

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

CATION COMPOSITION WITH STOICHIOMETRIC OXYGEN CONTENT

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Abstract—The equilibrium composition at the surface of the mixed spinel $\text{Co}_{1-y}\text{Fe}_{2+y}\text{O}_4$ is calculated as a function of the composition parameter y and of the degree of inversion. The ionic standard chemical potentials include the Born-Mayer repulsive energy and the vibrational contribution. The calculated results turn out to be weakly dependent on the bulk inversion, and indicate a pronounced tendency of iron to segregate at the surface. These results are compared and found to be in agreement with some experimental data obtained by AES. In a subsequent paper we will take into account the gas-phase and the charge-transfer effects.

1. INTRODUCTION

There is an increasing interest in the catalytic properties of mixed oxides, such as the non-stoichiometric ferrites $\text{Me}_{1-y}\text{Fe}_{2+y}\text{O}_4$, with particular attention to the dependence of their activity and selectivity on the oxide composition. Now it is clear that the equilibrium composition of the surface, on which catalytic properties directly depend, can be quite different from that of the bulk, this difference increasing with the deviation from stoichiometry. Indeed, since the operating temperature of these oxide catalysts is usually comparable or larger than the crystal Debye temperature, the actual surface composition is expected to be close to that predicted by equilibrium thermodynamics.

For this reason the study of surface segregation, an old thermodynamical problem approached one century ago by Gibbs[1], meets a revival, not only in his usual field of application, metallurgy[2, 3], but also in catalysis[4, 5]. However, in mixed oxides, the surface cation composition depends not only on the equilibrium with the bulk, but also on the equilibrium with the gas phase, namely on chemisorption and formation of surface oxygen vacant sites.

This work, consisting in two papers, reports on the theory and calculation of the equilibrium surface composition of $\text{Co}_{1-y}\text{Fe}_{2+y}\text{O}_4$ as function of the bulk composition and temperature, for y varying in the range where this crystal exists in the spinel phase[6, 7].

The present paper is mainly devoted to the calculation of the change of standard chemical potential due to the exchange between surface and bulk ions. Then, the surface composition and the surface inversion degree are evaluated, and compared with some preliminary

experimental results we have obtained by means of Auger electron spectroscopy (AES). This calculation represents a simple extension to the surface problem of the chemical works on the solid solutions of two isostructural oxides, particularly those of Kröger[8], Schmalzried[9] and Driessens[10]. Here, we have assumed that first, no oxygen exchange occurs between surface and gas-phase, and, second, Co^{3+} and Fe^{2+} are never present simultaneously in the lattice.

In practice, both these assumptions are not strictly valid. The gas-phase oxygen pressure is seen to have a remarkable influence on the equilibrium cation composition at the surface. Furthermore, the thermally activated charge transfer from Co^{2+} to Fe^{3+} yields a temperature dependent number of Co^{3+} - Fe^{2+} pairs, with appreciable effects on the surface composition in the region around stoichiometry. The gas-phase and the charge-transfer effects constitute the subject of the subsequent paper.

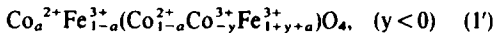
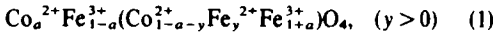
2. EQUILIBRIUM COMPOSITION OF THE SURFACE

The mixed oxide $\text{Co}_{1-y}\text{Fe}_{2+y}\text{O}_4$ is known to have the spinel structure. The inversion is complete for Fe_3O_4 ($y = 1$) and decreases continuously when iron is progressively replaced by cobalt; Co_3O_4 ($y = -2$) is a normal spinel. In spite of several recent Mössbauer studies[11-13], the inversion as function of y is not yet well known; indeed, the stoichiometric ferrite CoFe_2O_4 ($y = 0$) exhibits an inversion ranging from 96%[12] to 67%[13]. Such different values are perhaps due to different preparation techniques and temperatures.

A usual assumption is however that Co^{3+} and Fe^{2+} are never present simultaneously[13]. Therefore it is expected that as y decreases from +1 to 0, Fe^{2+} is progres-

sively replaced by Co^{2+} , while only for negative y , the ion Co^{3+} starts to replace Fe^{3+} . This means that a physical function of y usually has a discontinuous derivative at $y = 0$.

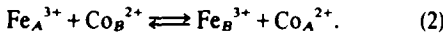
According to whether y is positive (iron excess) or negative (cobalt excess) we shall consider the two different formulas:



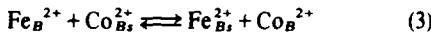
where cations inside or outside parentheses occupy octahedral or tetrahedral sites, respectively.

