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Chemical tuning of the optical band gap in spinel ferrites: CoFe_2O_4 vs NiFe_2O_4

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We measured the optical properties of epitaxial CoFe_2O_4 thin films and compared our findings with complementary electronic structure calculations and similar studies on the Ni analog. Our work reveals CoFe_2O_4 to be an indirect band gap material (1.2 eV, $X \rightarrow \Gamma$ in the spin-down channel) with a direct gap at 2.7 eV. The latter is robust up to 800 K. Compared to NiFe_2O_4 , the indirect gap is ≈ 0.5 eV lower, a difference we discuss in terms of size and covalency effects in spinel ferrites. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818315>]

Multifunctional, high Curie temperature (T_C) magnetic insulators are attracting attention due to their suitability for application. They naturally provide a non-zero magnetic moment along with spin-dependent band gaps that can be utilized in spintronics¹ as well as in spin-caloritronics.² Examples include spin-filters^{3,4} and spin-transfer torque devices.¹ Among the various candidate materials, the most noteworthy are strongly correlated spinel oxides (general formula AB_2O_4),⁵ particularly the spinel ferrites (general formula AFe_2O_4). While high quality single crystals are challenging to grow, thin film spinel ferrites have allowed researchers to investigate structural,⁶ electronic,^{7–10} and transport^{11–15} properties. Recent spectroscopic work on nickel ferrite (NiFe_2O_4) also revealed a hierarchy of band gaps,^{16,17} and a favorable overlap with the solar spectrum. CoFe_2O_4 is another high T_C material that presents an opportunity to quantify charge gaps and electronic structure trends within the spinel ferrite family. Prior theoretical work focused primarily on magneto-elastic properties and cation-ordering^{7–9,18} due to challenges both in accounting for electron correlation effects and the absence of reliable experimental gap values.

In this work, we bring together high quality film growth, optical properties work, and first principles calculations to investigate the electronic structure of CoFe_2O_4 . This system displays an indirect gap at 1.2 eV and a direct gap at 2.7 eV. In addition to resolving the long-standing band gap controversy in CoFe_2O_4 (with values between 0.11 and 2.6 eV quoted in the literature)^{19–21} and showing the robustness of the 2.7 eV gap on approach to T_C , we reveal how the charge gaps, electronic structure, and band dispersions change with chemical substitution. For instance, we find that the minority channel $X \rightarrow \Gamma$ indirect gap is almost 0.5 eV lower than that in the Ni analogue. The improved overlap with the solar spectrum, which offers electronic and light harvesting functions, combined with the modest temperature dependence of the 2.7 eV features, establishes CoFe_2O_4 as a robust magnetic semiconductor and a promising material for applications.

High quality epitaxial CoFe_2O_4 films were grown between 350 and 690 °C on (001)-orientated MgAl_2O_4 substrates using pulsed laser deposition.²² Optical measurements

were carried out using a Perkin-Elmer λ -900 spectrometer (0.41–6.53 eV) in both transmittance and reflectance mode, and the absorption ($\alpha(E)$) was determined via combined Glover-Tinkham and Kramers-Kronig techniques.^{23,24} The band gaps were extracted using methods established for traditional semiconductors as discussed in the text.²⁵ An open-flow cryostat was employed during variable temperature work. Electronic band structure calculations were performed with the Vienna *ab initio* simulation package (VASP)^{26,27} on a relaxed 14-atom primitive CoFe_2O_4 cell using LDA+ U and GGA+ U techniques ($U_{\text{eff}} = U - J = 4.5$ eV for Fe and 4.0 eV for Co)²⁸ and projector augmented-wave pseudopotentials.^{26,27,29} Additional 28-atom supercell calculations were performed to understand the effect of partial inversion on the electronic properties. We employed a plane wave cutoff of 500 eV and a Γ -centered $7 \times 7 \times 7$ \mathbf{k} mesh for the 14-atom density of states (DOS) and relaxation calculations.

