] and [Fe³⁺] content for the four major transitions which depend strongly on the Fe²⁺ content. The nonlinear dependence on [Fe²⁺] points to a pair interaction for all these transitions.⁸ Given their behavior on substitution of [Fe³⁺] with Al³⁺ the transitions at 0.56 and 1.94 eV involve also this ion, while the transitions at 3.11 and 3.93 eV involve (Fe³⁺). Consequently, four of the main transitions are assigned to intervalence charge transfer transitions (0.56 eV: [Fe²⁺]_{t_{2g}} → [Fe²⁺]_{t_{2g}}, 1.94 eV: [Fe²⁺]_{t_{2g}} → [Fe²⁺]_{e_g}, 3.11 eV: [Fe²⁺]_{t_{2g}} → (Fe²⁺)_e and 3.93 eV: [Fe²⁺]_{t_{2g}} → (Fe²⁺)_{t₂}). For the three major transitions remaining we propose a new assignment. These transitions are assigned to intersublattice charge transfer transitions (2.61 eV: (Fe³⁺)_{t₂} → [Fe²⁺]_{t_{2g}}, 3.46 eV: [Fe³⁺]_{e_g} → (Fe²⁺)_{t₂} and 3.94 eV: (Fe³⁺)_{t₂} → [Fe²⁺]_{e_g}), since the relative peak positions, the relative strengths and the linewidths of these transitions

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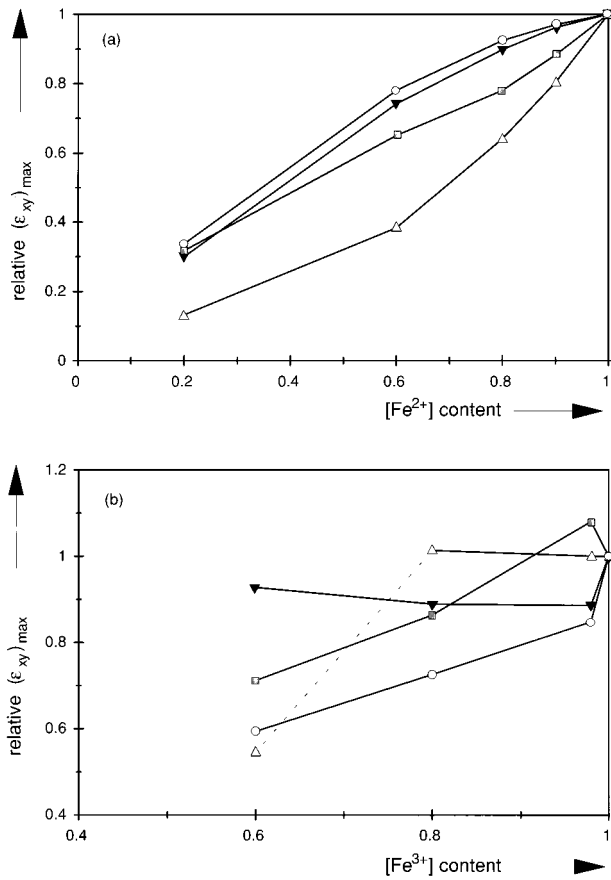


FIG. 1. Relative maximum ϵ'_{xy} value (a) vs $[\text{Fe}^{2+}]$ and (b) $[\text{Fe}^{3+}]$ content for the IVCT transition; (○) 0.56 eV, (□) 1.94 eV, (△) 3.11 eV, and (▼) 3.93 eV.

are consistent with the results reported for YIG.⁸ From this transition assignment for Fe_3O_4 the transition assignment for related ferrites such as MgFe_2O_4 and $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ can be derived. This assignment should be the same as that of Fe_3O_4 without the IVCT transitions as these involve Fe^{2+} , although one should allow for some shift in transition energy and differences in intensity. We used the dielectric tensor of MgFe_2O_4 from the literature⁹ and applied the same fit procedure. This yields three major MO transitions consistent with the ISCT transitions found in Fe_3O_4 and in YIG. Hence our assignment: 2.64 eV (Fe^{3+}) $t_2 \rightarrow [\text{Fe}^{2+}]t_{2g}$, 3.48 eV: $[\text{Fe}^{3+}]e_g \rightarrow (\text{Fe}^{2+})t_2$ and 3.97 eV: $(\text{Fe}^{3+})t_2 \rightarrow [\text{Fe}^{2+}]e_{2g}$. The same transitions are observed in $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$,^{2,10} however, at increased intensity and at higher energies compared to MgFe_2O_4 . The increased intensity is in part due to the increased amount of Fe^{3+} and in part due to the perturbation of the octahedral symmetry as a result of the small ion radius of Li^+ . The latter is also responsible for the increase in transition energy. The same shift in transition energy is observed for Al^{3+} substitution of Fe_3O_4 .⁷ Thus, also the MO-Kerr spectra of MgFe_2O_4 and $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ can be interpreted in a consistent manner with the proposed transition assignment given for Fe_3O_4 .