Iron excess ($y > 0$)

We consider the simultaneous equilibrium in the following three processes. The first two processes are the cation exchange between tetrahedral (A) and octahedral (B) sites, i.e. the inversion processes, occurring in the bulk and at the surface:



The third process is the cation exchange between the bulk and the surface layer (segregation process). According to formula (1) the only significant exchange process for $y > 0$ is that between divalent ions in octahedral sites, namely



where index s refers to surface layer. The equilibrium conditions for bulk and surface inversion processes and for the segregation process are respectively

$$\begin{cases} (1-y-a)(1-a) = a(1+a)e^{\delta/kT} \\ (1-y_s-a_s)(1-a_s) = a_s(1+a_s)e^{\delta_s/kT} \\ y(1-y_s-a_s) = y_s(1-y-a)e^{\Delta^{(2)}/kT} \end{cases} \quad (4)$$

where y , and a_s are the composition and inversion parameters at the surface, respectively.

In the present study, we assume that any cation exchange does not produce any elastic relaxation of the lattice, keeping the crystal volume constant. Therefore, δ , δ_s and $\Delta^{(2)}$ are the changes of Helmholtz free energy associated with the correspondent elementary exchange processes. They are expressed in terms of bulk and surface standard chemical potentials of the i th ion in sites A and B , $\mu_A^{(i)}$, $\mu_B^{(i)}$, $\mu_{A_s}^{(i)}$ and $\mu_{B_s}^{(i)}$, respectively, as follows

$$\delta = \mu_A^{(C2)} - \mu_A^{(F3)} - \mu_B^{(C2)} + \mu_B^{(F3)} \quad (5)$$

$$\delta_s = \mu_{A_s}^{(C2)} - \mu_{A_s}^{(F3)} - \mu_{B_s}^{(C2)} + \mu_{B_s}^{(F3)} \quad (5')$$

$$\Delta^{(2)} = \mu_{B_s}^{(F2)} - \mu_{B_s}^{(C2)} - \mu_B^{(F2)} + \mu_B^{(C2)} \quad (6)$$

where $F2$, $F3$, $C2$ and $C3$ stand for Fe^{2+} , Fe^{3+} , Co^{2+} and Co^{3+} , respectively.

A general form for the standard chemical potential of

an ion in a harmonic lattice is given by [14, 15]

$$\mu^{(i)} = u^{(i)} + kT \int_0^\infty d\omega \rho^{(i)}(\omega) \log [2 \sinh(\hbar\omega/2kT)] \quad (7)$$

where $u^{(i)}$ is the static potential energy of the i th ion in the crystal field, and $\rho^{(i)}(\omega)$ the frequency density of boson excitations (phonons and, below the Curie temperature, magnons) projected onto the i th ion coordinates. The static term includes the Coulomb interaction, the hard-core repulsive interaction and, below the Curie temperature T_c , the magnetic interaction.

The solution of the system (4) gives the three unknowns y , a , and a_s as functions of y , T and the cation standard chemical potentials.

For our purpose it is enough to consider the solutions of (4) for two extreme cases, corresponding to the perfectly random spinel ($\delta = \delta_s = 0$) and to the inverse spinel (δ and δ_s much larger than kT).

For a *random spinel*, we readily obtain

$$y_s = \frac{1}{2} [3 - \sqrt{9 - 8A/(1+A)}], \quad (8)$$

with

$$A = \frac{y(3-y)}{(1-y)(2-y)} e^{-\Delta^{(2)}/kT}, \quad (9)$$

and

$$a_s = \frac{1-y_s}{3-y_s}, \quad a = \frac{1-y}{3-y}. \quad (10)$$

For an *inverse spinel* we have

$$y_s = \frac{y}{y + (1-y)e^{\Delta^{(2)}/kT}} \quad (11)$$

and $a_s = a = 0$.

Cobalt excess ($y < 0$)

In this case we start from eqn (1'); a treatment analogous to that followed above yields the system

$$\begin{aligned} (1-a)^2 &= (1+y+a)a e^{\delta/kT} \\ (1-a_s)^2 &= (1+y_s+a_s)a_s e^{\delta_s/kT} \end{aligned} \quad (12)$$

$$(1+y_s+a_s)y = (1+y+a)y_s e^{\Delta^{(3)}/kT}$$

with

$$\Delta^{(3)} = \mu_{B_s}^{(C3)} - \mu_{B_s}^{(F3)} - \mu_B^{(C3)} + \mu_B^{(F3)}. \quad (13)$$