Figure 1 displays the 300 K absorption spectrum of the CoFe_2O_4 film grown at 690 °C (red) along with similar data on the Ni-analog (blue, from Ref. 16) for comparison. While there are many similarities in the response, there are important differences as well. One such difference is the absorption onset. $\alpha(E)$ for CoFe_2O_4 begins to rise much sooner than that of NiFe_2O_4 , a response that can be anticipated by examining the relative appearance of the two films (insets of Fig. 1). CoFe_2O_4 is overall darker when photographed in both transmittance and reflectance. For traditional semiconductors like silicon,²⁵ it is well established that plots of $(\alpha E)^2$ and $(\alpha E)^{0.5}$ vs energy reveal direct and indirect band gaps as

$$\alpha(E) = \frac{A}{E} (E - E_{g,\text{dir}})^{0.5} + \frac{B}{E} (E - E_{g,\text{ind}} + E_{ph})^2.$$

Despite their more complicated band structures, this approach is commonly extended to allow analysis of oxides.^{30,31} In CoFe_2O_4 , linear fits were obtained for both cases.

As shown in Fig. 1(b), a plot of $(\alpha E)^{0.5}$ vs. energy reveals an indirect band gap in CoFe_2O_4 at 1.17 ± 0.08 eV. This gap value is significantly smaller than that of NiFe_2O_4 (1.64 eV),¹⁶ as anticipated from the absorption spectrum and examination of the films themselves. We extract a coupling

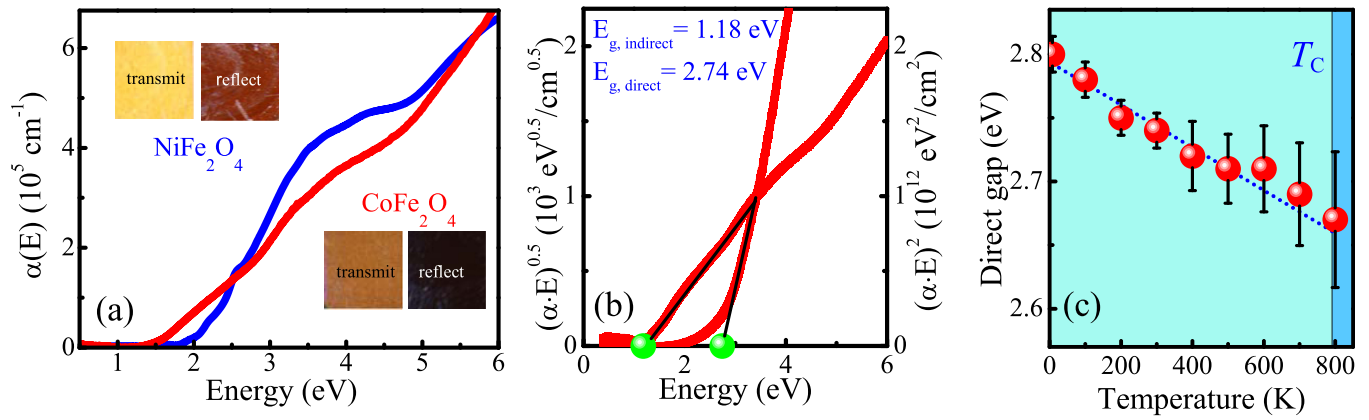


FIG. 1. 300 K absorption spectrum of CoFe_2O_4 and NiFe_2O_4 grown at 690°C . Insets: photos comparing transmittance and reflectance of CoFe_2O_4 and NiFe_2O_4 in a microscope with standard lamp. (b) Optical band gap analysis for the CoFe_2O_4 film. (c) Dependence of the direct band gap on measurement temperature upon approach to T_C at 795 K.

phonon energy²⁵ of 50–75 meV that corresponds to a O-Fe-O bending mode, similar to NiFe_2O_4 .¹⁶ The direct gap analysis (Fig. 1(b)) makes use of an $(\alpha E)^2$ vs. energy plot. It reveals a direct charge gap at 2.74 ± 0.10 eV. Comparing the indirect and direct gap values clearly reveals that CoFe_2O_4 displays a fundamental indirect energy gap, similar to the situation in NiFe_2O_4 . Prior optical work^{20,21} did not uncover the indirect gap excitation, so our findings are in sharp contrast with the reports that CoFe_2O_4 is a direct gap material. Notable also is the large difference between the indirect and direct gap in CoFe_2O_4 (see Table I).

