Synthetic spinels in the (Mg,Fe^{2+},Zn) $(Al,Fe^{3+})_2O_4$ system. II. Preliminary chemical and structural data of hercynite and magnesioferrite samples

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ABSTRACT. — Flux-grown spinel samples belonging to spinel s.s. – hercynite and spinel s.s. – magnesioferrite solid solutions were investigated by electron microprobe and single-crystal X-ray diffraction. Results confirmed the compositional homogeneity of the samples, and structural refinements gave final disagreement factors R ranging from 1.33 to 3.71%. The solid solution between spinel s.s. and hercynite is complete. The progressive substitution of Fe^{2+} for Mg does not affect the M-O distance (1.93 Å), but causes a T-O enlargement (from 1.92 to 1.97 Å) which is responsible for increments in both a_0 (from 8.0855 to 8.1646 Å) and u (from 0.2621 to 0.2642). The solid solution between spinel s.s. and magnesioferrite is incomplete at temperatures below 1000°C. Because of this, most of the samples examined belong to the spinel s.s. side, but the magnesioferrite end-member is also included. As a consequence of increasing Fe^{3+}, M-O increases linearly from 1.93 to 2.04 Å, whereas T-O remains almost constant. In this case, the a_0 variation (from 8.0855 to 8.3841 Å) is essentially due to the M-O increase, although $Fe^{3+} \leftrightarrow Al$ substitution involves both T and M sites.

RIASSUNTO. — Sono stati studiati mediante microsonda elettronica e diffrazione dei raggi X su cristallo singolo campioni di spinello sintetizzati tramite flux-growth ed appartenenti alle soluzioni solide spinello s.s. – ercinite e spinello s.s. – magnesioferrite. I risultati hanno confermato l'omogeneità composizionale dei campioni, mentre gli affinamenti strutturali hanno fornito valori dei fattori di disaccordo R variabili da 1.33 a 3.71%. La soluzione solida fra spinello s.s. ed ercinite è completa e la sostituzione progressiva di Fe^{2+} al posto del Mg non influenza la distanza M-O (1.93 Å), mentre determina un incremento di T-O (da 1.92 a 1.97 Å), che è responsabile dell'incremento sia di a_0 (da 8.0855 a 8.1646 Å) sia di u (da 0.2621 a 0.2642). La soluzione solida fra spinello s.s. e magnesioferrite è incompleta a temperature inferiori a 1000 °C. Per questo motivo la maggior parte dei campioni studiati appartiene al versante dello spinello s.s., ma è presente anche il termine estremo magnesioferrite. In conseguenza dell'incremento di Fe^{3+}, M-O cresce linearmente da 1.93 a 2.04 Å mentre T-O rimane circa costante. In questo caso l'aumento di a_0 (da 8.0855 a 8.3841 Å) è essenzialmente dovuto all'incremento di M-O, nonostante la sostituzione $Fe^{3+} \leftrightarrow Al$ coinvolga entrambi i siti T e M.

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Introduction

Spinels are a class of ubiquitous and important rock-forming minerals, and their widespread occurrence has long suggested their use as petrogenetic indicators (e.g., Spry and Scott, 1986). A large number of investigations on intracrystalline disorder in both natural and synthetic compounds has indicated their possible use for geothermometric purposes (e.g., Della Giusta et al., 1996; Lucchesi and Della Giusta, 1997; Princivalle et al., 1999).

Spinels are characterized by a very compact oxygen array with cations in tetrahedral (T) and octahedral (M) coordination and may be described by the $^{IV}(A_{1-i}B_i)^{VI}(B_{2-i}A_i)O_4$ structural formula, where IV and VI represent tetrahedrally- and octahedrally-coordinated sites, A and B are cations with variable valence, and i the inversion parameter. Normal spinels are those with $i = 0$ (e.g., $MgAl_2O_4$, $FeAl_2O_4$), inverse spinels those with $i = 1$, as $MgFe_2O_4$. A full discussion of spinel structure details was given by Hafner (1960) and Hill et al. (1979), and only the main features will be recalled in the following. The symmetry is cubic ($Fd3m$) with the single oxygen atom in the 32e position (3m point symmetry; u, u, u fractional coordinates); cations A and B are distributed in the tetrahedral and octahedral sites (8a, $\overline{4}$ 3m and 16d, $\overline{3}$ m symmetry, respectively, both with fixed coordinates). Modifications of T-O and M-O bond distances, to accommodate various chemical compositions and/or cation ordering, determine variations in cell edge a_0 and oxygen positional parameter u, according to the equations:

$$a_o = \left[5\,(T-O) + \sqrt{33\,(M-O)^2 - 8\,(T-O)^2}\right]\frac{8}{11\sqrt{3}} \quad (1)$$

$$u = \frac{\dfrac{3\,(M-O)^2}{4\,(T-O)^2} - 2 + \sqrt{\dfrac{33\,(M-O)^2}{16\,(T-O)^2} - \dfrac{1}{2}}}{6\left[\dfrac{(M-O)^2}{(T-O)^2} - 1\right]} \quad (2)$$