The solution of the system (12) for a *random spinel* ($\delta = \delta_s = 0$) gives

$$y_s = \frac{1}{2(1-A)} [4A - 3 + \sqrt{(9-8A)}], \quad (14)$$

where

$$A = \frac{y(3+y)}{(2+y)^2} e^{-\Delta^{(3)}/kT} \quad (15)$$

and

$$a_s = \frac{1}{3+y_s}, \quad a = \frac{1}{3+y} \quad (16)$$

For an *inverse spinel* ($\delta, \delta_s \gg kT$) we have

$$y_s = \frac{y}{(1+y)e^{\Delta^{(3)}/kT} - y}, \quad (-1 \leq y \leq 0) \quad (17)$$

and $a_s = a = 0$. By examining (1'), the restriction $y \geq -1$ is obvious. Indeed, for further replacement of iron with cobalt the system tends to a direct spinel structure. It is therefore instructive to derive y_s also for a perfectly *normal spinel* ($\delta, \delta_s \ll -kT$, namely $a_s = a = 1$). One finds

$$y_s = \frac{2y}{(2+y)e^{\Delta^{(3)}/kT} - y}, \quad (-2 \leq y \leq 0). \quad (18)$$

The qualitative behaviour of y_s vs y is shown in Fig. 1 for the special cases discussed above and for some representative values of $\Delta^{(i)}$.

It appears that the calculations for the random and for the inverse spinel configurations yield very similar results, indicating that the inversion degree has weak influence on the surface composition corresponding to a given y . It is however interesting to study such dependence for small values of y , i.e. for small deviations around the stoichiometric ferrite. In the region where y is linear in y , it is found

$$\frac{y_s}{y} = \begin{cases} \frac{1-a_s}{1-a} e^{-\Delta^{(2)}/kT} & \text{for } y \geq 0 \\ \frac{1+a_s}{1+a} e^{-\Delta^{(3)}/kT} & \text{for } y \leq 0 \end{cases} \quad (19)$$

where a_s and a are deduced from eqns (4) and (12) for $y_s = y = 0$. The factors $(1-a_s)/(1-a)$ and $(1+a_s)/(1+a)$

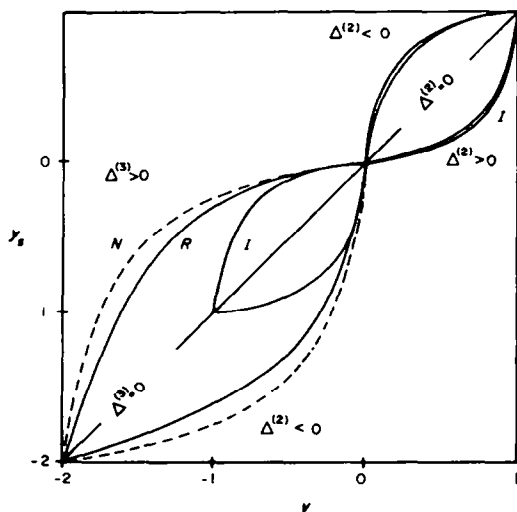


Fig. 1. Surface composition parameter y_s vs bulk composition parameter y of $\text{Co}_{1-y}\text{Fe}_{2+y}\text{O}_4$, for $\Delta^{(2)}/kT = \pm 2$ and $\Delta^{(3)}/kT = \pm 2$ and for different configurations: I = inverse spinel, R = random spinel, and N = normal spinel (broken line).

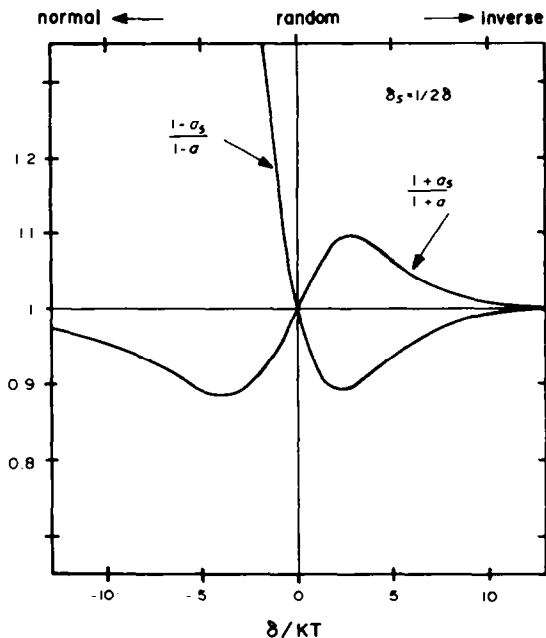


Fig. 2. The factors $(1-a_s)/(1-a)$ and $(1+a_s)/(1+a)$ as functions of the bulk inversion energy δ , calculated for $\delta_s = (1/2)\delta$.

express the deviations from the right and left derivatives, $\exp(-\Delta^{(2)}/kT)$ and $\exp(-\Delta^{(3)}/kT)$, respectively, valid for the random configuration ($a_s = a = 0$); they are plotted in Fig. 2 as function of the inversion energy δ . The calculation is performed by assuming $\delta_s = (1/2)\delta$ (see next section). It appears that for the physical cases (remember that CoFe_2O_4 has a configuration ranging between random and total inversion), the above deviations are always very close to unity, confirming that the surface composition is always weakly dependent on the inversion degree. In particular the right derivative for inverse configuration is the same as that for random configuration, while the left derivative is the same for all the three limit configurations.

