

Crystal structure of monoclinic ilvaite and the nature of the monoclinic-orthorhombic transition at high pressure

L. W. Finger and R. M. Hazen

Geophysical Laboratory, Carnegie Institution of Washington,
Washington, DC 20008, USA

Dedicated to the memory of Martin J. Buerger

Received: November 10, 1986

Ilvaite / Crystal structure / Phase transition

Abstract. Crystal structures of monoclinic ilvaite from Elba, Italy, and Seriphos, Greece, have been refined and an $\text{Fe}^{2+} - \text{Fe}^{3+}$ order parameter has been related to the monoclinic angle β . Lattice constants have been determined as a function of pressure in a diamond-anvil cell. At high pressure the β -angle decreases and the structure becomes orthorhombic. This transition, which is not first order, may be described as a λ -point, which has both order-disorder and displacive character. The electron disorders at the λ -point; however, there is residual short-range order above this point. One consequence is that the transition conditions observed by calorimetry are not necessarily the same as those of crystallography.

Introduction

Ilvaite, $\text{CaFe}^{3+}\text{Fe}_2^{2+}\text{Si}_2\text{O}_8(\text{OH})$ (previously known as lievrite), typically occurs as a late mineral in Ca–Fe–Si scarn deposits (Burt, 1972) or as an alteration product (Nasland et al., 1983). The structure of the mineral was studied by Takéuchi (1948) and Ito (1950), who proposed an incorrect model with distinct SiO_4 groups. Belov and Mokeeva (1954) found the correct basic structure, which contains Si_2O_7 dimers. The structure was further investigated by Beran and Bittner (1974) with X-ray film intensities and by Haga and Takéuchi (1976) with single-crystal neutron intensities. All above studies have assumed the symmetry to be orthorhombic, space

group *Pbnm*, even though high resolution powder studies (Bartholomé et al., 1968; and Dietrich, 1972) show the existence of a monoclinic polymorph of the mineral. In fact, the sample studied by Haga and Takéuchi (1976) has an angle of 90.18° (Takéuchi, personal communication, 1982).

The monoclinic symmetry was recognized by Finger et al. (1982) in a preliminary report of this study, and further refined by Takéuchi et al. (1983), Ghose et al. (1984a) and Ghose et al. (1985). The correct space group for most, if not all, ilvaite at room conditions is $P2_1/a$, which is a subgroup of *Pnam*, a reorientation of *Pbnm*.

Crystal structure refinement

Samples

Ilvaite selected for this study include samples from Elba, Italy (Dartmouth College No. DP631-7) and from Seriphos, Greece (National Museum of Natural History, Smithsonian Institution, Specimen No. B15334). The Elba sample has been studied by Ghose et al. (1985). A Seriphos sample obtained from the Harvard collection was used by Ghose et al. (1984a, b). This ilvaite has a larger β -angle at room conditions than found in the present study and it is, therefore, believed to be a different specimen.

Electron microprobe examination of the two samples resulted in the following chemical formulas: $\text{CaFe}_{2.73}\text{Al}_{0.12}\text{Mn}_{0.07}\text{Mg}_{0.04}\text{Si}_2\text{O}_8(\text{OH})$ for the Elba sample and $\text{CaFe}_{2.92}\text{Al}_{0.01}\text{Mn}_{0.02}\text{Mg}_{0.02}\text{Si}_2\text{O}_8(\text{OH})$ for the Seriphos sample.

Intensity collection and refinement

Prismatic crystals of the two samples were mounted on an automated Picker four-circle diffractometer equipped with a Mo X-ray tube ($\lambda = 0.70930 \text{ \AA}$). Lattice constants were refined from reflections ($37^\circ \leq 2\theta \leq 58^\circ$) centered using the eight-reflection centering technique of King and Finger (1979), which corrects the observed angles for many of the systematic errors. At this stage, no symmetry constraints were applied and a triclinic cell was determined. Two of the angles deviated from 90° by less than 0.01° , which is on the order of 2σ . The third angle was more than 15σ from 90° ; therefore, the symmetry was clearly monoclinic rather than orthorhombic. The deviations are of the order of tenths of a degree; thus it is understandable that the early studies failed to detect the correct symmetry. The monoclinic lattice constants (Table 1) were refined using the method of Ralph and Finger (1982).

Intensity data were measured for a hemisphere of reciprocal space to $60^\circ 2\theta$ using Nb-filtered Mo radiation with an ω scan technique. The integrated intensities were corrected for the Lorentz-polarization and

Table 1. Crystal data for Elba and Seriphos ilvaites.

Parameter	Elba	Seriphos
a , Å	13.0103(5) ^a	13.0056(6)
b , Å	8.8039(4)	8.7976(5)
c , Å	5.8517(3)	5.8539(5)
β , deg.	90.209(5)	90.105(6)
V , Å ³	670.26(6)	669.79(8)
Crystal size, mm	0.20 × 0.16 × 0.10	0.25 × 0.17 × 0.08
μ , cm ⁻¹	76.6	74.3
R	0.032	0.041
wR	0.040	0.034
No. obs. $I > 2\sigma_I$	1735	1598

^a Number in parentheses is the estimated standard deviation (1σ) and refers to the last decimal place quoted. This convention applies to all following tables.

absorption effects with the program of Burnham (1966) and the symmetry related structure factors were averaged. The numbers of observed reflections, crystal sizes and linear absorption coefficients are shown in Table 1.