Complete knowledge of cation distribution is crucial for full understanding of spinel properties: satisfactory results have been obtained by combining information from very accurate microprobe analyses and single-crystal X-ray diffraction (Lucchesi and Della Giusta, 1997; Lucchesi et al., 1998a, b, 1999). To exploit these data fully, the availability of an accurate and self-consistent set of bond distances specific for this class of oxides is fundamental. Improvements to the basic set of Shannon and Prewitt (1969) have been made by several authors (e.g., O'Neill and Navrotsky, 1983; Marshall and Dollase, 1984). Della Giusta et al. (1996), analysing a large number of spinels, recently proposed a whole self-consistent set of bond-distances relative to Mg, Al, Fe^{2+}, Fe^{3+} and Cr for octahedral and tetrahedral coordination. However, the presence of minor elements in natural spinels means that the fine details of spinel geometry are difficult to identify clearly. To overcome this disadvantage, synthetic single crystals with suitable composition were produced (Andreozzi 1999). This paper presents preliminary results of their crystal-chemical characterization.

Experimental

A flux growth method was used to obtain high-quality spinel crystals in the compositional field (Mg,Fe^{2+},Zn) $(Al,Fe^{3+})_2O_4$. Starting materials consisted of analytical grade MgO, ZnO, Fe_2O_3 and $Al(OH)_3$ powders, dehydrated and dried at 1000°C for 12 h before being mixed with $Na_2B_4O_7$, used as flux. About 5 g of material were thoroughly ground and mixed under acetone in an agate mortar and then transferred to a 10-cc platinum crucible with a lid. The mixtures were melted at 1200 °C either in air in a muffle furnace or in reduced conditions in a vertical furnace equipped with a multi-step temperature controller, and then cooled at linear rates of 1-4°C per hour to temperatures as low as 800°C (Andreozzi, 1999). The crucibles and contents were then removed and allowed to cool to

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TABLE 1

Parameters for X-ray data collection.

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Unit cell parameter determination:
Radiation (Å) — Mo-Kα_1 (0.70930)
Reflections used — 12 (Friedel pairs on both + 2θ and -2θ)
Range (2θ) — 83°-92°
Temperature (K) — 296

Diffraction intensity collection:
Radiation (Å) — Mo-Kα (0.71073)
Monochromator — High crystallinity graphite crystal
Range (2θ) — 3°-95°
Reciprocal space range — $0 \leq h,k,l \leq 17$
Scan method — ω
Scan range (2θ) — 2.4°
Scan speed (2θ/min) — Variable 2.93°-29.30°
Temperature (K) — 296

Data reduction:
Refinement — SHELXTL-PC
Corrections — Lorentz, Polarization
Absorption correction — Semi-empirical, 13 Ψscans (0°-95° 2θ)

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TABLE 2

Crystal data and results of crystal structure refinement of samples belonging to spinel s.s. – hercynite series.

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Sample	SP3/10a	He3a/b	He4b/d	He6a/e	He8a/h	He9a/h	He100c/a
a_0 (Å)	8.0855(2)	8.0937(3)	8.1071(3)	8.1221(3)	8.1406(3)	8.1494(4)	8.1646(3)
u	0.26213(5)	0.26215(5)	0.26278(5)	0.26308(5)	0.26362(6)	0.26377(7)	0.26416(8)
T-O (Å)	1.9204(4)	1.9227(4)	1.9347(4)	1.9425(4)	1.9545(5)	1.9588(6)	1.9679(7)
M-O (Å)	1.9283(4)	1.9301(4)	1.9287(4)	1.9301(4)	1.9307(5)	1.9317(6)	1.9325(7)
T m.a.n.	11.99(10)	13.87(9)	15.99(8)	18.32(10)	21.20(11)	22.64(18)	24.57(17)
M m.a.n.	12.82(7)	12.81(5)	13.00(4)	13.26(5)	13.67(4)	13.95(6)	14.55(7)
U_{11}T (Å^2×10^4)	42(2)	52(2)	54(1)	61(1)	65(1)	76(1)	78(1)
U_{11}M (Å^2×10^4)	43(2)	41(1)	44(1)	44(1)	42(1)	51(1)	50(2)
U_{11}O (Å^2×10^4)	75(2)	81(1)	80(1)	84(1)	87(1)	97(2)	99(2)
R (%)	3.71	2.65	1.68	1.68	1.75	2.66	2.31
N° reflections	147	147	147	149	149	149	149