3. THE CHANGE OF THE STANDARD CHEMICAL POTENTIAL

(a) Hard-core repulsion

The substitution of Fe^{3+} with Co^{3+} (cobalt excess) as well as of Co^{2+} with Fe^{2+} (iron excess) mostly produce a change in the hard-core repulsive energy between the cation and six oxygen ions of the octahedral cage. We neglect the change of the short-range interaction with further neighbours, as well as of the Coulomb energy via the elastic relaxation (producing a small local change of the oxygen parameter u). Parenthetically, the inclusion of the relaxation effects would introduce a dependence of the parameters $\Delta^{(i)}$ on the composition itself. Obviously no change in the direct Coulomb energy occurs, as the net changes of the substitutional and host ions are considered to be the same.

The simplest picture for the repulsion between two ions i and j is the Born-Mayer potential

$$u_R(r) = bc_{ij} e^{(r_0+r_i-r)/\rho} \quad (20)$$

where r is the interionic distance, r_i the crystal ionic radii, and $c_{ij} = 1 + z_i/n_i + z_j/n_j$ is the Pauling correction; z_i and n_i are the valence and the number of electrons in the outer shell of the i th ion. This potential has the peculiarity of giving reliable values for the repulsive energy of all the crystals belonging to a given family, with the same value of the repulsive parameter $\bar{\rho}$ and of the pre-exponential factor b , and with a single well-defined set of ionic radii [16].

Our task is to derive a set of ionic radii of Fe^{3+} , Fe^{2+} , Co^{3+} and Co^{2+} consistent with the equilibrium condition of Fe_3O_4 , CoFe_2O_4 , FeCo_2O_4 , Co_3O_4 and with the same value of b . The repulsive parameter chosen in this calculation is that used by Verwey *et al.* [17], $\bar{\rho} = 0.345 \text{ \AA}$. A convenient approximation is to put $C_{ij} = 1$ and use instead of r_i a set of effective ionic radii

$$\bar{r}_i = r_i + \bar{\rho} z_i / n_i.$$

The equilibrium condition for an inverse spinel (like Fe_3O_4 and CoFe_2O_4) and for a normal spinel (like FeCo_2O_4 [18] and Co_3O_4 [19]), read respectively as [17]

$$\frac{b}{\bar{\rho}} \left[4\sqrt{3} \left(u - \frac{1}{4} \right) \bar{e}_3 + 6 \left(\frac{5}{8} - u \right) (e_2 + e_3) \right] = \frac{Me^2}{a^2} \quad (21)$$

(inverse) where e_2 and e_3 refer to CoFe_2O_4 .

$$\frac{b}{\bar{\rho}} \left[4\sqrt{3} \left(u - \frac{1}{4} \right) \bar{e}_2 + 12 \left(\frac{5}{8} - u \right) e_3 \right] = \frac{Me^2}{a^2} \quad (21')$$

(normal)

where e is the electronic charge,

$$\bar{e}_{2,3} = \exp \left[\bar{r}_- + \bar{r}_{2,3} - a\sqrt{3} \left(u - \frac{1}{4} \right) \right] / \bar{\rho} \quad (22)$$

$$e_{2,3} = \exp \left[\bar{r}_- + \bar{r}_{2,3} - a \left(\frac{5}{8} - u \right) \right] / \bar{\rho} \quad (22')$$

and M is the Madelung constant, tabulated for different spinel structures and u values by Verwey *et al.* [20]. Starting from the ionic radii of Fe^{2+} ($r_2 = 0.830 \text{ \AA}$), Fe^{3+} ($r_3 = 0.670 \text{ \AA}$) and O^{2-} ($r_- = 1.40 \text{ \AA}$) [17], we calculate those of Co^{2+} and Co^{3+} from eqns (21) and (21'). The input data and the set of ionic radii are listed in Table 1. The changes in the repulsive energy $\Delta u_R^{(2)}$ due to substitution of Co^{2+} with Fe^{2+} , and $\Delta u_R^{(3)}$ due to substitution of Fe^{3+} with Co^{3+} in the octahedral site, are found to be

$$\Delta u_R^{(2)} = 6e_2 b (e^{\Delta r_2/\bar{\rho}} - 1) = 0.263 \text{ eV} \quad (23)$$

$$\Delta u_R^{(3)} = 6e_3 b (e^{\Delta r_3/\bar{\rho}} - 1) = -1.253 \text{ eV} \quad (23')$$

