

Interplay between oxygen vacancies and cation ordering in NiFe_2O_4

R. Arras, K. Sharma, and L. Calmels

*CEMES, Université de Toulouse, CNRS, 29 rue Jeanne Marvig, F-31055, Toulouse,
France*

(*Electronic mail: remi.arras@cemes.fr)

(Dated: 20 November 2023)

I. FORMATION ENERGIES OF NEUTRAL OXYGEN VACANCIES

We calculated the formation energy neutral of oxygen vacancies according to the following formula¹:

$$E_f [V_O^0] = E [\text{Host} + V_O^0] - E [\text{Host}] + \mu_O \quad (1)$$

where $E [\text{Host} + V_O^0]$ and $E [\text{Host}]$ are the total energies calculated by DFT methods, respectively for the defective and non-defective cubic cells. μ_O is the chemical potential of the oxygen atom removed to form the vacancy. For each of the studied compounds, μ_O deviates by $\Delta\mu_O$ from the energy $E_O^{\text{elem}} = \frac{1}{2}E_{O_2}$ calculated when oxygen is in its pure gas form: $\mu_O = E_O^{\text{elem}} + \Delta\mu_O$. It is possible to express the chemical potential of oxygen atoms as a function of experimental growth conditions^{2,3}:

$$\Delta\mu_O(T, P) = \frac{1}{2} \{ [H_0 + \Delta H(T)] - T [S_0 + \Delta S(T)] \} + \frac{1}{2} k_B T \ln\left(\frac{P}{P_0}\right) \quad (2)$$

where $\Delta H(T) = C_p(T - T_0)$, $\Delta S(T) = C_p \ln(T/T_0)$. $H_0 = 8.7 \text{ kJ mol}^{-1}$, $S_0 = 205 \text{ J mol}^{-1} \text{ K}^{-1}$ are tabulated values^{2,4} and $P_0 = 1 \text{ atm}$ and $T_0 = 298 \text{ K}$ are standard pressure and temperature.

Because we only considered the formation of neutral oxygen vacancies, no additional terms in Eq. 1 are required.

As shown in Fig. 1, the spreading of the formation-energy values calculated for all the non-equivalent oxygen sites with a given chemical environment (n_{Td}, n_{Oh}) is lower than the difference between the averaged formation energies of the different configurations, in particular if $\Delta n_{Td} = 1$. Table I shows moreover that the averaged formation energies of oxygen vacancies calculated for a given chemical environment does not strongly depend on the details of the supercell (inversion degrees or cation swaps S giving rise to this environment). This observation is certainly true as long as we keep the inversion degree λ close to 1, *i.e.* for cation distributions close to the perfectly inverse spinel structure. For too low values of λ , NFO could become metallic, which could totally change the physical properties of the system and the chemical potential μ_O chosen for our calculations could be not adapted anymore.