Crystal structure refinements were accomplished with program RFINE4 (Finger and Prince, 1975). The initial model for the Elba sample was formed by relaxing the mirror symmetry perpendicular to the c -axis of the orthorhombic pseudosymmetry as described by Finger et al. (1982). Neutral scattering factors and anomalous scattering factors were taken from *International Tables for X-ray Crystallography*, Volume IV (1974). The list of refined parameters included anisotropic thermal coefficients for all atoms but hydrogen, positional coordinates, and an isotropic extinction coefficient. The final R -factors are listed in Table 1 and the refined atomic coordinates are presented in Table 2. Anisotropic thermal parameters are presented in Table 3 and principal axes are in Table 4. The longest axis of the ellipsoid tends to be parallel to the c -axis, as would be expected from the $\text{Fe}^{2+} - \text{Fe}^{3+}$ disorder. In addition, twinning associated with previous transitions from the high-temperature orthorhombic state would also contribute to this effect.

Discussion

In the orthorhombic structure, there are mirror planes perpendicular to the c -axis at heights of $1/4$ and $3/4$. The seven-coordinated calcium, one six-coordinated iron, both silicon atoms, five of the oxygens and the hydrogen atom are located on this mirror plane with Wyckoff position (4c). One octahedral cation and two oxygens are not on the mirror plane and have Wyckoff position (8d). In the monoclinic form, the mirror symmetry is

Table 2. Refined atomic coordinates and equivalent isotropic temperature factors for Elba and Seriphos ilvaïtes.

Atom	x	y	z	B_{eq}^a
M(11) ^b	0.89013(3) ^c	0.05000(5)	0.00784(8)	0.44(1)
	0.89012(5)	0.05043(7)	0.00783(10)	0.63(1)
	0.8890(10)	0.0494(19)	0.0095(19)	0.63
M(12)	0.88998(3)	0.05172(5)	0.49229(8)	0.41(1)
	0.89007(5)	0.05136(7)	0.4922(1)	0.60(1)
	0.8900(9)	0.0548(18)	0.4903(20)	0.63
M(2)	0.94089(4)	0.74010(5)	0.24895(8)	0.45(1)
	0.94103(4)	0.74039(7)	0.2494(1)	0.59(1)
	0.9406(7)	0.7396(10)	0.2481(25)	0.00
Ca	0.81281(5)	0.37031(7)	0.75233(11)	0.46(1)
	0.81271(6)	0.37021(9)	0.7512(2)	0.63(1)
	0.8092(16)	0.3662(19)	0.7558(52)	1.63
Si(1)	0.95957(7)	0.3688(1)	0.2494(2)	0.26(1)
	0.95961(9)	0.3690(1)	0.2496(2)	0.43(2)
	0.9585(16)	0.3669(25)	0.2451(59)	1.57
Si(2)	0.67938(6)	0.2273(1)	0.2516(2)	0.27(1)
	0.67938(9)	0.2272(1)	0.2508(2)	0.46(2)
	0.6785(17)	0.2260(23)	0.2464(60)	1.57
O(1)	0.0098(2)	0.0295(3)	0.7397(4)	0.69(4)
	0.0097(2)	0.0300(3)	0.7453(5)	0.89(5)
	0.0085(13)	0.0306(19)	0.7309(35)	1.57
O(21)	0.9370(2)	0.2726(3)	0.0164(4)	0.45(3)
	0.9367(2)	0.2723(4)	0.0172(5)	0.60(4)
	0.9348(15)	0.2736(33)	0.0106(34)	1.57
O(22)	0.9356(2)	0.2728(3)	0.4826(4)	0.43(3)
	0.9360(2)	0.2727(4)	0.4823(5)	0.66(4)
	0.9363(14)	0.2751(36)	0.4795(33)	1.57
O(3)	0.7775(2)	0.1096(3)	0.2544(4)	0.43(3)
	0.7776(2)	0.1095(4)	0.2527(5)	0.64(4)
	0.7770(11)	0.1098(15)	0.2545(39)	1.57
O(41)	0.6709(2)	0.3281(3)	0.0188(4)	0.51(3)
	0.6707(2)	0.3293(4)	0.0190(5)	0.61(4)
	0.6721(18)	0.3277(28)	0.0191(34)	1.57
O(42)	0.6703(2)	0.3309(3)	0.4819(4)	0.50(3)
	0.6708(2)	0.3301(4)	0.4818(5)	0.61(4)
	0.6709(17)	0.3320(29)	0.4771(33)	1.57
O(5)	0.5852(2)	0.1007(3)	0.2528(4)	0.47(3)
	0.5852(2)	0.1009(3)	0.2509(5)	0.54(4)
	0.5854(11)	0.1004(16)	0.2605(38)	1.57
O(6)	0.6020(2)	0.0260(3)	0.7515(4)	0.64(4)
	0.6013(2)	0.0260(3)	0.7511(5)	0.79(5)
	0.6006(11)	0.0214(17)	0.7543(37)	1.57

Table 2. (Continuation)

Atom	x	y	z	B_{eq}^a
O(7)	0.7978(2)	0.1097(3)	0.7453(4)	0.40(3)
	0.7979(3)	0.1092(4)	0.7478(5)	0.77(5)
	0.7963(13)	0.1069(16)	0.7492(38)	1.57
H	0.753(4)	0.090(7)	0.754(10)	0.6(12) ^c
	0.740(5)	0.068(7)	0.756(12)	0.1(13)
	0.7355(23)	0.0621(33)	0.7402(73)	3.06

^a B_{eq} is the isotropic temperature factor equivalent to the refined anisotropic ellipsoid.

^b The order of entries is: Elba, this study; Seriphos, this study; and Seriphos, Ghose et al. (1984).

^c Only an isotropic temperature factor was refined for H.

relaxed and the positions with multiplicity of eight split into two distinct sites. As a result all positions have a multiplicity of four with Wyckoff position (4e).