Table 1. Crystal data entering the calculation of repulsive energy

Crystal spinel type	Fe_3O_4 inverse	CoFe_2O_4 inverse	Co_2FeO_4 normal	Co_3O_4 normal
a (\AA)	8.3963 ^(a)	8.393 ^(b)	8.254 ^(c)	8.094 ^(d)
u	0.379 ^(a)	0.381 ^(e)	0.386 ^(f)	0.392 ^(d)
r_- (\AA)	1.40 ^(g)	1.40 ^(g)	1.40 ^(g)	1.40 ^(g)
r_{2+} (\AA)	0.83 ^(g)	0.825	0.825	0.825
r_{3+} (\AA)	0.67 ^(g)	0.67 ^(g)	0.64	0.63
\bar{r}_- (\AA)	1.36	1.36	1.36	1.36
\bar{r}_{2+} (\AA)	0.89	0.88	0.88	0.88
\bar{r}_{3+} (\AA)	0.74	0.74	0.71	0.70
M	130.95 ^(h)	131.05 ^(h)	134.48 ^(f)	137.50 ^(h)
	$\bar{\rho} = 0.345 \text{ \AA}^{(g)}$		$b = 2.70 \text{ eV}$	

a) Wyckoff R.W.G., "Crystal Structures", vol. II, Interscience (1960).

b) See ref. 7.

c) Greenwood N.N., "Ionic Crystals, Lattice Defects and Nonstoichiometry" (Butterworth, London 1968) p. 96.

d) See ref. 19.

e) Prince E., Phys. Rev. **102**, 674 (1956).

f) Interpolated between CoFe_2O_4 and Co_3O_4 .

g) See ref. 17.

h) See ref. 20.

(b) *Change in phonon energy*

The change of the standard chemical potential $\Delta\mu_p$ associated with the vibrational energy change induced by the ion substitution has been thoroughly investigated in several works [14, 21]. The perturbation due to the ion substitution consists in a local change of the cation mass M_+ and of nearest neighbour force constant f , respectively described by the parameters $\epsilon = -\Delta M_+/M_+$ and $\gamma = \Delta f/f$. We write

$$\Delta\mu_p = kT \int_0^\infty d\omega \Delta\rho(\omega) \log \left(2 \sinh \frac{\hbar\omega}{2kT} \right) \quad (24)$$

where the change of the phonon density can be expressed in terms of the resonant denominator $D(\omega)$ as

$$\Delta\rho(\omega) = -\frac{1}{\pi} \text{Im} \frac{d}{d\omega} \log D(\omega). \quad (25)$$

For simplicity, we regard the crystal as a set of three orthogonal linear chains, in order to have the factorization

$$D(\omega) = D_{(-)}^3(\omega) D_{(+)}^3(\omega) \quad (26)$$

where [13]

$$D_{(-)}(\omega) = 1 + \gamma[1 + (1 - \epsilon)M_+\omega^2/f] + [\epsilon(1 + \gamma) + \gamma(1 - \epsilon)M_+\omega^2/f]\omega^2 g_{(-)}(\omega^2) \quad (27)$$

and

$$D_{(+)}(\omega) = 1 + (\gamma f/M_-)g_{(+)}(\omega^2) \quad (28)$$

are the resonant denominators for odd-symmetry and even-symmetry modes; M_+ and M_- are the cation and anion masses and $g_{(\pm)}(\omega^2)$ are the phonon unperturbed Green functions for even and odd modes, projected onto the perturbation subspace. All the information on the lattice dynamics of the host lattice (the stoichiometric CoFe_2O_4) is contained in the Green functions, their imaginary parts being the projected unperturbed phonon densities for even and odd symmetry modes. In order to evaluate the magnitude of $\Delta\mu_p$, we replace the phonon spectrum with a delta function centered on an average frequency $\bar{\omega}$ (Einstein model), writing

$$\text{Im} \hat{g}_{(-)}(\omega^2) \sim \text{Im} g_{(+)}(\omega^2) \sim \pi \delta(\omega^2 - \bar{\omega}^2). \quad (29)$$

Furthermore, since the difference of mass and ionic radius between iron ions and cobalt ions are small, no resonant or local mode is expected from the ion substitution ($D \approx 1$), so that we can write

$$\text{Im} \frac{d}{d\omega} \log D \sim \frac{d}{d\omega} \text{Im} D. \quad (30)$$

