

STUDY OF THE EQUILIBRIUM SURFACE COMPOSITION OF $\text{Co}_{1-y}\text{Fe}_{2+y}\text{O}_4$ —II

THE ROLE OF VACANT AND CHEMISORBED OXYGEN AND CHARGE TRANSFER EFFECT

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Abstract—In Part I of this work we have calculated the equilibrium cation composition at the surface of $\text{Co}_{1-y}\text{Fe}_{2+y}\text{O}_4$ considering a stoichiometric oxygen content. In this paper we extend our model to include the effect on the cation surface composition of the equilibrium with the gas-phase. We take into account both the formation of surface oxygen vacancies and chemisorption. This model allows for an interpretation of AES experimental data obtained after different thermal treatments under gas fluxes or in UHV. While all previous calculations were based on the assumption that Co^{3+} and Fe^{2+} ions are never present simultaneously, here we discuss finally the effects of the charge transfer from Co^{2+} to Fe^{3+} .

1. INTRODUCTION

In Part I[1] we have approached the study of the surface equilibrium composition and inversion in the non-stoichiometric ferrite $\text{Co}_{1-y}\text{Fe}_{2+y}\text{O}_4$ under the simplifying assumptions that no oxygen exchange occurs between surface and gas phase, and, second, Co^{3+} and Fe^{2+} are not present simultaneously in the crystal. In practice, both these assumptions are not strictly valid. Indeed, the gas-phase oxygen pressure is seen to have a remarkable influence on the equilibrium cation-composition. Moreover, as early as 1959, Jonker [2] has interpreted the semiconducting properties of the non-stoichiometric cobalt ferrites, associating conduction electrons and holes with Fe^{2+} and Co^{3+} ions, respectively. This implies that, at finite temperature, and around the stoichiometric composition, small amount of these ions exist simultaneously, due to the thermally induced charge transfer from Co^{2+} to Fe^{3+} .

In this paper we investigate both the above effects and their role in the cation composition at the surface. The equilibrium between surface and gas-phase oxygen implies chemisorption and formation of surface oxygen vacant sites, i.e. a deviation of the surface oxygen amount from stoichiometry. Both these mechanisms are included in the present model, and are needed in the interpretation of the experimental data obtained from the same series of $\text{Co}_{1-y}\text{Fe}_{2+y}\text{O}_4$ samples used in Part I after various treatments under gas fluxes or in UHV. The calculation of the charge-transfer effects on the surface cation composition yields a small correction of the relationship between bulk and surface composition, in the region around stoichiometry. However this charge-transfer model enables us to give a qualitative picture of the electronic structure at the surface.

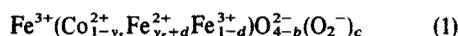
2. EFFECTS OF VACANT AND CHEMISORBED OXYGEN

Exchange of oxygen between surface and gas phase can take place both as a lattice oxygen loss and as chemisorption of molecular oxygen.

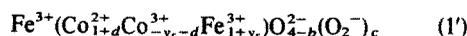
In the first process two electrons per oxygen atoms are left in the crystal and captured by the trivalent cations of the surface. More precisely, the electrons are trapped by Fe^{3+} in the iron-excess case ($y_s > 0$), while in the cobalt-excess case ($y_s < 0$) the trapping is assumed to occur only at Co^{3+} ion, due to its larger affinity. Here we work in the *inverse spinel* configuration, and assume that only the trivalent cations in octahedral sites are involved.

For the second process, we adopt a model in which molecular oxygen is chemisorbed as O_2^- . In this case the electron is provided by Fe^{2+} for $y_s > 0$, and by Co^{2+} for $y_s < 0$ (when Fe^{2+} ions are not available).

Hence we write the equilibrium surface compositions as



for $y_s > 0$, and



for $y_s < 0$, where $d = 2b - c$ can be either positive or negative; b and c are functions of the gas-phase pressure and temperature.

The equilibrium conditions between surface and bulk read

$$\frac{1 - y_s}{1 - y} \frac{y}{y_s + d} = e^{\Delta(2)/kT} \quad (y > 0) \quad (2)$$

$$\frac{1 + y_s}{1 + y} \frac{y}{y_s + d} = e^{\Delta(3)/kT} \quad (y < 0) \quad (2')$$

where $\Delta^{(2)}$ and $\Delta^{(3)}$, the changes of standard chemical potential for the exchange between bulk and surface of divalent and trivalent ions, respectively, are defined in Part I.