Estimated standard deviation (±1σ) in brackets; m.a.n. = mean atomic number.

room temperature. Sodium borate flux was removed by dissolution in hot dilute hydrochloric acid, and spinel crystals were hand-picked under a binocular microscope. The products consisted of transparent, variously coloured octahedra approximately 0.1-1.0 mm across. The amounts of spinel recovered from each run ranged from 50 to 150 mg, corresponding to some hundred single crystals. The largest crystals sometimes contained imperfections, cracks and inclusions, whereas medium-sized to small crystals generally

TABLE 3

Chemical composition of samples belonging to spinel s.s. – hercynite series.
Average of eight to fourteen electron microprobe analyses.

Sample	SP3/10a	He3a/b	He4b/d	He6a/e	He8a/h	He9a/h	He100c/a
FeO_{tot}	–	5.4(1)	13.7(3)	22.6(5)	33.0(3)	38.0(4)	44.7(2)
MgO	28.5(3)	24.7(4)	19.3(2)	13.8(3)	7.34(8)	4.2(2)	0.03(2)
Al_2O_3	71.0(3)	69.6(5)	66.8(2)	63.4(3)	59.8(1)	58.0(3)	55.5(4)
Total	99.5	99.7	99.8	99.8	100.1	100.2	100.2
FeO_{calc}	–	5.0(4)	13.0(3)	20.9(4)	30.4(1)	35.0(3)	40.9(2)
Fe_2O_{3calc}	–	0.4(4)	0.8(3)	1.9(3)	2.9(3)	3.3(4)	4.2(3)
Total	99.5	99.7	99.9	100.0	100.4	100.5	100.6
Cations on basis of 4 oxygens							
Fe^{2+}	–	0.102(9)	0.274(6)	0.459(9)	0.699(3)	0.825(7)	0.999(1)
Mg	1.011(6)	0.90(1)	0.726(6)	0.541(9)	0.301(3)	0.175(7)	0.001(1)
Al	1.992(4)	1.99(1)	1.984(5)	1.963(6)	1.941(6)	1.929(9)	1.908(6)
Fe^{3+}	–	0.008(8)	0.016(5)	0.037(6)	0.059(6)	0.071(9)	0.092(6)
Total	3.003	3.000	3.000	3.000	3.000	3.000	3.000

Estimated standard deviation (±1σ) in brackets.

TABLE 4

Crystal data and results of crystal structure refinement of samples belonging to spinel s.s. –
magnesioferrite series.

Sample	SP3/10a	MgF1a/6c	MgF2c/12a	MgF100f/fa
a_0 (Å)	8.0855(2)	8.1199(4)	8.1758(3)	8.3841(3)
u	0.26213(5)	0.26181(6)	0.26093(4)	0.25652(8)
T-O (Å)	1.9204(4)	1.9241(8)	1.9249(6)	1.9099(15)
M-O (Å)	1.9283(4)	1.9388(4)	1.9587(3)	2.0428(8)
T m.a.n.	11.99(10)	13.62(8)	15.74(4)	24.49(29)
M m.a.n.	12.82(7)	13.62(4)	14.86(3)	20.07(18)
$U_{11}T(Å^2×10^4)$	42(2)	46(2)	46(1)	31(1)
$U_{11}M(Å^2×10^4)$	43(2)	41(1)	50(1)	37(1)
$U_{11}O(Å^2×10^4)$	75(2)	80(2)	89(1)	48(2)
R (%)	3.71	2.32	1.33	2.47
N° reflections	147	149	149	164

Estimated standard deviation (±1σ) in brackets; m.a.n. = mean atomic number.

appeared to be of gem quality, homogeneous and inclusion-free. Some of these high-quality crystals were selected for X-ray study.

Small equidimensional fragments of the crystals were selected, cemented on a glass capillary and mounted, for X-ray data collection, on a Siemens P4 automated four-circle single-crystal diffractometer.

Experimental conditions are listed in Table 1 and further details may be found in Lucchesi *et al.* (1997).