By means of these approximations, the integral (24) can be explicated as

$$\Delta\mu_p \approx \frac{3}{4} [\epsilon + \gamma(1 + \chi) + \epsilon\gamma(1 - \chi)] \hbar\bar{\omega} \cotg \frac{\hbar\bar{\omega}}{2kT} \quad (31)$$

where we have set $\chi = M_+/M_-$ and $\bar{\omega}^2 = f/M_-$. The short-range force constant f is just the second derivative of $u_R(r)$ between the host and neighbour ions, namely $f = u_R/\bar{\rho}^2$ and then $\gamma = \Delta u_R/u_R \approx \Delta \bar{f}/\bar{f}$. For Fe^{2+} replacing Co^{2+} , $\epsilon = 0.0524$ and $\gamma = 0.0157$, while for Co^{3+} replacing Fe^{3+} , $\epsilon = -0.0553$ and $\gamma = -0.1709$.

For $\bar{\omega}$ we use the experimental transverse optical frequency of CoFe_2O_4 , $\bar{\omega} = 7.1 \times 10^{13}$ rad sec^{-1} , obtained from neutron inelastic scattering [22].

We perform the calculation of $T = 1089$ K, the quenching temperature for the samples used in the present experiments. It is found

$$\Delta\mu_p^{(2)} = 0.022 \text{ eV} \quad \text{and} \quad \Delta\mu_p^{(3)} = -0.111 \text{ eV}. \quad (32)$$

(c) *Surface strain effects and estimation of $\Delta^{(1)}$*

In this calculation we do not consider the change in the magnetic interaction, the temperature T being well above the Curie temperature.

By summing the above contributions (23) and (32) we obtain for substitutions in the bulk

$$\Delta\mu^{(2)} = 0.285 \text{ eV} \quad \text{and} \quad \Delta\mu^{(3)} = -1.364 \text{ eV}. \quad (33)$$

A similar calculation for the surface layer is more complicated, particularly for the dynamical terms. For our purposes, however, we need just an average value of $\Delta\mu_s^{(1)}$, as we deal with fine powders. As the major contributions to $\Delta\mu^{(1)}$ come from the static nearest-neighbour interaction, the dynamical part being a small correction, we attribute to $\Delta\mu_s^{(1)}$ a value proportional to the coordination number at the surface. However, such average does not allow to escape the important problem of the surface strain caused by the elastic relaxation. This is expected to have an appreciable influence on $\Delta^{(1)}$.

We consider the effect of surface strain on $\Delta^{(2)}$ through the change in the strain-induced perturbation of the chemical potentials, $\delta\mu_s^{(F2)} - \delta\mu_s^{(C2)}$. In the harmonic approximation

$$\delta\mu_s = -\frac{z_o^2}{2} \frac{\partial^2}{\partial z^2} (u_C + u_R), \quad (34)$$

where z_o is the cation relaxation along the z -axis normal to the surface, u_C and u_R are Coulomb and repulsive potentials acting on the surface cation, respectively. All atoms interacting with the surface cation along a direction forming an angle α with the z -axis give contributions like

$$\frac{\partial}{\partial z^2} (u_C + u_R) = (u_C'' + u_R'') \cos^2 \alpha + \frac{1}{r} (u_C' + u_R') \sin^2 \alpha \quad (35)$$

where one or two primes denote first- or second-order derivative with respect to interionic distance, respectively. The summation over all atoms yields $u_C' + u_R' = 0$ because of equilibrium. Taking into account that u_R and u_C are respectively proportional to $\exp(-r/\bar{\rho})$ and to r^{-1} , we get

$$\frac{\partial^2}{\partial z^2} (u_C + u_R) = \frac{u_R}{\bar{\rho}^2} \left(1 - \frac{2\bar{\rho}}{r_o} \right) \cos^2 \alpha, \quad (36)$$

where r_o is the nearest-neighbour (oxygen) distance. In order to perform an average on all the possible surface coordinations, we replace $\cos^2 \alpha$ with its mean value

$$\langle \cos^2 \alpha \rangle = \frac{2}{3} c_s, \quad (37)$$

where c_s is the average fractional coordination at the surface, and obtain

$$\delta \mu_s = -\frac{c_s z_o^2}{3 \bar{\rho}^2} \left(1 - \frac{2\bar{\rho}}{r_o} \right) u_R. \quad (38)$$

As the difference between Fe^{2+} and Co^{2+} ionic radii is small, we assume that c_s and δ are the same for the two ions. Within this approximation we get the simple expression

$$\Delta^{(2)} = -(1 - c_s^*) \Delta \mu^{(2)} \quad (39)$$

where the effect of surface strain is contained in the effective surface coordination c_s^* given by

$$\frac{c_s^*}{c_s} = 1 - \left(1 - \frac{2\bar{\rho}}{r_o} \right) \frac{z_o^2}{3\bar{\rho}^2}. \quad (40)$$

Unfortunately, we have no information around c_s and δ . In the near future the experimental knowledge of these parameters should be within reach of Extended X-Ray Absorption Fine Structure (EXAFS) analysis with synchrotron radiation and perhaps of Mössbauer spectroscopy. For the moment we are content with a qualitative discussion.