There has been considerable confusion regarding the naming of the split sites. The two cation designations that result have been described as M(1a) and M(1b) by Finger et al. (1982), Fe(11) and Fe(12) by Takéuchi et al. (1983), M(11) and M(12) by Ghose et al. (1984a), and M(Ao) and M(Am) by Ghose et al. (1985). The latter designation is derived from the feldspar nomenclature of Megaw (1956). We do not believe this form to be an improvement and will employ the designations of Ghose et al. (1984a).

Selected interatomic distances for Elba and Seriphos ilvaites are presented in Table 5. Of particular interest are the differences in the mean distances for M(11) and M(12), which is a manifestation of the ordering of $Fe^{2+} - Fe^{3+}$. Following the example of Takéuchi et al. (1983), the mean bond distances and an ionic radius model can be used to compute the degree of ordering of the iron in the two sites. In the present study, the radii of Shannon (1976) were used to compute cation occupancies and the associated order parameter (Takéuchi et al., 1983). Because of the presence of impurities, it was necessary to normalize the calculated occupancies. The order parameters for the samples of Takéuchi et al. (1983) were recalculated and the variation of order parameter with β is shown in Figure 1. The solid point in this diagram, which is taken from the 305 K data of Ghose et al. (1984a), was not used in the least-squares fitting. The equation of this line is $\eta = 1.64(3)|\beta - 90|$.

High-pressure results

Experimental

Single crystals of ilvaites from Elba and Seriphos were mounted in a diamond-anvil pressure cell (Merrill and Bassett, 1974) in the manner

Table 3. Anisotropic thermal factors for ilvaïtes from Elba and Seriphos.

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M(11) ^b	55(2)	157(6)	355(13)	-2(3)	-1(4)	22(6)
	102(3)	103(7)	632(16)	6(4)	-56(5)	25(9)
M(12)	48(2)	149(6)	337(13)	-0(3)	17(4)	-20(6)
	92(3)	102(7)	628(16)	6(4)	-35(5)	-26(9)
M(2)	66(2)	131(5)	373(13)	-10(3)	-6(4)	-10(6)
	107(3)	72(7)	600(17)	-3(4)	-40(5)	-9(9)
Ca	53(3)	141(7)	452(16)	10(4)	9(5)	-1(8)
	92(4)	85(10)	734(23)	17(6)	-35(7)	8(12)
Si(1)	31(4)	112(9)	183(20)	-3(5)	11(7)	15(11)
	75(6)	60(13)	438(30)	5(7)	-49(10)	-27(15)
Si(2)	35(4)	107(9)	192(21)	2(5)	13(7)	-8(11)
	79(5)	79(13)	447(28)	4(7)	-40(9)	-12(16)
O(1)	79(12)	212(27)	643(65)	26(14)	7(22)	-8(32)
	118(16)	164(42)	992(88)	2(21)	-70(29)	-38(49)
O(21)	81(11)	181(25)	193(56)	-19(13)	10(19)	-51(29)
	107(14)	146(36)	455(79)	-21(19)	-38(25)	-16(42)
O(22)	65(11)	189(25)	220(56)	-16(13)	16(19)	22(29)
	111(14)	134(36)	588(83)	-26(19)	-2(26)	6(42)
O(3)	49(11)	175(24)	303(55)	30(13)	13(20)	-47(29)
	82(15)	127(33)	716(81)	25(19)	-78(27)	-6(43)
O(41)	73(11)	165(26)	389(57)	22(13)	14(20)	26(30)
	127(16)	120(34)	441(77)	24(20)	-21(26)	48(41)
O(42)	88(12)	149(25)	330(56)	23(13)	-6(20)	-42(30)
	100(15)	138(35)	524(78)	-6(19)	-31(26)	-81(42)
O(5)	49(10)	168(24)	428(57)	6(14)	27(20)	-25(31)
	67(15)	66(32)	706(77)	20(18)	-45(26)	14(43)
O(6)	71(11)	148(26)	730(63)	-36(13)	-7(22)	-11(31)
	108(15)	71(37)	1042(85)	-18(19)	-81(28)	-14(44)
O(7)	33(11)	178(25)	377(57)	-13(14)	13(20)	-31(30)
	114(16)	163(35)	754(84)	-23(21)	-64(29)	-17(47)

^a Thermal factors are scaled by 10^5 . The temperature factor is $\exp\{-\sum \Sigma h_i h_k \beta_{jk}\}$.

^b The order of the entries is the Elba sample followed by the Seriphos data.

described by Hazen and Finger (1982) using a methanol-ethanol mixture as the pressure transmitting fluid. Pressures were measured with the ruby fluorescence technique. Unit-cell data were determined by centering 12 to 20 reflections using the eight-position technique of King and Finger (1979) and refining the unit cell with monoclinic constraints (Ralph and Finger, 1982). The data for the Elba sample are presented in Table 6 and the volume

Table 4. Principal axes for thermal ellipsoids of ilvaites from Elba and Seriphos.