Unit cell parameters (Tables 2 and 4) were obtained after centering 12 independent reflections, and their Friedel pairs were chosen in the 83° < 2θ < 92° range on both sides of the direct beam, with MoKα₁ radiation (λ = 0.70930 Å). One-eighth of the reciprocal space was examined within the range 3° - 95° 2θ, for intensity collection, with the continuous ω scan method and 2.4° fixed scan range at 296 K, with MoKα radiation (λ = 0.71073 Å), monochromatized with a high-crystallinity graphite crystal. Scan speed was variable, from 2.93° to 29.30° 2θ/min., depending on reflection intensity, estimated with a pre-scan. Background was measured with a stationary counter and crystal at the beginning and end of each scan, in both cases for half the scan time. Three standard reflections were monitored every 47 measurements.

The SHELXTL-PC program package allowed data reduction. Intensities were corrected for polarization and Lorentz effects. Absorption was corrected with a semi-empirical method, using intensities from the ψ-scans of 13 non-equivalent reflections collected in the range 10° - 90° 2θ. Reflections with I > 2σ(I) were considered as observed and the original set of 624 data was reduced to 147-149 independent reflections. No significant deviations from *Fd*3*m* symmetry were noted: the appearance of forbidden space-group reflections such as {200} was attributed, on the basis of ψ-scan checks, to double reflections (Tokonami and Horiuchi, 1980). Variable parameters were scale factor, oxygen coordinate, mean atomic numbers (m.a.n.) of T and M sites, isotropic secondary extinction coefficient and thermal factors (Tables 2 and 4). The starting oxygen coordinate was that proposed by Princivalle *et al.* (1989), setting the origin at $\bar{3}m$. Isotropic secondary extinction was corrected according to Larson's (1970) algorithm. No chemical constraints were used during refinement. Fully ionized scattering curves for all elements were used, since they

proved to furnish the best values of conventional agreement factors over all sinθ/λ intervals and the best coherence between observed and calculated F(222), the latter structure factor only being sensitive to M and O site occupancies. This combination gave satisfactory agreement (within 1%) between total m.a.n. values obtained by structural refinement and electron microprobe analysis. Off-diagonal thermal factors were extremely small and of the same magnitude as their σ, when not forced to zero by symmetry, and thus only U_{11} are reported. Three cycles of isotropic refinement were followed by anisotropic cycles until convergence. The R values were very satisfactory (Tables 2 and 4).

It has been already observed (Andreozzi, 1999) that the chemical composition of flux-grown crystals often deviates from the starting oxide mixture, so that the former needs to be analytically determined. After X-ray data collection, the crystals were mounted on glass slides and polished for electron microprobe analysis on a Cameca-Camebax instrument (WDS method) with the PAP data reduction program. Instrumental and analytical details are reported in Lucchesi *et al.* (1997). No fewer than eight point analyses for each sample were performed to check for homogeneity. Synthetic oxide standards (MgO, FeO, Al₂O₃) were used, and a synthetic MgAl₂O₄ spinel served as a reference. The absence of boron was confirmed by nuclear reaction analysis (alpha particle emission stimulated by a proton beam) of SP3 crystals (Kristiansson *et al.*, 1999). Fe^{2+} and Fe^{3+} contents were calculated on the basis of the spinel formula with 3 cations for 4 oxygens (Tables 3 and 5).

RESULTS

The synthetic crystals investigated here represent spinel s.s. – hercynite (samples He) and spinel s.s. – magnesioferrite (samples MgF) solid solutions. Sample SP3/10a, which represents the spinel s.s. end-member and the common start of both series, is colourless;

TABLE 5

Chemical composition of samples belonging to spinel s.s. – magnesioferrite series. Average of eight to fourteen electron microprobe analyses.

Sample	SP3/10a	MgF1a/6c	MgF2c/12a	MgF100f/fa
FeO_{tot}	–	10.31(2)	26.0(9)	72.6(5)
MgO	28.5(3)	26.36(2)	24.7(2)	19.0(2)
Al_2O_3	71.0(3)	60.19(3)	46.5(9)	–
Total	99.5	96.86	97.2	91.6
FeO_{calc}	–	0.38(2)	1.2(3)	1.6(3)
Fe_2O_{3calc}	–	11.04(2)	27.6(9)	78.9(5)
Total	99.5	97.96	100.0	99.5
Cations on basis of 4 oxygens				
Fe^{2+}	–	0.008(5)	0.025(7)	0.044(8)
Mg	1.011(6)	0.992(5)	0.975(3)	0.956(8)
Al	1.992(4)	1.791(6)	1.450(5)	–
Fe^{3+}	–	0.210(5)	0.550(7)	2.000(1)
Total	3.003	3.001	3.000	3.000

Estimated standard deviation ($\pm 1\sigma$) in brackets.

hercynite samples are variously coloured, from pale lilac to sky blue, deep green and black. Magnesioferrite samples show a smaller variety of colours, ranging from reddish-brown to dark brown and black.

