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Optical Properties of Mixed Cobalt Ferrites

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Abstract. The optical properties of Co and Mg ferrigallate spinels have been studied near the magnetic transition. The cluster (CoFeO)₃⁵⁺ is characterized by a strong intensification of iron pair excitations and by the existence in ferrimagnetic compounds of a large electronic transition assigned to Co²⁺ → Fe³⁺ metal-metal charge transfer at 1.70-1.75 eV.

The optical spectra of transition-group metal ions have been the subject of intense investigations attempted in order to obtain a fundamental understanding of the varied colors and luminescent properties exhibited by the internal transitions in different crystalline environments. Some much more intense absorptions are due to electron transfer: LMCT (ligand-metal charge transfer), IVCT (intervalence charge transfer) and MMCT (metal-metal charge transfer). The purpose of this paper is to present the influence of superexchange interactions on the optical spectrum of the cluster (CoFeO)₃⁵⁺ in the spinel structure. The compounds chosen to illustrate the influence of superexchange interactions on the Co²⁺ → Fe³⁺ metal-metal charge transfer belong to the CoFeₓGaₙ₋ₓO₄ system. In order to get a better insight of the local environment of cobalt and iron in these spinels, the EXAFS spectra were recorded at the Fe and Co K-edge and analyzed. The structural parameters do not reveal important fluctuations of M-O distances in the analyzed compounds (x = 0, 0.5, 1, 1.4, 2).

4-fold coordination 6-fold coordination
Fe-O (nm) 0.204 ± 0.002 0.199 ± 0.002
Co-O (nm) 0.192 ± 0.002 0.191 ± 0.002

Co²⁺ → Fe³⁺ transfer and superexchange interactions in mixed cobalt ferrites.

The substitution of the tetrahedral and octahedral Fe³⁺ ions by non-magnetic Ga³⁺ ions in Li₃Fe₂O₄ [1] and MgFe₂O₄ (Fig. 1) provides a possibility for experimentally distinguishing transitions from various sites. From these studies the following conclusions may be drawn:
- in Li₃Fe₂O₄ and MgFe₂O₄ ferrites the ligand field transitions unaffected by a double exciton process are strongly enhanced by the A-B interactions. The band at 19000 cm⁻¹ (2.35 eV) is a composite of the ⁴A₁ → ⁴T₁ (⁴G) ligand field transition of tetrahedral Fe³⁺ and ⁴A₁ + ⁴A₁ → ⁴T₁ + ⁴T₁ (⁴G) pair transition.
- the gallium substitution influences the nature of interactions : as the gallium content is increased, the intersublattice interaction weaken and the intrasublattice become stronger facilitating a canted spin alignment on the octahedral sites. This phenomenon induces a strong intensification of pair transitions : ⁴A₁ → ⁴E₁ ⁴A₁, 2 ⁴A₁ → ⁴T₁ + ⁴T₂ near 21500 cm⁻¹ (2.66 eV) and 2 ⁴A₁ → (⁴E₁, ⁴A₂) + ⁴T₁ near 28500 cm⁻¹ (3.53 eV)
- in paramagnetic compounds, the absorption coefficient k for the Fe³⁺ ion in tetrahedral coordination is ten times higher than that of octahedral Fe³⁺.

The influence of a strong antiferromagnetic coupling on the electronic spectrum (0.5-4 eV) of gallium-substituted cobalt ferrites containing Fe³⁺ and Co²⁺ cations octahedral coordinated has been studied. The analysis of the difference spectra CoFeₓGaₙ₋ₓO₄ - CoGaₙ₋ₓO₄ and CoFeₓGaₙ₋ₓO₄ - MgFeₓGaₙ₋ₓO₄ (fig. 2, x = 0) reveals for ferrimagnetic compounds (0 ≤ x ≤ 1) in the range 1.5-3 eV a strong enhancement of iron (III) pair transition and the existence of an intense electronic transition assigned to the Co²⁺ + Fe³⁺ → Co³⁺ + Fe²⁺ intervalence charge transfer at 1.70-1.75 eV (Table1).
Fig. 1. UV-Vis-NIR spectra of iron (II) in the MgFe$_2$Ga$_x$O$_4$ system near the magnetic transition:
(1) $x = 0$; (2) $x = 0.6$; (3) $x = 1$ and (4) $x = 1.5$