Atom	Elba			Seriphos				
	Ampl.	Angle with			Ampl.	Angle with		
		<i>a</i>	<i>b</i>	<i>c</i>		<i>a</i>	<i>b</i>	<i>c</i>
M(11)	0.068(2)	4(7)	86(7)	90(8)	0.063(2)	97(3)	10(4)	97(2)
	0.075(1)	92(10)	46(8)	136(8)	0.087(2)	148(3)	100(4)	120(2)
	0.082(1)	93(4)	44(8)	46(8)	0.111(1)	121(2)	87(2)	31(2)
M(12)	0.062(2)	20(5)	94(5)	109(4)	0.063(2)	93(4)	6(2)	85(2)
	0.074(1)	105(6)	141(9)	125(8)	0.086(1)	158(3)	91(4)	111(3)
	0.080(1)	78(4)	129(9)	42(8)	0.107(1)	111(3)	96(2)	22(3)
M(2)	0.069(2)	57(7)	33(7)	87(6)	0.053(3)	88(2)	3(2)	88(2)
	0.077(1)	41(9)	117(8)	118(11)	0.090(1)	146(4)	87(2)	124(4)
	0.082(1)	68(9)	107(7)	29(11)	0.102(1)	124(4)	91(2)	34(4)
Ca	0.065(2)	25(7)	115(7)	95(3)	0.056(3)	102(4)	13(4)	93(2)
	0.076(2)	114(7)	155(7)	87(6)	0.088(2)	161(3)	103(4)	104(3)
	0.089(2)	84(4)	89(6)	6(4)	0.114(2)	105(3)	90(2)	15(3)
Si(1)	0.049(4)	147(15)	100(8)	58(15)	0.047(5)	91(7)	7(5)	83(5)
	0.058(3)	123(15)	77(14)	143(15)	0.071(3)	144(5)	86(8)	125(6)
	0.067(3)	91(10)	16(12)	74(12)	0.095(3)	126(5)	96(3)	36(5)
Si(2)	0.069(2)	57(7)	33(7)	87(6)	0.056(5)	92(8)	4(4)	87(6)
	0.077(1)	41(9)	117(8)	118(11)	0.075(3)	144(6)	90(9)	126(6)
	0.082(1)	68(9)	107(7)	29(11)	0.094(3)	126(6)	94(4)	36(6)
O(1)	0.076(7)	32(14)	122(14)	94(9)	0.080(10)	88(22)	6(15)	84(9)
	0.096(6)	122(14)	148(14)	92(25)	0.096(7)	161(8)	86(23)	108(8)
	0.106(5)	88(15)	93(22)	4(13)	0.135(6)	108(7)	95(6)	19(7)
O(21)	0.054(9)	90(12)	72(11)	18(11)	0.071(10)	68(14)	29(23)	71(23)
	0.078(6)	142(18)	126(18)	79(14)	0.086(8)	112(22)	63(25)	144(21)
	0.092(5)	128(18)	42(17)	104(9)	0.102(6)	148(16)	79(15)	60(19)
O(22)	0.059(8)	111(19)	102(12)	24(20)	0.069(10)	73(12)	18(12)	91(12)
	0.075(6)	149(20)	108(19)	114(20)	0.100(6)	148(153)	75(32)	118(185)
	0.088(5)	112(18)	22(17)	86(12)	0.101(6)	116(174)	81(50)	28(185)
O(3)	0.054(9)	142(15)	62(9)	66(16)	0.063(10)	124(19)	37(22)	101(11)
	0.073(6)	120(17)	97(17)	149(17)	0.081(8)	135(18)	126(22)	113(10)
	0.090(6)	69(11)	29(9)	109(15)	0.118(6)	115(8)	95(8)	25(8)
O(41)	0.071(7)	136(21)	46(22)	93(34)	0.062(11)	103(9)	24(13)	110(15)
	0.079(6)	67(34)	71(33)	149(24)	0.090(8)	95(18)	112(15)	158(15)
	0.090(6)	55(17)	50(17)	59(24)	0.106(6)	14(10)	80(11)	99(17)
O(42)	0.067(7)	106(17)	41(19)	53(25)	0.066(10)	79(14)	29(13)	64(11)
	0.078(6)	122(20)	66(24)	138(26)	0.091(7)	151(25)	69(17)	109(25)
	0.092(6)	37(17)	58(13)	107(16)	0.103(7)	117(26)	108(14)	33(18)
O(5)	0.061(8)	20(14)	101(16)	107(11)	0.046(14)	110(16)	21(16)	95(7)
	0.080(6)	106(18)	155(29)	109(30)	0.076(8)	155(14)	111(16)	103(9)
	0.089(6)	78(13)	112(30)	26(24)	0.113(6)	104(8)	90(7)	14(8)
O(6)	0.062(8)	47(11)	43(11)	87(5)	0.051(14)	79(10)	11(11)	87(5)
	0.090(6)	43(11)	133(11)	90(10)	0.092(7)	159(8)	79(11)	107(6)
	0.113(5)	92(8)	92(8)	3(5)	0.138(5)	108(6)	90(4)	18(6)
O(7)	0.051(9)	10(9)	81(11)	96(12)	0.076(9)	66(17)	26(19)	79(11)
	0.077(7)	89(14)	127(23)	143(23)	0.095(8)	141(16)	64(19)	116(13)
	0.088(6)	79(9)	142(23)	54(24)	0.120(6)	118(12)	88(9)	28(12)

Table 5. Selected interatomic distances in ilvaïtes from Elba and Seriphos.