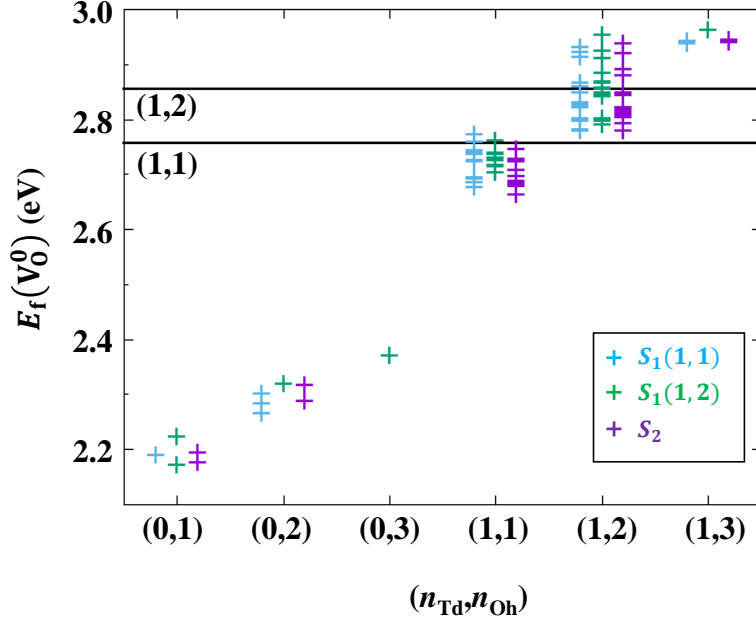


FIG. 1. Formation energies of neutral oxygen vacancies $E_f(V_O^0)$ calculated for all the 32 non-equivalent oxygen atoms in the three kinds of cation swaps giving rise to the partially-inverse spinel structures with $\lambda = 0.875$. The black lines correspond to the calculated formation energies calculated with the perfectly inverse spinel structure ($\lambda = 1$).

TABLE I. Total spin magnetic moment M_S per f.u. of NFO and formation energy E_f of a neutral oxygen vacancy as a function of the inversion degree λ and of the oxygen site described by $[n_{Td}(\text{Fe}), n_{Oh}(\text{Fe})]$ (the multiplicity n_i of these sites in the cubic supercell is also given for information).

λ		M_S (μ_B)	$[n_{Td}(\text{Fe}), n_{Oh}(\text{Fe})]$	n_i	$E_f(V_O^0)$ (eV)
0		7.69	(0,3)	32	0.019
0.875	$S_1(1,1)$	2.5	(0,1)	1	2.190
			(0,2)	3	2.284
		2.75	(1,1)	11	2.722
			(1,2)	15	2.844
			(1,3)	2	2.939
		average			
0.875	$S_1(1,2)$	2.5	(0,1)	2	2.197
			(0,2)	1	2.318
		2.75	(0,3)	1	2.370
			(1,1)	10	2.726
			(1,2)	17	2.859
			(1,3)	1	2.962
average				2.747	
0.875	S_2	2.5	(0,1)	2	2.186
			(0,2)	2	2.302
		2.75	(1,1)	10	2.706
			(1,2)	16	2.837
			(1,3)	2	2.943
			average		
$\lambda = 1$		2.0	(1,1)	16	2.756
			(1,2)	16	2.855
		average			

II. BINDING ENERGY OF THE OXYGEN VACANCY/CATION SWAP COMPLEXES

The binding energy of a defect complex is given by the equation¹:

$$E_b = E(\text{complex}) - \sum_i E[\text{Defect}(i)] \quad (3)$$

which corresponds for our system to:

$$E_b = \min\{E_f(\lambda = 7/8, \zeta = 1/8)\} - \min\{\Delta E(\lambda = 7/8, \zeta = 0)\} - \min\{E_f(\lambda = 1, \zeta = 1/8)\} \quad (4)$$

III. DEPENDENCY OF THE RESULTS ON THE VALUES OF U_{eff}

We checked whether the preference of the oxygen vacancies for Ni-rich environment that we calculated may come from the values of the U_{eff} parameters, chosen to get a band gap close from the experimental one.⁵ The value of U_{eff} applied on Ni-3d bands is lower than the one used for Fe atoms, which makes the Ni-rich environment around the vacancy more favorable. Increasing $U_{\text{eff}}(\text{Ni})$ to 5 eV (keeping $U_{\text{eff}}(\text{Fe}) = 4.0$ eV) indeed cancels the increase of the V_{O}^0 formation energy when the number of first-neighbor Oh sites occupied by Fe atoms [$n_{\text{Oh}}(\text{Fe})$] also increases, *i.e.* for this value of $U_{\text{eff}}(\text{Ni})$, the presence of oxygen vacancies will not depend on the Ni/Fe distributions in the Oh sites. However, for this higher value of $U_{\text{eff}}(\text{Ni})$, the formation of V_{O}^0 remains easier near a Ni_{Td} atom, even if the bonding energy increases from -0.566 eV ($U_{\text{eff}}(\text{Ni}) = 2.5$ eV) to -0.367 eV ($U_{\text{eff}}(\text{Ni}) = 5.0$ eV). Due to the large value of this bonding energy, we can state that our main conclusion should remain true for a large range of $U_{\text{eff}}(\text{Ni})$ values.