Fig. 2. Difference spectra (curve 3) between CoFe$_2$O$_4$ (1) and CoGa$_2$O$_4$ (2) and between CoFe$_2$O$_4$ and MgFe$_2$O$_4$ (curve 4)

Table 1. Analysis of the difference spectra. Energy in eV and assignment of the observed bands

| $x$ | Fe$^{3+}$ 6$A_1 \rightarrow 4T_1$ MMCT (Co$^{3+} \rightarrow$ Fe$^{3+}$) Fe$^{3+}$ 6$A_1 \rightarrow 4T_2$ Fe$^{3+}$ pair transition $\theta_\alpha$ (°C) of the CoFe$_{1-x}$Ga$_x$O$_4$ spinels |
|-----|---------------------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|
| 0   | 1.18                                                         | 1.74 (1)                                                      | 2.48 (1)                                                        | 520                                                             |
| 0.5 | ~1.24                                                        | 1.74 (0.98)                                                   | 2.45-2.60 (0.94)                                                | 357                                                             |
| 1   | ~1.24                                                        | 1.74 (0.75)                                                   | 2.42-2.60 (0.98)                                                | 194                                                             |
| 1.5 | 1.21                                                         | 1.70 (0.26)                                                   | 2.48 (0.58)                                                     | 0                                                               |

| $x$ | Co$^{2+}$ d-d MMCT Co$^{2+}$ d-d Fe$^{3+}$ 6$A_1 \rightarrow 4T_2$ Co$^{2+}$ 4$A_2 \rightarrow 4T_1$($^3P$) main components ($\Gamma_8$) |
|-----|---------------------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|
| 0   | 0.74-0.91                                                    | 1.70                                                          | 2.03 (0.81)                                                     |                                                                 |
| 0.5 | 0.74-0.91                                                    | 1.82 (0.93)                                                   | 2.03 (0.81)                                                     |                                                                 |
| 1   | 0.74-0.91                                                    | 1.86 (0.93)                                                   | 2.03 (0.89)                                                     |                                                                 |
| 1.5 | 0.74-0.91                                                    | 1.91 (0.80)                                                   | 2.06 (0.80)                                                     |                                                                 |

CoGa$_2$O$_4$ 0.74-0.91 1.91 (0.96) 2.07 (0.98) 1.74 (1) ; 2.48 (1) : (1) absorbance (arbitrary unit)

These data may be correlated with the magneto-optical properties of cobalt ferrites. The polar Kerr observed in CoFe$_2$O$_4$ around 2 eV is mainly due to the MMCT transition. In substituted CoFe$_{2-x}$M$_x$O$_4$, the shift of the negative peak near 2 eV on the polar Kerr rotation spectra to the high energies is assigned to a major contribution of the $^4A_2 \rightarrow ^4T_1$ ($^3P$) Co$^{2+}$ tetrahedral transition ($M = Al$, Cr):

- CoFe$_2$O$_4$: 1.80 [2]
- CoFe$_{1.8}$Al$_{0.2}$O$_4$: 1.90-2.15 [3]
- CoFeCr$_2$O$_4$: 1.97 [2]
- CoFe$_{1.1}$Mn$_{0.9}$O$_4$: 1.95-2.30 [3]
- CoFe$_{1.1}$Mn$_{0.9}$O$_4$: 1.93 [2]

The reinvestigation of the optical properties of MgFe$_2$O$_4$ leads to the conclusion that the magneto-optical properties of this ferrite in the 2-5 eV range may be correlated with Fe$^{3+}$ tetrahedral and pair-transitions up to 4 eV and LMCT transitions above 4 eV.

References