Elba		Seriphos	
Atoms	Distance	Atoms	Distance
M(11)–O(1)	2.086(2)	M(11)–O(1)	2.069(3)
–O(1)	2.222(2)	–O(1)	2.196(3)
–O(21)	2.053(2)	–O(21)	2.045(3)
–O(3)	2.126(2)	–O(3)	2.115(3)
–O(41)	2.114(2)	–O(41)	2.106(3)
–O(7)	<u>2.017(2)</u>	–O(7)	<u>2.004(3)</u>
Mean	2.103	Mean	2.089
M(12)–O(1)	2.017(2)	M(12)–O(1)	2.038(3)
–O(1)	2.133(2)	–O(1)	2.155(3)
–O(22)	2.036(2)	–O(22)	2.037(3)
–O(3)	2.080(3)	–O(3)	2.088(3)
–O(42)	2.102(2)	–O(42)	2.107(3)
–O(7)	<u>1.976(2)</u>	–O(7)	<u>1.985(3)</u>
Mean	<u>2.057</u>	Mean	<u>2.069</u>
M(2)–O(1)	2.128(2)	M(2)–O(1)	2.119(3)
–O(21)	2.229(2)	–O(21)	2.232(3)
–O(22)	2.246(2)	–O(22)	2.243(3)
–O(41)	2.270(2)	–O(41)	2.277(3)
–O(42)	2.287(2)	–O(42)	2.286(3)
–O(6)	<u>1.966(2)</u>	–O(6)	<u>1.965(3)</u>
Mean	2.188	Mean	2.187
Ca–O(21)	2.392(2)	Ca–O(21)	2.400(3)
–O(22)	2.408(2)	–O(22)	2.407(3)
–O(3)	2.413(2)	–O(3)	2.411(3)
–O(41)	2.449(2)	–O(41)	2.451(3)
–O(42)	2.457(2)	–O(42)	2.451(3)
–O(5)	2.424(2)	–O(5)	2.425(3)
–O(7)	<u>2.303(2)</u>	–O(7)	<u>2.304(3)</u>
Mean	3.407	Mean	2.407
Si(1)–O(21)	1.630(2)	Si(1)–O(21)	1.631(3)
–O(22)	1.636(2)	–O(22)	1.634(3)
–O(5)	1.657(2)	–O(5)	1.655(3)
–O(6)	<u>1.599(2)</u>	–O(6)	<u>1.593(3)</u>
Mean	1.630	Mean	1.628
Si(2)–O(3)	1.644(2)	Si(2)–O(3)	1.644(3)
–O(41)	1.629(2)	–O(41)	1.631(3)
–O(42)	1.632(2)	–O(42)	1.632(3)
–O(5)	<u>1.656(2)</u>	–O(5)	<u>1.653(3)</u>
Mean	1.640	Mean	1.640
H–O(6)	2.04(6)	H–O(6)	1.84(7)
–O(7)	0.62(6)	–O(7)	0.84(7)

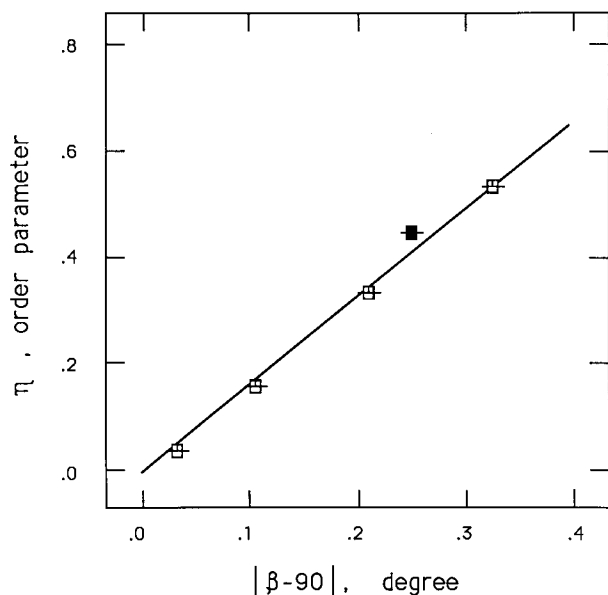


Fig. 1. The order parameter derived from average bond distances as a function of the monoclinic angle. The open points are from the present study and from Takéuchi et al. (1983). The filled point, derived from Ghose et al. (1984a), was not used in the least-squares fit.

Table 6. Unit-cell and order parameters as a function of pressure for Elba ilvaite.

P (GPa)	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	OP ^a
0.0001 ^b	13.0103(5)	8.8039(4)	5.8517(3)	90.209(5)	670.26(6)	0.34(1)
0.0001 ^b	13.008(1)	8.806(1)	5.853(2)	90.23(2)	670.4(2)	0.38(3)
0.0001	13.012(3)	8.8059(6)	5.855(2)	90.26(3)	670.9(3)	0.43(5)
0.5	12.997(2)	8.7985(6)	5.843(1)	90.21(2)	668.2(2)	0.34(3)
0.8	12.991(3)	8.7957(7)	5.836(1)	90.21(3)	666.9(2)	0.34(5)
0.9	12.991(2)	8.7951(5)	5.833(1)	90.20(2)	666.5(2)	0.33(3)
1.0 ^c	12.988(3)	8.7912(8)	5.832(2)	90.17(3)	665.8(2)	0.28(5)
1.0	12.992(3)	8.7927(8)	5.830(2)	90.19(3)	666.0(3)	0.31(5)
1.1 ^c	12.987(5)	8.791(1)	5.831(3)	90.18(5)	665.7(4)	0.29(9)
1.3	12.981(3)	8.7871(7)	5.824(1)	90.12(3)	664.4(2)	0.19(5)
1.6	12.982(2)	8.7855(6)	5.818(1)	90.07(2)	663.5(2)	0.10(3)
1.9 ^c	12.973(3)	8.7794(7)	5.812(1)	90.05(3)	662.0(2)	0.07(5)
2.6	12.955(5)	8.769(1)	5.798(3)	90.01(5)	658.6(4)	0.00(9)
3.3	12.947(3)	8.7562(8)	5.779(1)	90.03(3)	655.2(2)	0.04(5)
5.7 ^c	12.898(9)	8.722(3)	5.734(5)	90.01(9)	645.0(7)	0.00(15)

^a OP is the order parameter. See the text for details.