IV. ATOMIC SPIN MAGNETIC MOMENTS AND MAGNETIC ORDERINGS

In this section, we detail the variations of magnetic moments of the different cations as a function of the presence or not of an atomic swap (λ) and/or a neutral oxygen vacancy (ζ) in spinel crystals described by the formula $(\text{Ni}_{1-\lambda}^{2+}\text{Fe}_{\lambda}^{3+})_{\text{Td}}[\text{Ni}_{\lambda}^{2+}\text{Fe}_{2-\lambda}^{3+}]_{\text{Oh}}(\text{O}^{2-})_{4-\zeta}$. The changes of spin magnetic moments of the Ni or Fe cations (Table II) are consistent with the changes in the DOS curves shown in the main paper and they help to understand the charge reorganization.

We also verified that the ground-state ferrimagnetic ordering remains stable when the cation inversion degree is decreased and/or when an oxygen vacancy is present. As we can see in Ta-

TABLE II. Averaged atomic spin magnetic moments calculated for different NiFe_2O_4 spinel structures characterized by the oxygen stoichiometry ζ and the inversion degree λ . With $\lambda = 0.875$, the results correspond to the structure with the swap labeled $S_1(1,1)$. With $\zeta = 0.875$, the oxygen vacancy is formed in the most stable oxygen site (1,1) ($\lambda = 1$) and (0,1) ($\lambda = 0.875$). The results are given for a supercell of 56 atoms, which possesses 24 cations, among which 8 are located in Td sites and 16 in Oh sites. The multiplicity is given between parentheses for every chemical species.

ζ	λ	$M(\text{Ni}_{\text{Oh}})$ ($\mu_{\text{B}}/\text{atom}$)	$M(\text{Fe}_{\text{Oh}})$ ($\mu_{\text{B}}/\text{atom}$)	$M(\text{Ni}_{\text{Td}})$ ($\mu_{\text{B}}/\text{atom}$)	$M(\text{Fe}_{\text{Td}})$ ($\mu_{\text{B}}/\text{atom}$)	M_{tot} ($\mu_{\text{B}}/8 \text{ f.u.}$)
0	1	1.553 (8)	4.037 (8)	-	-3.884 (8)	16
0	0.875	1.560 (7)	4.040 (9)	-1.504 (1)	-3.884 (7)	22
0.125	1	1.425 (2) + 1.557 (6)	3.906 (1) + 4.037 (7)	-	-3.440 (1) + -3.884 (7)	16
0.125	0.875	1.380 (2) + 1.552 (5)	3.538 (1) + 4.025 (8)	-1.473 (1)	3.884 (7)	20

ble III, the energy differences ΔE between the different orderings which have been tested and the ferrimagnetic ground state only display small changes for the different atomic structures and our calculations confirm that the ferrimagnetic ground state is robust because of the strong Td-O-Oh antiferromagnetic coupling J_{AB} . As we nonetheless calculated a slight reduction of the energy difference between the ferrimagnetic ground state and the ferromagnetic ordering when decreasing the inversion degree or adding oxygen vacancies, as compared to the perfect structure, we can expect an associated decrease of J_{AB} , which would certainly result in a reduction of the Curie temperature.

TABLE III. Total spin magnetic moment and energy difference between the different magnetic orderings and the ground-state (GS) magnetic ordering calculated for every structure.