The present results enable us to discuss two series of experimental data obtained from samples kept 6.5 hr under a N_2 or He flux at 1273 K; in practice, small amounts of oxygen are present in the gas fluxes, which contaminate the surface. The cobalt-to-iron and the oxygen-to-cation ratios measured at the surface of our six samples are reported in Table 1 for the above two experimental conditions. The average values of the oxygen-to-cation ratio

$$\frac{O}{Co+Fe} = \frac{1}{3}(4-b+2c)$$

are 1.56 for N_2 flux treatment and 1.58 for He flux treatment, against 1.33 for the ideal case. Hence we have an oxygen excess at the surface due to chemisorption. A reasonable fit of the experimental data is obtained with $d = -0.15$ and $d = -0.06$, for the two above sets of measurements. Combining these values with those of the oxygen-to-cation ratios we find a small number (few percent) of surface oxygen vacancies, largely compensated by chemisorption: we obtain $b = 0.13$, $c = 0.40$ for N_2 treated samples and $b = 0.21$, $c = 0.47$ for He treated samples. Experimental data and theoretical curves are shown in Fig. 1.

A third set of experimental data, obtained after cleaning the sample surface by 0.5 hr heating in ultra high vacuum (UHV), is reported in Table 1 and in Fig. 1(c). In this case, the oxygen-to-cation ratio has an average value of 1.38 and cobalt excess always occurs at the surface.

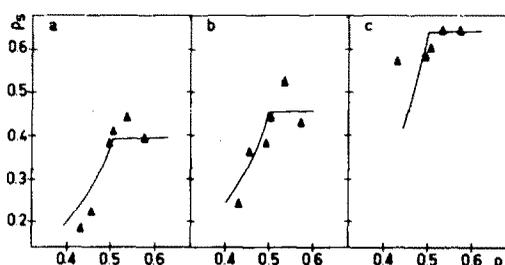


Fig. 1. Experimental surface Co/Fe ratio ρ_s vs bulk ratio ρ . Curves represent the result of theoretical calculations. (a) after treatment at 1273 K in N_2 flux; (b) after treatment at 1273 K in He flux; (c) after treatment at 1073 K in UHV.

Now the fitting of these data with eqn (2) is quite poor, the point at $\rho \approx 0.43$ being quite far from the theoretical curve. Nevertheless we obtain $b = 0.16$, a value quite close to those found for the samples treated with N_2 and He, and $c = 0.15$, which is instead quite lower than the values found above, because of the surface decontamination. It is interesting to remark that now $c \approx b$, which means that at the surface we have, more or less, as many chemisorbed oxygen molecules as vacant oxygen lattice sites. This could be interpreted as due to the fact that oxygen molecules chemisorbed at vacant oxygen lattice sites are tightly bounded, in such a way they survive to the surface cleaning procedure by UHV heating.

3. CHARGE TRANSFER EFFECTS

Till now we have worked under the assumption that Fe^{2+} and Co^{3+} are never present simultaneously. As a consequence the calculated surface composition exhibits a discontinuous derivative at $y = 0$ due to the sharp change from the iron-excess regime, where Fe^{2+} is present, to the cobalt-excess regime, where Co^{3+} is present.

However, the present model is not rigorously valid. According to the classical description of semiconducting properties of Co ferrites given by Jonker [2], Fe^{2+} and Co^{3+} ions behave as donor- and acceptor-like centres respectively, in such a way that $Co_{1-y}Fe_{2+y}O_4$ is either an n -type or a p -type semiconductor according to whether y is positive or negative. In practice, the number of carriers corresponds to the number of Fe^{2+} and Co^{3+} ions. Hence, also in the intrinsic case ($y = 0$) it is expected that, at finite temperature, some pair of Fe^{2+} and Co^{3+} coexist, because the electron transfer from Co^{2+} to Fe^{3+} requires only 0.55 eV [2]. This picture can now be extended to the surface case, to give a single model of the surface electronic structure. We study the effect of the charge transfer (i.e. of the coexistence of Co^{3+} and Fe^{2+}) on the surface composition in the inverse spinel configuration, and without including any gas-phase oxygen perturbation. As usual, we assume that the charge transfer occurs only between ions in the octahedral sites. We consider the formula



where $z = y + \beta$; it is valid in the bulk for both $y > 0$ and $y < 0$. The same formula is written for the surface with $z_s = y_s + \beta_s$ and β_s .