The crystals compare well with natural spinels in terms of quality of diffraction effects, and have the advantage of being simple and controlled in their composition. No indications of cation vacancies were found by comparison of structural and chemical data, since both total m.a.n. and total number of electrons from chemical analysis are in agreement with stoichiometry (Tables 2-5).

$MgAl_2O_4$ - $Fe^{2+}Al_2O_4$

All samples in the $MgAl_2O_4$ - $Fe^{2+}Al_2O_4$ solid solution were found to be chemically homogeneous. Their chemical composition is dominated by the $Fe^{2+} \leftrightarrow Mg$ substitution, which is complete through the solid solution (Table 3). Minor Fe^{3+} up to 0.09 atoms per formula unit (apfu) is present, substituting for Al. Fe^{3+} contents increase with total Fe, and the calculated Fe^{3+}/Fe^{2+} ratios are in full agreement with Mössbauer data (work in progress).

Both structural parameters a_0 and u increase linearly with the hercynite molar fraction, i.e., with Fe^{2+} content (fig. 1). Among bond distances, M-O remains almost constant, ranging from 1.928 to 1.933 Å, whereas T-O shows the largest variation, increasing linearly with Fe^{2+} from 1.920 to 1.968 Å (fig. 2). As a consequence, the a_0 variation from 8.0855 to 8.1646 Å is essentially due to the T-O increase. As well as bond distances, both T and M m.a.n. increase at different rates with respect to hercynite contents: that is, the M m.a.n. increase is limited, from 12.82 to 14.55, whereas that of T m.a.n. almost doubles from spinel s.s. to hercynite, values being 11.99 and 24.57, respectively (Table 2).

$MgAl_2O_4$ - $MgFe^{3+}_2O_4$

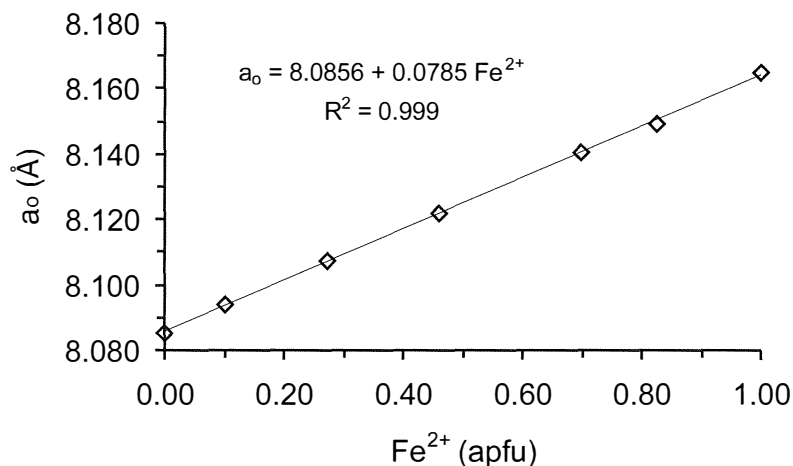The magnesioferrite samples are chemically homogeneous and characterized by the

Fig. 1a – Linear correlation between cell parameter a_0 and Fe^{2+} contents in samples belonging to spinel s.s. – hercynite series. Solid line shows best fit with experimental data. Symbol dimensions: approx ±1σ.
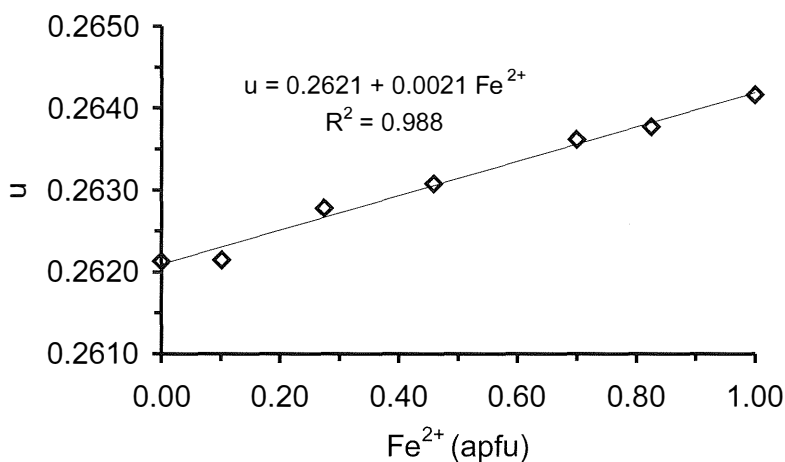
Fig. 1b – Linear correlation between oxygen positional parameter u and Fe^{2+} contents in samples belonging to spinel s.s. – hercynite series. Solid line shows best fit with experimental data. Symbol dimensions: approx ±1σ.