ζ	λ		Magnetic ordering	M ($\mu_B/f.u.$)	ΔE (eV/f.u.)
0.0	1.0	Ferrimagnetic (GS)	$(Fe\downarrow)_{Td}(Ni\uparrow Fe\uparrow)_{Oh}$	2.000	0.000
		Ferromagnetic	$(Fe\uparrow)_{Td}(Ni\uparrow Fe\uparrow)_{Oh}$	12.003	0.856
		Ferrimagnetic	$(Fe\uparrow)_{Td}(Ni\downarrow Fe\uparrow)_{Oh}$	8.002	0.530
		Ferrimagnetic	$(Fe\uparrow)_{Td}(Ni\uparrow Fe\downarrow)_{Oh}$	2.000	0.293
		Antiferromagnetic	$(Fe_{0.5}\downarrow Fe_{0.5}\uparrow)_{Td}(Ni_{0.5}\uparrow Ni_{0.5}\downarrow Fe_{0.5}\uparrow Fe_{0.5}\downarrow)_{Oh}$	0.000	0.382
0.125	1.0	Ferrimagnetic (GS)	$(Fe\downarrow)_{Td}(Ni\uparrow Fe\uparrow)_{Oh}$	2.000	0.000
		Ferromagnetic	$(Fe\uparrow)_{Td}(Ni\uparrow Fe\uparrow)_{Oh}$	11.749	0.785
		Ferrimagnetic	$(Fe\uparrow)_{Td}(Ni\downarrow Fe\uparrow)_{Oh}$	7.999	0.542
		Ferrimagnetic	$(Fe\uparrow)_{Td}(Ni\uparrow Fe\downarrow)_{Oh}$	1.750	0.305
		Antiferromagnetic	$(Fe_{0.5}\downarrow Fe_{0.5}\uparrow)_{Td}(Ni_{0.5}\uparrow Ni_{0.5}\downarrow Fe_{0.5}\uparrow Fe_{0.5}\downarrow)_{Oh}$	0.006	0.398
0.0	0.875	Ferrimagnetic (GS)	$(Fe_{0.875}\downarrow Ni_{0.125}\downarrow)_{Td}(Ni_{0.875}\uparrow Fe_{1.125}\uparrow)_{Oh}$	2.750	0.000
		Ferromagnetic	$(Fe_{0.875}\uparrow Ni_{0.125}\uparrow)_{Td}(Ni_{0.875}\uparrow Fe_{1.125}\uparrow)_{Oh}$	11.999	0.792
		Ferrimagnetic	$(Fe_{0.875}\downarrow Ni_{0.125}\uparrow)_{Td}(Ni_{0.875}\uparrow Fe_{1.125}\uparrow)_{Oh}$	3.250	0.033
		Ferrimagnetic	$(Fe_{0.875}\uparrow Ni_{0.125}\downarrow)_{Td}(Ni_{0.875}\uparrow Fe_{1.125}\uparrow)_{Oh}$	11.500	0.752
0.125	0.875	Ferrimagnetic (GS)	$(Fe_{0.875}\downarrow Ni_{0.125}\downarrow)_{Td}(Ni_{0.875}\uparrow Fe_{1.125}\uparrow)_{Oh}$	2.500	0.000
		Ferromagnetic	$(Fe_{0.875}\uparrow Ni_{0.125}\uparrow)_{Td}(Ni_{0.875}\uparrow Fe_{1.125}\uparrow)_{Oh}$	11.747	0.768
		Ferrimagnetic	$(Fe_{0.875}\downarrow Ni_{0.125}\uparrow)_{Td}(Ni_{0.875}\uparrow Fe_{1.125}\uparrow)_{Oh}$	3.000	0.047
		Ferrimagnetic	$(Fe_{0.875}\uparrow Ni_{0.125}\downarrow)_{Td}(Ni_{0.875}\uparrow Fe_{1.125}\uparrow)_{Oh}$	11.252	0.714

REFERENCES

- ¹C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, “First-principles calculations for point defects in solids,” *Rev. Mod. Phys.* **86**, 253 (2014).
- ²J. Osorio-Guillén, S. Lany, S. V. Barabash, and A. Zunger, “Magnetism without magnetic ions: Percolation, exchange, and formation energies of magnetism-promoting intrinsic defects in CaO,” *Phys. Rev. Lett.* **96**, 107203 (2006).
- ³K. Reuter and M. Scheffler, “Composition, structure, and stability of RuO₂(110) as a function of oxygen pressure,” *Phys. Rev. B* **65**, 035406 (2001).
- ⁴R. C. Weast and M. J. Astle, eds., *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, 1979).
- ⁵K. Sharma, L. Calmels, D. Li, A. Barbier, and R. Arras, “Influence of the cation distribution, atomic substitution, and atomic vacancies on the physical properties of CoFe₂O₄ and NiFe₂O₄ spinel ferrites,” *Phys. Rev. Mater.* **6**, 124402 (2022).