The data obtained for the transition assignment of Fe_3O_4 and the assignment itself can be applied to the investigation

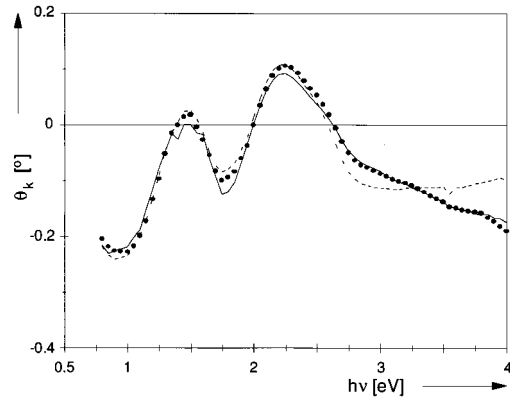


FIG. 2. The measured Kerr rotation spectrum of 115 nm Fe_3O_4 layer on MgAl_2O_4 (100) (—) vs the theoretical spectrum of a perfect layer (----) and the fitted spectrum (···).

of the stoichiometric quality of thin layers of Fe_3O_4 . The polar Kerr spectra between 0.7 and 4.0 eV were measured of thin layers of Fe_3O_4 deposited by oxidic molecular beam epitaxy (MBE)¹¹ on MgAl_2O_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_3O_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_3O_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.^{12,13}

Since the Verwey transition is often taken as an indication for the stoichiometric quality of Fe_3O_4 ,^{14,15} we also determined the Verwey temperature, T_V , of the 40, 115, and 360 nm thick layers on MgAl_2O_4 ; see Fig. 3. T_V was identified through changes in resistivity, ρ , with temperature, T . We take as a measure for T_V the temperature at which the derivative of the ρ/T vs T^{-1} is maximum.¹⁶ For the 360 nm thick layer this leads to $T_V = 122 \pm 1$ K, equal to the bulk value. For the 115 nm layer T_V is 109 ± 1 K. For the 40 nm thick layer a barely discernable T_V at 107 ± 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 ρ are found.

Oxidation of the *total* layer might lead to the observed reduction in T_V .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_3O_4 layer is 8.398 ± 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_V in this case. However, the difference in thermal expansion coefficients between substrate and the Fe_3O_4 film could give rise to the observed increased reduction of T_V for thinner layers. Hence,

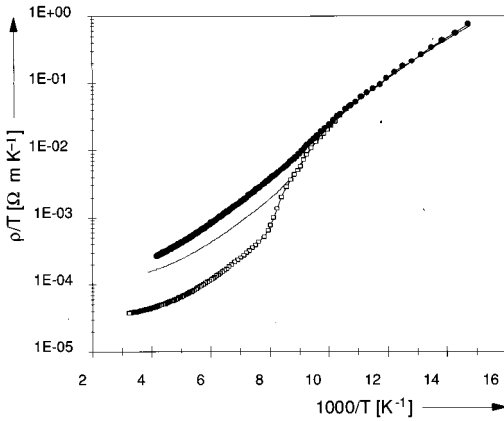


FIG. 3. Specific resistivity divided by temperature, ρ/T , of thin layers of Fe_3O_4 on MgAl_2O_4 as a function of inverse temperature, T^{-1} . (●) 40 nm, (○) 115 nm, and (□) 360 nm.

as strain due to differences in thermal expansion coefficient influences T_V ,¹⁷ this parameter may not be suited to assess the stoichiometric quality of epitaxial thin Fe_3O_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 $\lambda=514$ and 633 nm versus the Fe_3O_4 thickness, $t_{\text{Fe}_3\text{O}_4}$, for a wedge of Fe_3O_4 grown on MgO (100) covered with a 2 nm $\text{MgO}/3$ nm NiO capping layer. MgO was chosen as substrate as previous work has shown that growth on this substrate results in proper Fe_3O_4 .¹⁸ 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 interference shifts the MO-Kerr spectrum of thin Fe_3O_4 layers to the blue; a capping layer may enhance this effect. Furthermore, the Fe_3O_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_3O_4 can be assigned to

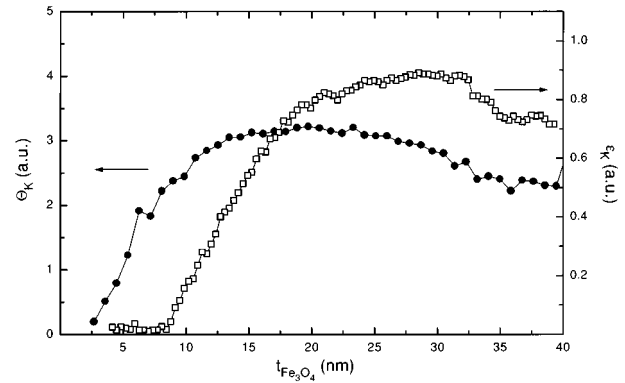


FIG. 4. Comparison of the Kerr effect vs Fe_3O_4 layer thickness, $t_{\text{Fe}_3\text{O}_4}$, for a wedge-shaped Fe_3O_4 sample at two wavelengths, λ . (□) ellipticity ϵ_K at 633 nm; (●) rotation Θ_K at 514 nm.

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_2O_4 and $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ can be assigned consistently. Two applications of this understanding of the MO-Kerr spectrum of Fe_3O_4 have been shown in the field of thin oxides: first in a stoichiometry analysis of an Fe_3O_4 layer, second, in the wavelength selection in MO-Kerr effect studies of such layers.

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