substitution $Fe^{3+} \leftrightarrow Al$ (Table 5). The very small substitution of Fe^{2+} for Mg indicated by electron microprobe analysis is not always in agreement with Mössbauer data and therefore needs to be confirmed by further investigations (work in progress). The synthetic samples do not cover the entire solid solution between spinel s.s. and magnesioferrite because of the miscibility gap existing at low temperature (Lehmann and Roux, 1986; Turnock and Eugster, 1962). In fact, we obtained crystals with magnesioferrite contents up to 30% and then the magnesioferrite end-member (Andreozzi, 1999). Sample MgF2c/12a is close to the upper limit of the spinel side because it contains 0.55 apfu of Fe^{3+}, i.e., 27.5% magnesioferrite (Table 5).

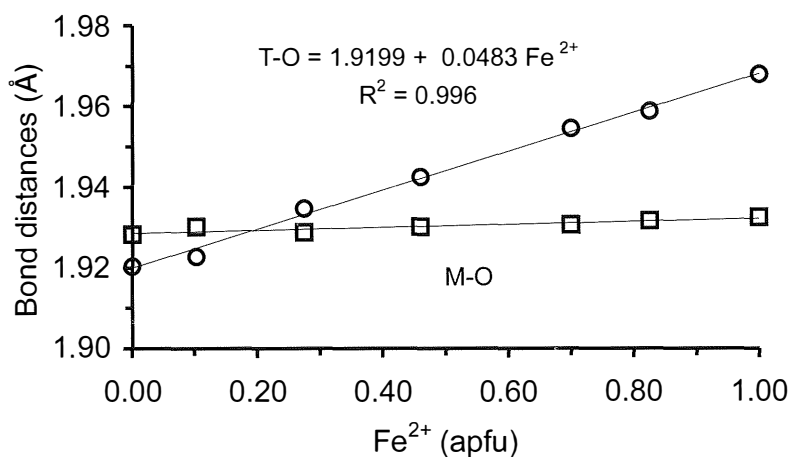Cell parameter a_0 linearly increases with the

Fig. 2 – Linear correlations between bond distances and Fe^{2+} contents in samples belonging to spinel s.s. – hercynite series. Solid lines show best fit with experimental data. Symbol dimensions: approx ±2σ.

magnesioferrite molar fraction, i.e., with Fe^{3+} contents, whereas oxygen positional parameter u linearly decreases (fig. 3). This is in agreement with literature data, and the values measured for a_0 in our samples are in excellent agreement with those calculated using the linear equation of Sharma et al. (1973). Among bond distances, although T-O shows a slight shortening from spinel s.s. (1.920 Å) to magnesioferrite (1.909 Å) with a peak in between (1.925 Å, sample MgF2c), it is close to remaining constant, whereas M-O shows the largest variation, increasing linearly with Fe^{3+} from 1.928 to 2.043 Å (fig. 4). In this case, the a_0 variation (from 8.0855 to 8.3841 Å) is essentially due to M-O increase. Both T and M m.a.n. increase with magnesioferrite contents, more markedly in T site than in M site, values ranging from 11.99 to 24.49 and from 12.82 to 20.07, respectively (Table 4), suggesting partitioning of Fe^{3+} in both T and M sites.

DISCUSSION

Both spinel s.s. and hercynite are normal spinels, meaning that at low temperature inversion i is close to zero (Harrison et al., 1998; Andreozzi et al., 2000). Consequently,