An upper limit of z_o is given by the overlap with the nearest-neighbour ions, defined as the difference between the sum of ionic radii and the nearest-neighbour distance, i.e. $z_o \leq r_+ + r_- - r_o$. For both Co^{2+} and Fe^{2+} the overlaps are of the order of 0.2 Å, which gives

$$c_s^* \cong 0.93 c_s.$$

We see that the effective surface coordination is a 7% smaller than c_s because of relaxation. A correspondent increase affects $\Delta^{(2)}$, which simply means that *surface strain favours segregation*. As concerns c_s , we note that in ideal surfaces it is usually larger than 1/2, but its value is reduced in presence of edges, vertices, steps, etc. Therefore in order to derive some numerical results we use $c_s^* = 1/2$, from which

$$\Delta^{(1)} = \Delta \mu_s^{(1)} - \Delta \mu^{(1)} \cong -\frac{1}{2} \Delta \mu^{(1)}. \quad (41)$$

We are now able to calculate the surface composition as function of the bulk composition. Hereafter it is convenient to consider the cobalt to iron ratios

$$\rho = \frac{1-y}{2+y} \quad \text{and} \quad \rho_s = \frac{1-y_s}{2+y_s}. \quad (42)$$

In Fig. 3 we plot ρ_s as function of ρ around the stoi-

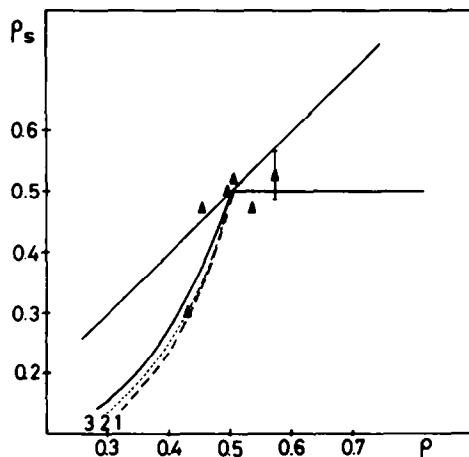


Fig. 3. Surface cobalt-to-iron ratio, ρ_s , vs the corresponding value in the bulk, ρ . The AES experimental values (Δ) are overimposed to the theoretical curves for both random and inverse spinel configurations and for two different temperatures.

chiometric ratio $\rho = 1/2$, for both the inverse and the random spinel configurations.

It appears that for iron excess ($\rho < 1/2$), the fractional amount of iron at the surface is quite larger than that in the bulk, while for cobalt excess very small deviations from stoichiometry are observed at the surface. Such behaviour is simply due to the fact that the ionic radius of Fe^{2+} is only slightly larger than that of Co^{2+} , whereas the radius of Co^{3+} is quite smaller than that of Fe^{3+} .

4. COMPARISON WITH EXPERIMENTAL RESULTS

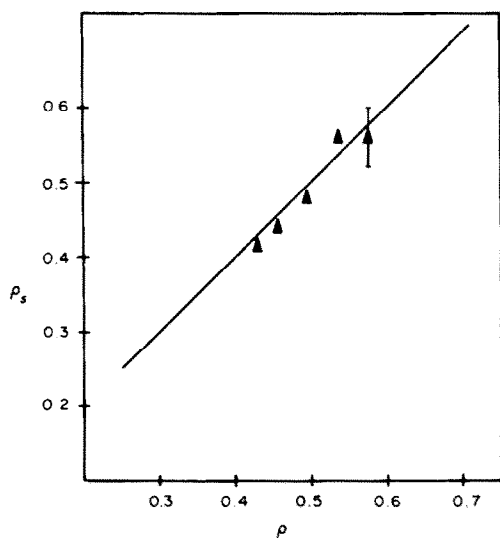
The cobalt ferrite samples were prepared by mixing proper quantities of Fe_2O_3 and CoCO_3 , at 1340 K for 12 hr [23]. The Auger analyses were performed at room temperature in a PHI LEED-AES system, equipped with a cylindrical mirror analyzer, a 5 keV integral electron gun and a 1 keV sputter ion gun at a base pressure 1.33×10^{-7} Pa. Details in experimental conditions and methods are given elsewhere [24].