Table 1. Carrier concentration at the surface of $Co_{1-y}Fe_{2+y}O_4$

ρ	z	β	z_s	β_s	ρ_s	v_s	ϵ_F	L_D
0.3	0.313	0.006	0.676	4.12×10^{-6}	0.121	0.371	0.182	3.88
0.4	0.158	0.015	0.461	1.01×10^{-5}	0.219	0.386	0.109	5.27
0.5	0.051	0.051	0.196	3.53×10^{-5}	0.366	0.397	0	6.86
0.6	0.017	0.142	0.073	1.01×10^{-4}	0.477	0.398	-0.098	4.49
0.7	0.009	0.244	0.039	2.13×10^{-4}	0.472	0.392	-0.152	4.35

Table 2. Surface compositions expressed in terms of Co/Fe and O/(Co+Fe) ratios obtained by AES after: (a) sputter ion etching until Co/Fe constant; (b) heating to 1273 K for 6.5 hr in N_2 flux; (c) as (b) but in He flux; (d) heating to 1073 K for 0.5 hr in UHV

Sample	a)		b)		c)		d)	
	Co/Fe	O/(Co+Fe)	Co/Fe	O/(Co+Fe)	Co/Fe	O/(Co+Fe)	Co/Fe	O/(Co+Fe)
1	0.42	1.23	0.18	1.51	0.24	1.61	0.57	1.43
2	0.44	1.10	0.22	1.41	0.36	1.44	0.52	1.36
3	0.48	1.32	0.38	1.45	0.38	1.54	0.58	1.38
4	-	-	0.41	1.48	0.44	1.49	0.60	1.27
5	0.56	1.17	0.44	1.86	0.52	1.49	0.64	1.44
6	0.56	1.25	0.39	1.62	0.43	1.89	0.64	1.36
average		1.21	average	1.56	average	1.58	average	1.38

The thermal equilibrium with respect to the cobalt-iron exchange between bulk and surface is reached when

$$\frac{z_s}{1-z_s} = \frac{z}{1-z} e^{-\Delta^{(2)}/kT} \quad (3)$$

With regard to the charge transfer processes in the bulk and at the surface we have two additional equilibrium conditions

$$\frac{z\beta}{(1-z)(1-\beta)} = e^{\gamma/kT}, \quad \frac{z_s\beta_s}{(1-z_s)(1-\beta_s)} = e^{\gamma_s/kT} \quad (4)$$

where

$$\gamma = \mu_{\square}^{(F3)} - \mu_{\square}^{(C3)} - \mu_{\square}^{(F2)} + \mu_{\square}^{(C2)} - \delta_3;$$

δ_3 is the third ionization potential difference between cobalt and iron in the crystal. A similar expression holds for γ_s , where the chemical potentials are those at the surface, while δ_3 is assumed to be the same. Hence

$$\gamma - \gamma_s = \Delta^{(2)} + \Delta^{(3)}.$$

Combining eqns (3, 4) we have an equation for β_s :

$$\frac{\beta_s}{1-\beta_s} = \frac{\beta}{1-\beta} e^{-\Delta^{(3)}/kT}. \quad (5)$$

As δ_3 is expected to be quite lower than the correspondent value for free atoms (2.85 eV)[3], the direct evaluation of γ is quite difficult. However, we can relate γ to the gap energy E_g of the stoichiometric ferrite. In the intrinsic case ($y=0$) we have the same amount β_0 of Co^{3+} and Fe^{2+} , given by

$$\beta_0 = (1 + e^{-\gamma/2kT})^{-1} \approx e^{\gamma/2kT}.$$

On the other hand, β_0 corresponds to the number of transferred electrons per atom, i.e.

$$\beta_0 \approx e^{-E_g/kT}.$$

Thus $\gamma \approx -E_g$. According to the classical model due to Jonker, a lower bound for E_g is represented by the

energy separation between Fe^{2+} donor and Co^{3+} acceptor levels, namely $2\Delta = 0.55$ eV [2], while an estimate of E_g could be the sum of 2Δ plus the electron and hole activation energies, $q_1 = 0.175$ eV and $q_2 = 0.475$ eV respectively, which gives $\gamma = -1.2$ eV. An upper bound for E_g is obtained by giving δ_3 the value for free atoms; in this case $\gamma = -1.79$ eV.