Mg and Fe^{2+} are essentially ordered in T site and Al is ordered in M site, according to the ideal crystal-chemical formula $^{IV}(Mg, Fe^{2+})^{VI}(Al)_2O_4$. Because of this, along the spinel s.s. – hercynite series the chemical substitution $Fe^{2+} \leftrightarrow Mg$ principally involves T site. The observed T-O increase towards hercynite may be explained according to the difference between $^{IV}Fe^{2+}$ and ^{IV}Mg cation-to-oxygen distances, i.e., 1.996 and 1.964 Å, respectively (bond distances from Lucchesi et al., 1997). The small increase in the M-O bond distance (fig. 2) may be due to the very slight $Fe^{3+} \leftrightarrow Al$ substitution, since bond distance $^{VI}Fe^{3+}$-O is larger than that of ^{VI}Al-O (2.020 and 1.909 Å, respectively). For hercynite contents of about 20%, T-O and M-O bond distances take on the same value, about 1.93 Å (fig. 2), and the corresponding u value is 0.2625, in agreement with geometrical requirements in spinel structure. This value is in fact independent of spinel bulk chemistry, being only dependent on structural geometry, and $u = 0.2625$ is the limit value of equation (2) when T-O and M-O tend to the same value, whatever it may be. In the spinel s.s. – magnesioferrite series, u is relatively close to 0.2625 only for sample SP3 (which shows comparable T-O and M-O distances) and
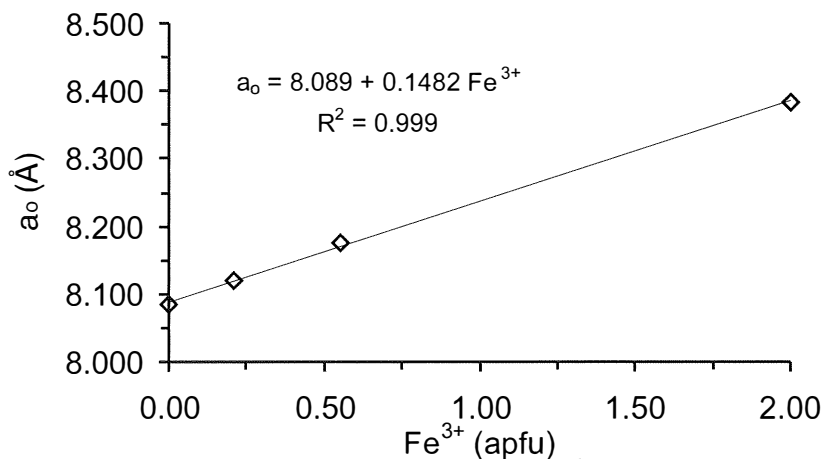
Fig. 3a – Correlation between cell parameter a_0 and Fe^{3+} contents in samples belonging to spinel s.s. – magnesioferrite series. Solid line shows best fit with experimental data. Symbol dimensions: approx ±2σ.
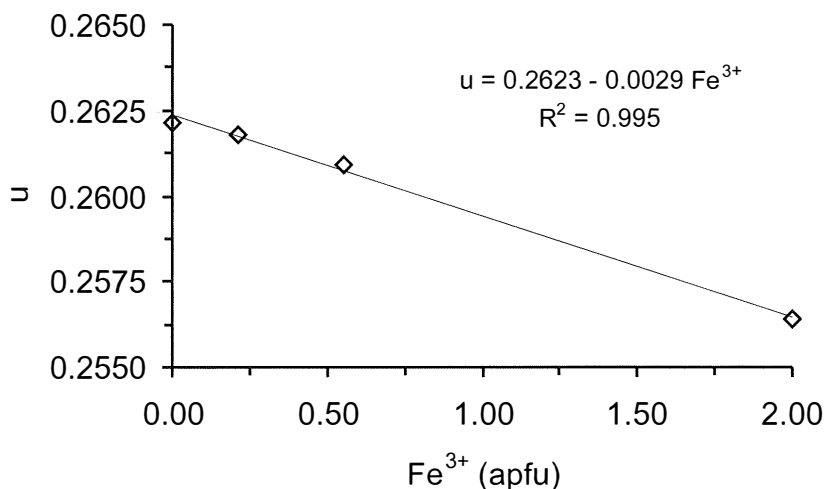

Fig. 3b – Correlation between oxygen positional parameter u and Fe^{3+} contents in samples belonging to spinel s.s. – magnesioferrite series. Solid line shows best fit with experimental data. Symbol dimensions: approx ±2σ.

progressively deviates from this value in all the other samples, for which the two bond distances become very different (fig. 4).