^b These unit-cell parameters were measured for crystals in air. The crystal was in a diamond-anvil cell for all other cases.

^c Data measured on a Huber diffractometer with graphite monochromator. A Picker unit with unfiltered radiation was used for all other cases.

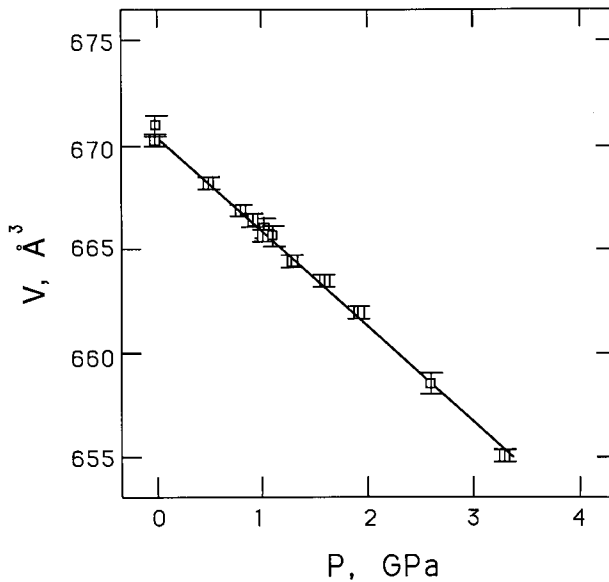


Fig. 2. Volume as a function of pressure for ilvaite from Elba. No first-order discontinuity is observable at the transition pressure of 1.5–1.6 GPa.

Table 7. Unit-cell and order parameters as a function of pressure for Seriphos ilvaite.

P (GPa)	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	OP ^a
0.0001 ^b	13.0056(6)	8.7976(5)	5.8539(5)	90.105(6)	669.79(8)	0.17(1)
0.0001 ^b	13.0148(3)	8.805(1)	5.8495(3)	90.11(3)	670.31(8)	0.18(5)
1.2	12.981(1)	8.786(3)	5.8268(7)	90.00(1)	664.6(2)	0.00(2)
2.7	12.9466(7)	8.765(2)	5.7947(6)	90.002(7)	657.5(1)	0.00(1)
4.5	12.906(2)	8.736(4)	5.759(1)	90.02(2)	649.3(3)	0.03(3)
0.0001 ^c	13.007(1)	8.804(1)	5.8494(1)	90.000(5)	669.6(6)	0.00(1)

^a OP is the order parameter. See the text for details.

^b This unit-cell was measured for a crystal in air. The crystal was in a diamond-anvil cell for all other cases.

^c Unit cell measured after crystal had been taken to 4.5 GPa. The crystal has an orthorhombic cell as a result of twinning.

as a function of pressure is plotted in Figure 2. Although the sample transformed from monoclinic to orthorhombic at a pressure lower than 1.9 GPa, there is no evidence for a discontinuity in the volume; therefore, no first-order character was detected within the precision of these experiments. Although we expected the sample to undergo twinning upon pressure release, the transition pressure was exceeded several times with no evidence

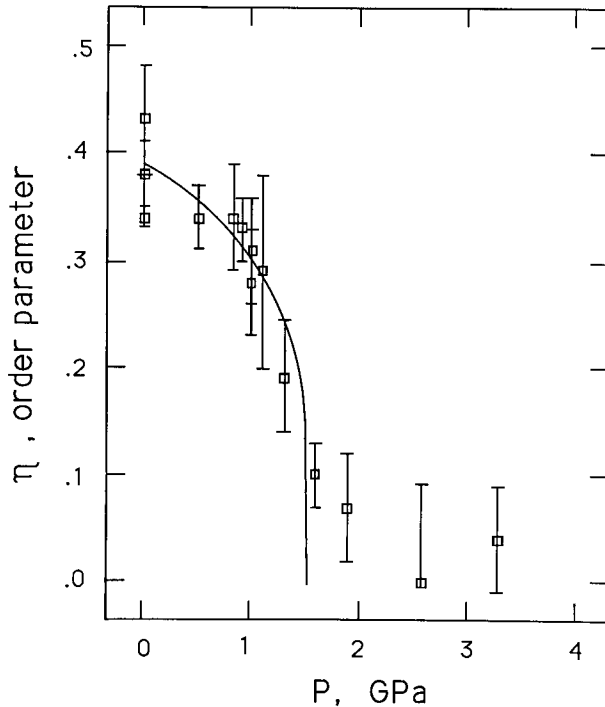


Fig. 3. Order parameter as a function of pressure for ilvaite from Elba. The curve of the predicted value for the long-range order parameter is generated by a Landau-type expression with a critical exponent of $1/4$.

for any change in the twinning. The Seriphos sample, which contains only a small amount of impurity (Table 7), transformed at a lower pressure, consistent with the smaller initial magnitude of the monoclinic angle. Furthermore, this sample was twinned after pressure release and had orthorhombic cell geometry. It seems likely that the presence of a large number of impurity atoms, particularly Al^{3+} , is responsible for "locking in the orientation" of the monoclinic phase, which restricts the twinning.