The surface compositions were determined from the measured peak-to-peak heights in the $dN(E)/dE$ energy diagrams of the 510 eV peak of oxygen, 598 eV peak of iron and 775 eV peak of cobalt, with the method of elemental sensitivity factors [25]. In Table 2 we report for each sample the bulk Co/Fe ratio obtained from X-ray emission spectroscopy, the atomic surface analysis (in %) and the Co/Fe surface ratio. The presented values are the means on several measurements (up to 6) both on the same and different pellets for each bulk composition. In Fig. 3, together with the calculated curves, the experimental ρ_s are plotted. In Table 2 are also reported the Co/Fe ratio obtained by ion bombardment of the samples until a constant value was reached. The constant value of ρ was gradually achieved in an average time of 60 min.

The Co/Fe ratios obtained fit enough well with the expected straight line of the bulk composition, as it is shown in Fig. 4. Relative sputtering yields up to 900 eV are not available for Co and Fe, but the measurements made by Laegreid and Wehner [26] up to 600 eV indicate that it is reasonable to consider negligible an enrichment

Table 2. Experimental bulk and surface composition data

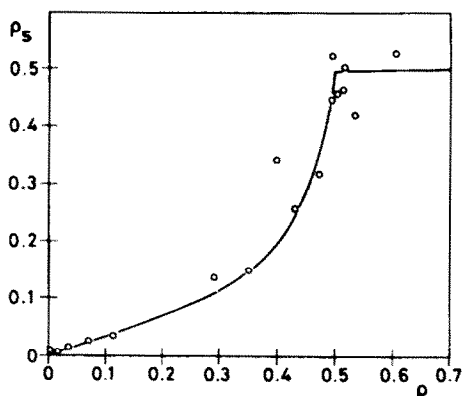
Sample	ρ	Surface composition			ρ_s	ρ_s (after sputtering)
		O (%)	Fe (%)	Co (%)		
1	0.43	59.2	31.5	9.3	0.30	0.42
2	0.455	57.3	28.9	13.8	0.48	0.44
3	0.495	57.5	28.3	14.2	0.50	0.48
4	0.505	57.3	28.0	14.7	0.52	n.d.
5	0.535	60.5	26.9	12.6	0.47	0.56
6	0.575	59.8	26.2	14.0	0.53	0.56

Fig. 4. Surface cobalt-to-iron ratio, ρ_s , vs the corresponding value in the bulk, ρ , after Ar^+ ion sputtering.

due to the ion bombardment. Therefore, we can assume the Auger compositions obtained after sputtering as the true bulk compositions.

The experimental values in Fig. 3 with their standard errors are all in agreement with the calculated curves (both inverse and random cation distribution in spinel structure at 1089 K) apart for the higher Co/Fe value for the sample No. 2. We cannot say if it is due to the intrinsic experimental difficulty to obtain good composition data by AES applied to this type of samples or to other causes, i.e. the imperfect preparation. It is apparent by this fact that, almost in a certain degree, the chosen preparation procedure gives samples in thermodynamic equilibrium.

We have made the Auger analysis also of several other samples obtained by coprecipitation at relatively low temperature ($T = 363$ K). The surface composition of these samples, apart from a few exceptions, exhibits the expected dependence on the bulk composition predicted by theory (Fig. 5). It is however evident that on the wide range from $\rho = 0$ to $\rho = 1/2$, we cannot expect to have a constant value for $\Delta^{(2)}$. We recall that in several similar crystals the intrinsic dependence of bulk inversion free enthalpy on the composition parameter y has been investigated [10]; it is found a linear dependence on y is

Fig. 5. Experimental surface composition vs bulk composition of coprecipitated samples of $\text{Co}_{1-y}\text{Fe}_{2+y}\text{O}_4$ all over the range $0 < \rho < 0.6$, and theoretical fitting (see text).

usually enough to give a good fit of the experimental data. Such a linearity seems to hold also for surface composition: indeed a good theoretical fit is obtained all over the range $0 < \rho < 1/2$ with

$$\Delta^{(2)}/kT = -2.07 + 1.41y. \quad (43)$$

The good fit indicates, with only few exceptions, a close correlation between bulk and surface composition, which means that also these coprecipitated samples are close to the equilibrium configuration.

These experimental data agree with the prediction that for the stoichiometric ferrite ($y = 0$) no surface segregation occurs ($y_s = 0$). This is related to the experimental observation that in all these samples the oxygen-to-cation ratio is close to the stoichiometric ratio, 1.33. In the subsequent paper we will show that surface segregation occurs also at $y = 0$ when the percentage of surface oxygen is altered by suitable treatments of the samples.

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