The magnesioferrite end-member is an inverse spinel, meaning that at low temperature inversion i is very close to 1 (O'Neill *et al.*, 1992). Consequently, half the Fe^{3+} is ordered in T site and the other half in M site, together with Mg, according to the ideal crystal-chemical formula $^{IV}(Fe^{3+})^{VI}(MgFe^{3+})O_4$. If this inverse character is also maintained when magnesioferrite forms a solid solution with spinel s.s., chemical substitution $Fe^{3+} \leftrightarrow Al$ all along the series must involve both T and M sites. With this in mind, enlargement of M site towards magnesioferrite may easily be explained by substitution of Mg and Fe^{3+} for Al, since in spinels both ^{VI}Mg-O and $^{VI}Fe^{3+}$-O
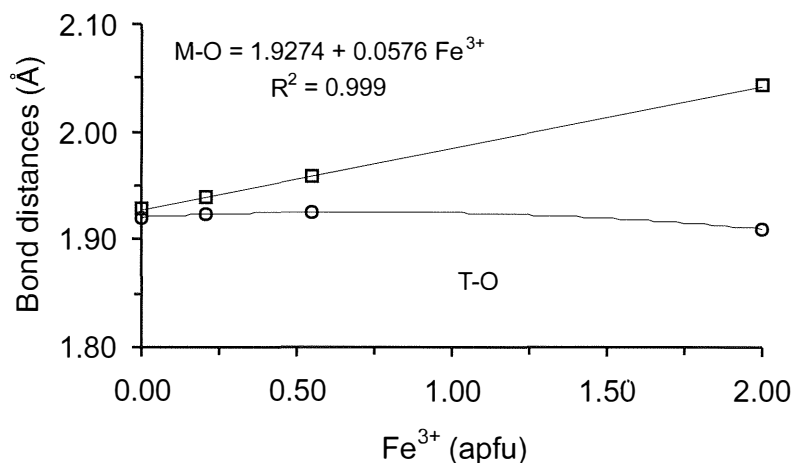
Fig. 4 – Correlations between bond distances and Fe^{3+} contents in samples belonging to spinel s.s. – magnesioferrite series. Solid lines show best fit with experimental data. Symbol dimensions: approx $\pm 2\sigma$.
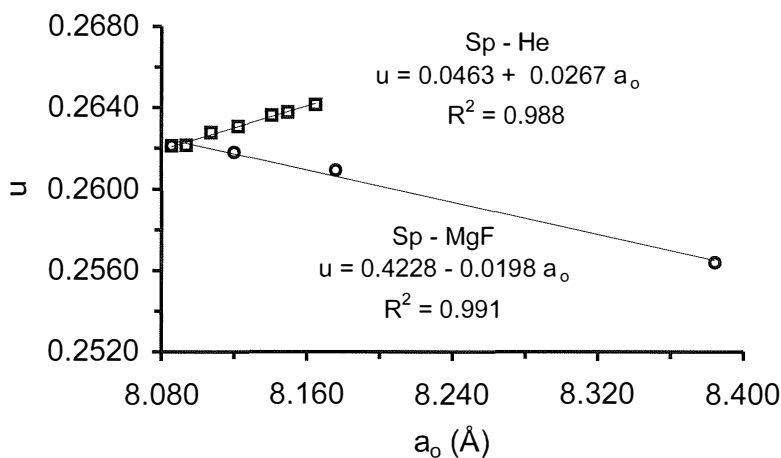

Fig. 5 – Correlations between oxygen positional parameter u and cell parameter a_O in samples belonging to the series spinel s.s. – hercynite (Sp – He) and spinel s.s. – magnesioferrite (Sp – MgF). Solid lines show best fit with experimental data. Symbol dimensions: approx $\pm 2\sigma$.

bond distances are larger than that of ^{VI}Al-O. Similarly, contraction of T site in the magnesioferrite end-member may be explained by substitution of $^{IV}Fe^{3+}$ for ^{IV}Mg, because the former has a smaller bond distance than the latter (Lucchesi *et al.*, 1997). Instead, the small expansion of T site in the first half of the series (fig. 4) cannot be explained only by

substitution of $^{IV}Fe^{3+}$ for ^{IV}Mg. Because of the temperatures involved in the flux growth process, a certain degree of inversion, i.e., of cation disorder, must be considered for our spinel samples. According to literature data, inversion expected at 800°C (the closure temperature recorded by most of our crystals) is about 23% for spinel s.s. and 75% for

magnesioferrite end-members (Andreozzi *et al.*, 2000; O'Neill *et al.*, 1992). In addition, the influence of the second coordination sphere on T-site bond distance must be taken into account, because it has recently been shown that the presence of Fe^{3+} in the M site of franklinite causes an increase in the $^{IV}Zn-O$ distance (Lucchesi *et al.*, 1999).

It is well-known that, in spinels, the two structural parameters a_0 and u are independent and mainly influenced by chemical composition and cation distribution, respectively. Nevertheless, when the thermal history is the same for all samples and chemical composition varies progressively along a binary join, as in this case, the two parameters show a very good linear correlation (fig. 5). The opposite slope taken by the equations in the two series is noteworthy, and is justified by the normal and inverse characters of hercynite and magnesioferrite samples, respectively.

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