In Fig. 2 we show the calculated cobalt-to-iron ratio at the surface, $\rho_s = (1-y_s)/(2+y_s)$, vs the bulk ratio $\rho = (1-y)/(2+y)$ for the three values $\gamma = -0.55$, -1.20 and -1.79 eV and for $T = 1089$ K. The charge transfer effects are apparent in the region around the stoichiometric value $\rho = \frac{1}{2}$, where they produce a further iron enrichment at the surface. Such effects are very sensitive on the gap energy E_g ; the influence of the charge transfer on the surface composition is large for $E_g = 0.55$ eV, but it can be neglected for $E_g = 1.79$ eV. However, the experimental data seem to indicate a small charge-transfer effect, i.e. a gap energy of the order of larger than 1 eV.

Under the assumption that the carrier concentrations in each layer correspond to the concentrations of Fe^{2+} and Co^{3+} , we can build up a simple picture of the surface electronic structure as function of the bulk composition. In Table 1 the bulk and surface carrier concentrations z , β , z_s and β_s are given for some values of ρ . The calculation is based on Jonker data for $T = 1069^\circ\text{K}$; ϵ_F is the shift of the Fermi energy with respect to the intrinsic case ($z = \beta$; i.e. $\rho = \frac{1}{2}$). The surface band bending V_s and

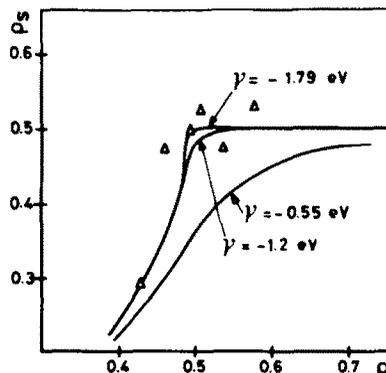


Fig. 2. Calculated surface Co/Fe ratio ρ_s vs bulk ratio ρ , for different values of γ . Triangles represent experimental results.

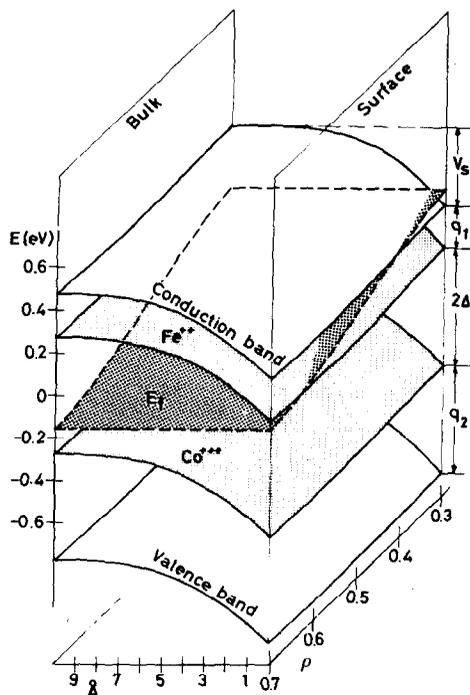


Fig. 3. Representation of the band structure from bulk to surface as function of the bulk composition ρ .

the Debye length L_D are obtained from the approximate equations

$$V_s \approx \frac{1}{2} kT \log \frac{z_s \beta}{\beta_s z'}, \quad L_D \approx \left(\frac{a^3 \epsilon kT}{8e^2 \beta + z} \right)^{1/2},$$

where $\epsilon \approx 10$ is the experimental dielectric constant[4] and $a^3/8$ is the part of the unit cell containing one molecule. A picture of the band structure from bulk to surface as function of the bulk composition is shown in Fig. 3. The light gray surfaces represent the donor and acceptor bands whose distances from the conduction and valence bands are q_1 and q_2 , respectively, while the dark gray one represents the Fermi level. It is interesting to note that the cobalt rich samples, which according to Jonker exhibit a p -type conductivity, present an inversion layer, whose thickness is of only few atomic layers. In other words, the surface conductivity is n -type, and several electrons are available for chemisorption of oxygen or nitrogen oxide.

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