We can assign the excitations in Fig. 1(a) using the results from our first principles electronic structure calculations (Fig. 2). The strongly hybridized Co + O valence edge permits both $Op \rightarrow$ transition metal d charge transfer and intersite metal $d \rightarrow$ metal d charge-transfer-like transitions. Interestingly, the localized Co states near the valence band edge can make intersite $d \rightarrow d$ excitations comparable in strength to those of $p \rightarrow d$ origin. Clearly, transitions in the minority channel (Co + O \rightarrow $\text{Fe}(O_h)$) define the absorption edge and the fundamental indirect gap, similar to the situation in NiFe_2O_4 . The strong band above 3 eV is due to a combination of majority and minority channel excitations. In the majority channel, Co $d \rightarrow \text{Fe}(T_d)$ d and O $p \rightarrow \text{Fe}(T_d)$ d dominate, whereas in the minority channel, $Op \rightarrow \text{Fe}(O_h) + \text{Co } d$ and Co $d \rightarrow \text{Fe}(O_h) + \text{Co } d$ excitations are allowed in addition to the fundamental transitions. This band edge determines the character of the direct gap. The latter can be in either spin channel. The most likely candidates are listed in Table I.

Interestingly, the optical absorption spectra of films grown at 520 and 365°C are virtually identical to that of films grown at 690°C (Fig. 1). This is different from what is found in NiFe_2O_4 thin films.¹⁶ While surprising on first inspection, this finding can be understood by recalling the dissimilar evolution of the unit cell structure with growth temperature in the two materials.²² X-ray diffraction measurements show that NiFe_2O_4 films become progressively strained due to an increase in the out-of-plane lattice parameter at lower growth temperatures. By contrast, CoFe_2O_4 films grow almost strain-free between 300 and 700°C .²² We conclude that the optical properties of spinel ferrites are more sensitive to unit cell parameter changes than film epitaxy. The insensitivity of the band gap to growth temperature supports this supposition.

We also carried out variable temperature optical measurements between 4 and 800 K. The latter is very close to T_C . The temperature dependence of the direct gap in CoFe_2O_4 is shown in Fig. 1(c). It displays a systematic quasi-linear decrease from 2.80 eV at 4.2 K to 2.67 eV at 800 K. Overall, the direct gap softens by only 0.13 eV over the temperature range investigated and remains robust on approach to $T_C = 795$ K. This insensitivity to temperature and robustness on approach to T_C implies relatively weak charge-spin coupling in CoFe_2O_4 compared to other multifunctional oxides like BiFeO_3 .^{33–35} The modest temperature dependence can probably be understood in terms of thermal broadening effects, which creates virtual states between the valence band maximum and conduction band minimum,

TABLE I. Experimental and theoretical optical band gap values of CoFe_2O_4 (in eV).

	Experimental gaps	Band gap	LSDA+U	GGA+U
Indirect	1.2 (from $(\alpha E)^{0.5}$ vs E plot)	$E_{g\min}(X \rightarrow \Gamma)$	0.9	1.5
Direct	2.7 (from $(\alpha E)^2$ vs E plot)	$E_{g\min}(X \rightarrow X)$	1.0	1.6
		$E_{g\min}(\Gamma \rightarrow \Gamma)$	1.4	2.0
		$E_{g\min}(W \rightarrow W)$	1.9	2.3
		$E_{g\max}(\Gamma \rightarrow \Gamma)$	1.9	2.1