Nature of the monoclinic-orthorhombic transition

The calibration of the order parameter in terms of the monoclinic angle (Fig. 1) has been used to convert the unit-cell data of Table 6 as shown in Figure 3. The shape of this curve is compatible with that of a λ -transition (Carpenter, 1985). This type of behaviour occurs when there is a mixture of order-disorder and displacive transitions (Thompson and Perkins, 1981). At a critical point, a long-range order parameter, which is associated with

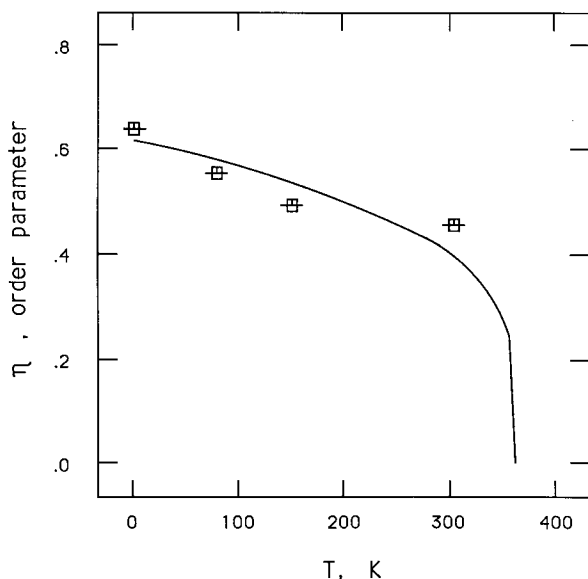


Fig. 4. Order parameter as a function of temperature for the data of Ghose et al. (1984a). The curve is for a Landau exponent of $1/4$.

the order-disorder phenomena, goes to zero whereas a short-range order parameter, associated with the displacive behaviour, persists above the critical point. For this type of transition, a calorimetry experiment will be sensitive to the change in enthalpy and the λ -shape in C_p at the critical point, whereas a crystallography experiment will observe the completion of the transition only when there is no short-range order. As a result, the two techniques may report different values for the transition conditions.

Although Landau theory (Thompson and Perkins, 1981; Ghose, 1985; Carpenter, 1985) does not apply for λ -transition, it can be used to describe the behavior of the long-range order parameter in the vicinity of the critical point. In this formalism, $\eta \propto (P_C - P)^\beta$, where P_C is the critical pressure and β is the Landau exponent, which should be the inverse of an integer. If a mean-field effect describes the influence on the order parameter, β would be $1/2$. For values of $1/3$ or $1/4$, local fluctuations of β and the order parameter become important.

The data of Table 6 with $P \leq 1.3$ GPa were fitted to the Landau equation with various values for the exponent. Only an exponent of $1/4$ gave reasonable results. The curve in Figure 3 corresponds to $\eta = 0.35(P_C - P)^{1/4}$ with $P_C = 1.54$ GPa.

Evans and Amthauer (1980) have shown that the Mössbauer spectra of ilvaite at high pressure and at high temperature are identical; therefore, a

similar transition is believed to be responsible. At high temperature, the small barrier for electron hopping (0.11 eV, Litterst and Amthauer, 1984) is exceeded. At high pressure as M(11) and M(12) become closer together, the height of the barrier is reduced until hopping takes place at room temperature. To test the critical exponent for the high-temperature transition, the order parameter has been computed for the refined bond distances of Ghose et al. (1984a) at various temperatures. These data have been fitted with a $(T_c - T)^{1/4}$ curve as shown in Figure 4. This result predicts a transition temperature of 360 K, which is in reasonable agreement with the value of 333–343 K obtained by Ghose et al. (1984b), particularly when the lack of data near the critical point is considered. Note, however, that the correlation between monoclinic angle and order parameter does not hold for temperatures well below the transition temperature (Ghose, 1984a).

Clapeyron slope

It is difficult to determine the Clapeyron slope from the present data on ilvaite because the high-temperature and high-pressure experiments were performed on different materials and the critical pressures and temperatures appear to be dependent upon impurity content and sample history. We have shown that the high-pressure transformation is the same as the that observed at high temperature; therefore, dP/dT , the Clapeyron slope, must be negative and is -0.02 to -0.03 GPa K^{-1} .

For a second-order transition, $dP/dT = \Delta S/\Delta V$, the usual formulation for the Clapeyron slope, is invalid as both the entropy and the volume are continuous at the transition. It is necessary, therefore, to employ the second-order equation, $dP/dT = \Delta\alpha/\Delta\beta$ (Thompson and Perkins, 1981), where α and β are the coefficients of isobaric thermal expansion and isothermal compression, respectively. The precision of the present study is not sufficient to quantify a change of slope in the volume versus pressure (Fig. 2). There is, however, some indication of a greater compressibility above the transition which would make $\Delta\beta$ less than zero. We would predict, therefore, that $\Delta\alpha$ is greater than zero.

Discussion

Comparison of X-ray and Mössbauer results

Ilvaite has been the subject of numerous ^{57}Fe Mössbauer spectral studies (Herzenberg and Riley, 1969; Gerard and Grandjean, 1971; Grandjean and Gerard, 1975; Heilmann et al., 1977; Nolet and Burns, 1978, 1979; Amthauer and Evans, 1978; Yamanaka and Takéuchi, 1979; Evans and

Amthauer, 1980; Litterst and Amthauer, 1984). Each of these studies has assumed an orthorhombic structure with Fe^{2+} in an octahedron of fourfold multiplicity corresponding to M(2), and Fe^{2+} and Fe^{3+} in an eightfold site, which corresponds to an average of M(11) and M(12). With a single exception, the absorption spectra were evaluated assuming Lorentzian line shapes. This assumption is valid only if the electron exchange is much slower than the mean life time of the excited ^{57}Fe nuclear level. Litterst and Amthauer (1984) showed this assumption to be incorrect and developed an expression for the resonant absorption that included a relaxation rate due to electron hopping that varied with temperature. The activation energy for the process was 0.11 eV.

