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M. Lenglet, F. Hochu, J. Dürr. Optical Properties of Mixed Cobalt Ferrites. Journal de Physique IV Proceedings, 1997, 07 (C1), pp.C1-259-C1-260. 10.1051/jp4:19971100 . jpa-00254721

HAL Id: jpa-00254721

<https://hal.science/jpa-00254721>

Submitted on 4 Feb 2008

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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 $(\text{CoFeO}_{10})^{15-}$ is characterized by a strong intensification of iron pair excitations and by the existence in ferrimagnetic compounds of a large electronic transition assigned to $\text{Co}^{2+} \rightarrow \text{Fe}^{3+}$ 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 $(\text{CoFeO}_{10})^{15-}$ in the spinel structure. The compounds chosen to illustrate the influence of superexchange interactions on the $\text{Co}^{2+} \rightarrow \text{Fe}^{3+}$ metal-metal charge transfer belong to the $\text{CoFe}_{2-x}\text{Ga}_x\text{O}_4$ 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

$\text{Co}^{2+} \rightarrow \text{Fe}^{3+}$ transfer and superexchange interactions in mixed cobalt ferrites.

The substitution of the tetrahedral and octahedral Fe^{3+} ions by non-magnetic Ga^{3+} ions in $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ [1] and MgFe_2O_4 (Fig. 1) provides a possibility for experimentally distinguishing transitions from various sites. From these studies the following conclusions may be drawn :

- in $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ and MgFe_2O_4 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 ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2$ (${}^4\text{G}$) ligand field transition of tetrahedral Fe^{3+} and ${}^6\text{A}_1 + {}^6\text{A}_1 \rightarrow {}^4\text{T}_1 + {}^4\text{T}_1$ (${}^4\text{G}$) 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 : ${}^6\text{A}_1 \rightarrow {}^4\text{E}_1$ ${}^4\text{A}_1$, $2 {}^6\text{A}_1 \rightarrow {}^4\text{T}_1 + {}^4\text{T}_2$ near 21500 cm^{-1} (2.66 eV) and $2 {}^6\text{A}_1 \rightarrow ({}^4\text{E}_1, {}^4\text{A}_1) + {}^4\text{T}_1$ near 28500 cm^{-1} (3.53 eV)
- in paramagnetic compounds, the absorption coefficient k for the Fe^{3+} ion in tetrahedral coordination is ten times higher than that of octahedral Fe^{3+} .

The influence of a strong antiferromagnetic coupling on the electronic spectrum (0.5-4 eV) of gallium-substituted cobalt ferrites containing Fe^{3+} and Co^{2+} cations octahedral coordinated has been studied. The analysis of the difference spectra $\text{CoFe}_{2-x}\text{Ga}_x\text{O}_4 - \text{CoGa}_2\text{O}_4$ and $\text{CoFe}_{2-x}\text{Ga}_x\text{O}_4 - \text{MgFe}_{2-x}\text{Ga}_x\text{O}_4$ (fig. 2, $x = 0$) reveals for ferrimagnetic compounds ($0 \leq x \leq 1$) 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 $\text{Co}^{2+} + \text{Fe}^{3+} \rightarrow \text{Co}^{3+} + \text{Fe}^{2+}$ intervalence charge transfer at 1.70-1.75 eV (Table1).

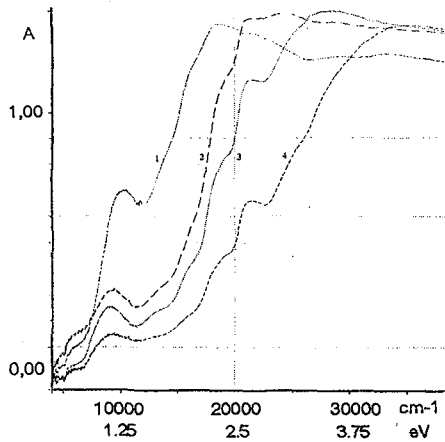


Fig. 1. UV-Vis-NIR spectra of iron (III) in the $\text{MgFe}_{2-x}\text{Ga}_x\text{O}_4$ system near the magnetic transition : (1) $x = 0$; (2) $x = 0.6$; (3) $x = 1$ and (4) $x = 1.5$

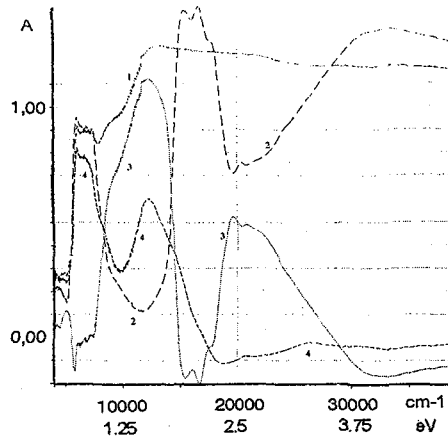


Fig. 2. Difference spectra (curve 3) between CoFe_2O_4 (1) and CoGa_2O_4 (2) and between CoFe_2O_4 and MgFe_2O_4 (curve 4)

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

CoFe _{2-x} Ga _x O ₄ - CoGa ₂ O ₄					
x	Fe ³⁺ ⁶ A ₁ → ⁴ T ₁	MMCT (Co ²⁺ → Fe ³⁺)	Fe ³⁺ ⁶ A ₁ → ⁴ T ₂ and ⁶ A ₁ → ⁴ E ₁ , ⁴ A ₁	Fe ³⁺ pair transition	θ _c (°C) of the CoFe _{2-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)	2.79	0
CoFe _{2-x} Ga _x O ₄ - MgFe _{2-x} Ga _x O ₄					
x	Co ²⁺ d-d	MMCT	Co ²⁺ d-d	Fe ³⁺ ⁶ A ₁ → ⁴ T ₂	Fe ³⁺ pair transition
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)	2.38	2.72
1.5	0.74-0.91	1.91 (0.80)	2.06 (0.80)	2.40	2.85
Co ²⁺ ⁴ A ₂ → ⁴ T ₁ (⁴ P) main components (Γ ₈)					
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_2O_4 around 2 eV is mainly due to the MMCT transition. in substituted $\text{CoFe}_{2-x}\text{M}_x\text{O}_4$, 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 $\ ^4\text{A}_2 \rightarrow \ ^4\text{T}_1(^4\text{P})$ Co^{2+} tetrahedral transition ($\text{M} = \text{Al}, \text{Cr}$) :

	CoFe_2O_4	$\text{CoFe}_{1.2}\text{Al}_{0.8}\text{O}_4$	CoFeCrO_4	$\text{CoFe}_{1.1}\text{Mn}_{0.9}\text{O}_4$
Energy (eV)	1.80 [2]	1.90-2.15 [3]	1.97 [2]	1.95-2.30 [3]
			1.93 [2]	1.70 [2]

The reinvestigation of the optical properties of MgFe_2O_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

[1] Hochu F., Lenglet M., Jørgensen C.K., *J. Solid State Chem.* **120** (1995) 244-253.
[2] Abe M., Gomi M., *J. Appl. Phys.* **53** (1982) 8172-8174.
[3] Peters W.L., Martens J.W.D., *J. Appl. Phys.* **53** (1982) 8178-8180.