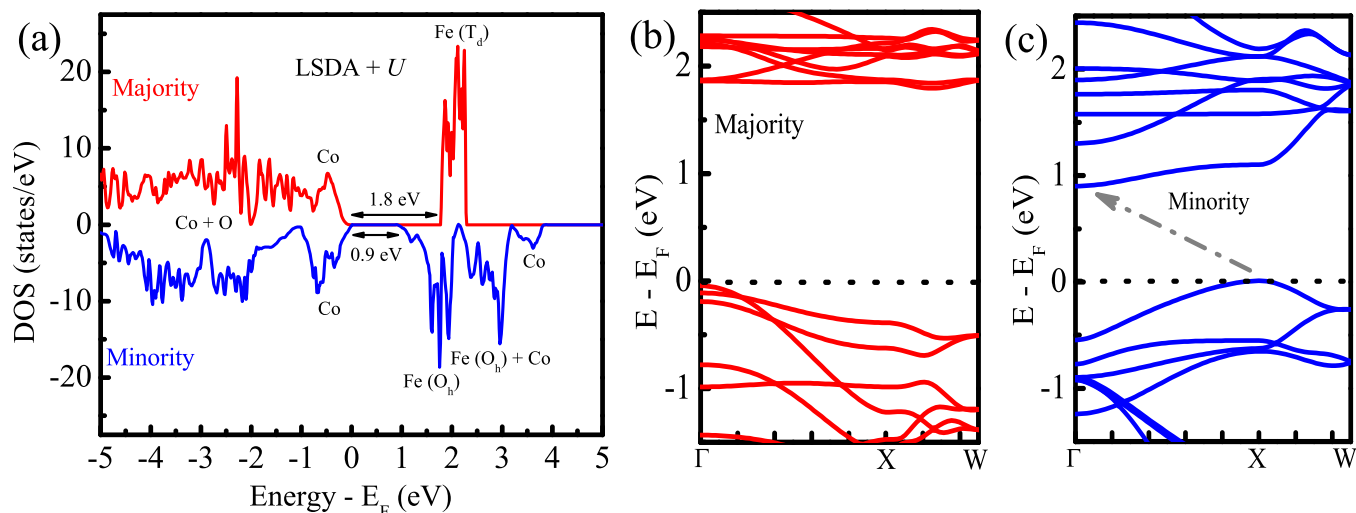


FIG. 2. (a) Density of states of CoFe_2O_4 calculated using the LSDA+ U method. Energy bands along Γ -X-W for (b) minority and (c) majority channels. The minority channel exhibits an indirect gap between X and Γ . In both channels, the lowest conduction band is nearly flat over a wide region, a character that probably leads to many nearly-degenerate transitions.

reducing the average gap value. That the semiconducting character of this spinel ferrite remains robust up to very high temperature certainly broadens the utility of this material.

Figure 2(a) displays the density of states as obtained with LSDA+ U . Comparison with GGA+ U is reported in Table I. Due to the agreement between these methods (mainly a rigid shift that changes the gap values), we shall only discuss LSDA+ U results here. Our calculations correctly capture the semiconducting nature of CoFe_2O_4 . The majority and minority channels are spin-split both in the valence and conduction bands, and the gap is found to be much larger in the majority channel (1.8 eV) than in the minority channel (0.9 eV). We also verified that the octahedral sites strongly prefer antiferromagnetic alignment with the tetrahedral sites, consistent with the super-exchange picture and irrespective of the inversion factor. In the fully inverted structure, the Fe^{3+} moments are completely compensated, and the net moment arises only from Co^{2+} ($3\mu_B/\text{f.u.}$), consistent with previous reports.⁹ Both Co^{2+} and Fe^{3+} are in the high-spin configuration. The density of states is qualitatively similar to that of the Ni-analogue¹⁶ except for the difference in band gap values (Fig. 2(a)). Like NiFe_2O_4 , we see narrow conduction band states belonging to minority octahedral Fe and Co d states and majority tetrahedral Fe d states. The valence band can be separated into strongly localized Fe states 7-8 eV below the Fermi level (not shown in figure) and a broad hybridized band of Co and O states near E_F . The most perceptible difference between CoFe_2O_4 and NiFe_2O_4 is stronger presence of localized Co states at the valence band edge, whereas in NiFe_2O_4 , the Ni states are more hybridized. The projected density of states is provided in Fig. S1.³⁶

To analyze the nature of the gap, we plot the LSDA+ U bands along the lines Γ -X-W for the minority and majority channels (Figs. 2(b) and 2(c)). The majority channel conduction band is practically dispersionless, whereas the valence band maximum is clearly at the Γ point. This difference yields a direct gap at 1.9 eV. There are additional indirect gaps very close to this energy, notably from Γ to between X

and W point (1.8 eV). We find more dispersive valence bands in the minority channel of CoFe_2O_4 compared to NiFe_2O_4 , with a clear indirect gap candidate between X ($k = \frac{2\pi}{a}[100]$) and Γ , the difference in energy being 0.9 eV. This result agrees quite well with recent literature reports.¹⁵ There are also direct gaps very close to this indirect gap. Notable ones are at X (1.0 eV), Γ (1.4 eV), and W (1.9 eV) (Table I). Overall there is reasonable agreement with the experimental result that the fundamental gap is indirect, which theory assigns to the minority channel.³⁷

Motivated by experimental reports of 70%-80% partial inversion in CoFe_2O_4 powder samples and nanoparticles,^{32,38,39} we performed additional relaxation and density-of-states calculations on a 75% inverted structure by swapping an octahedral Co with a tetrahedral Fe site while preserving the antiferromagnetic tetrahedral-octahedral spin alignment. Our main findings are as follows. First, energetically we find that this partially inverted configuration has higher energy compared to the fully inverted case (~ 70 meV/f.u.) implying that these are metastable states. Second, the magnetic moment is higher ($4.0\mu_B/\text{f.u.}$) as the extra moment from the uncompensated Fe lattice outweighs the loss in moment at the Co site. Enhanced magnetization values, sometimes observed in thin films,^{10,22} can thus be rationalized by invoking the presence of these metastable, partially inverted configurations. Electronically, we find that partial inversion introduces tetrahedral Co states at the majority channel valence band-edge which reduces the gap to 1.3 eV. The minority valence band-edge, however, remains largely unchanged, i.e., octahedral Co states occupy the band-edge, just like the fully inverted configuration, and the tetrahedral Co states are deeper. The conduction band-edge character in both channels is also similar to the fully inverted case, i.e., tetrahedral and octahedral Fe states define the majority and minority band-edges, respectively. As a result, the minority channel gap is largely unaffected and widens slightly to 1.0 eV. Taken together, our calculations show that partial inversion has a limited effect

on the fundamental minority channel gap and mainly changes the band-edge character of the majority channel via appearance of tetrahedral Co states. The band edges in the two different configurations are shown in Fig. S2.³⁶

The difference in the optical and electronic properties between CoFe_2O_4 and NiFe_2O_4 is quite analogous to the trend observed between CoO and NiO . It is well known that NiO has a larger band gap than CoO (4.0 vs 2.4 eV),⁴⁰ increased hybridization,⁴¹ and a higher magnetic ordering temperature (530 vs 291 K). A similar mechanism is likely at work in the spinel ferrites since the occupied Fe states are deeper and well localized in both systems and do not affect the interaction between $\text{Ni}(\text{Co})$ and oxygen. The smaller NiFe_2O_4 unit cell compared to that of CoFe_2O_4 (8.34 vs 8.39 Å) results in a shorter Ni-O bond length which promotes covalency and, in turn, greater hybridization and super-exchange interaction, which manifest in a higher Curie temperature. The band gap trend can probably be traced to the fact that the Ni^{2+} ($3d^8$) ion is smaller than the Co^{2+} ion ($3d^7$)⁴² which creates deeper Ni^{2+} states due to stronger electrostatic interaction. Therefore the energy gap between occupied and unoccupied levels widens going from CoFe_2O_4 to NiFe_2O_4 , other factors being equal.

Finally, our work reveals that the band gap hierarchy of CoFe_2O_4 is quite similar to that of Si—the most investigated indirect band gap material.⁴³ It also has a strong overlap with the solar spectrum. CoFe_2O_4 and other spinel oxides have much lower band gaps than many other complex oxides, such as room temperature ferroelectric perovskites (BaTiO_3 or PbTiO_3 for example) where the charge gaps are typically over 3 eV.⁴⁴ Extension to other members of the spinel ferrite family will be a subject of further investigation.

To summarize, we measured the optical response of epitaxial CoFe_2O_4 thin films and compared our findings with complementary first-principles calculations. This spinel oxide is a minority channel indirect band gap material. We extract a 1.2 eV indirect gap and a higher energy direct gap at 2.7 eV. The latter is robust on approach to the 795 K Curie temperature, a consequence of weak charge-spin coupling. A comparison with similar work on the Ni analog reveals that the band gaps are significantly lower in CoFe_2O_4 , a trend that we attribute primarily to ionic size effects. This opens up the possibility of band gap tuning via chemical substitution and strain in the spinel ferrites, along with wider applications that many high T_C oxides enjoy.

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³⁵By contrast, CoFe_2O_4 displays strong spin-lattice interactions.³²

³⁶See supplementary material at <http://dx.doi.org/10.1063/1.4818315> for additional electronic structure data.

³⁷The LSDA+*U* and GGA+*U* methods underestimate the higher gaps considerably compared to our experimental data. Underestimation of gap values is a well-known shortcoming of the method which can be improved, in principle, by using computationally expensive techniques (such as hybrid functionals and/or the many-body GW method). An alternate possibility is the presence of optically forbidden transitions between valence and conduction bands.

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