With the electron hopping model, only three sets of hyperfine parameters are required to explain the pattern at all temperatures. At the transition, the slopes of the isomer shift and quadrupole splitting for the line assigned to Fe^{2+} in the M(11) and M(12) sites change. There are, however, no differences in the number of lines nor in the line widths other than those attributed to changes in the relaxation time.

This interpretation is difficult to explain in terms of the crystallography. The (8d) orthorhombic site is clearly split into two distinct fourfold sites. The mean, time-averaged bond distances are 2.089 Å and 2.069 Å for the two positions in the Seriphos ilvaite, one of the samples studied by Litterst and Amthauer (1984). The distortion parameters defined by Robinson et al. (1971) are not greatly different for the two sites and appear to be more important than the average distances in determining the hyperfine parameters. This sample also has a relatively small deviation from orthorhombic geometry and a relatively low degree of order at room temperature. A better test of the Litterst and Amthauer model would be obtained by studying the temperature variation of the Mössbauer spectra for the Elba or Tsumo (Takéuchi et al., 1983) samples.

Summary

Because of the interest in electron hopping, the small deviation from orthorhombic geometry, and the subtle phase transition, ilvaite has been the subject of numerous studies employing various techniques. Although our understanding of the relationships among these effects is fairly good, the problems of the interactions between impurities and the studied properties reiterate the necessity of working with properly characterized samples.

Acknowledgements. This work was supported, in part, by NSF Grants EAR-8419982 and EAR-8319209. The manuscript was greatly improved by the suggestions of C.T. Prewitt. We also thank Dartmouth College and the National Museum of Natural History, Smithsonian Institution for their kind donation of samples, and John M. Hughes for his part in the initiation of the study.

References

- Amthauer, G., Evans, B. J.: Single crystal and high pressure ^{57}Fe Mössbauer studies of ilvaite, $\text{CaFe}_2^+ \text{Fe}^{3+} (\text{Si}_2\text{O}_7/\text{O}/\text{OH})$ at 298 K. *Phys. Chem. Minerals* **3** (1978) 55–56.
- Bartholomé, P., Duchesne, J. C., van der Plas, L.: Sur une forme monoclinique de l'ilvaite. *Ann. Soc. Géol. Belgique* **90** (1968) 779–788.
- Belov, N., Mokeeva, V. I.: Kristallicheskaya struktura ilvaita. *Trudy Inst. Kristallogr. Akad. Nauk SSSR* **9** (1954) 47–102.
- Beran, A., Bittner, H.: Untersuchungen zur Kristallchemie des Ilvaites. *Tschermaks Mineral. Petrogr. Mitt.* **21** (1974) 11–29.
- Burnham, C. W.: Computation of absorption corrections and the significance of end effect. *Am. Mineral.* **51** (1966) 159–167.
- Burt, D. M.: The facies of some Ca–Fe–Si skarns in Japan. *Carnegie Inst. Washington Year Book* **71** (1972) 185–188.
- Carpenter, M. A.: Order-disorder transformations in mineral solid solutions. *Rev. Mineral.* **14** (1985) 187–223.
- Dietrich, V.: Ilvait, Ferroantigorit und Greenalith als Begleiter oxidisch-sulfidischer Vererzungen in den Oberhalbsteiner Serpentiniten. *Schweiz. Mineral. Petrog. Mitt.* **52** (1972) 57–74.
- Evans, B. J., Amthauer, G.: The electronic structure of ilvaite and the pressure and temperature dependence of its ^{57}Fe Mössbauer spectrum. *J. Phys. Chem. Solids* **41** (1980) 985–1001.
- Finger, L. W., Prince, E.: A system of Fortran IV computer programs for crystal structure computations. *Nat. Bur. Stand. (U.S.), Tech. Note* **854** (1975) 133.
- Finger, L. W., Hazen, R. M., Hughes, J. M.: Crystal structure of monoclinic ilvaite. *Carnegie Inst. Washington Year Book* **81** (1982) 386–388.
- Gerard, A., Grandjean, F.: Observation by Mössbauer effect of an electron hopping process in ilvaite. *Solid State Commun.* **9** (1971) 1845–1849.
- Ghose, S.: Lattice dynamics, phase transitions and soft modes. *Rev. Mineral.* **14** (1985) 127–163.
- Ghose, S., Hewatt, A. W., Marezio, M.: A neutron powder diffraction study of the crystal and magnetic structures of ilvaite from 305 K to 5 K — a mixed valence iron silicate with an electronic transition. *Phys. Chem. Minerals* **11** (1984a) 67–74.
- Ghose, S., Hewatt, A. W., Marezio, M., Dang, N. V., Robie, R. A., Evans, H. T.: Electron and spin ordering and associated phase transitions in ilvaite, a mixed valence iron silicate. *Trans. Am. Geophys. Union* **65** (1984b) 289.
- Ghose, S., Sen Gupta, P. K., Schlemper, E. O.: Electron ordering in ilvaite, a mixed-valence iron silicate: crystal structure refinement at 138 K. *Am. Mineral.* **70** (1985) 1248–1252.
- Grandjean, F., Gerard, A.: Analysis by Mössbauer spectroscopy of the electronic hopping process in ilvaite. *Solid State Commun.* **16** (1975) 553–556.
- Haga, N., Takéuchi, Y.: Neutron diffraction study of ilvaite. *Z. Kristallogr.* **144** (1976) 161–174.
- Hazen, R. M., Finger, L. W.: *Comparative Crystal Chemistry*. John Wiley and Sons, Chichester (1982) 231.
- Heilmann, I. U., Olsen, N. B., Olsen, J. S.: Electron hopping and temperature dependent oxidation states of iron in ilvaite studied by Mössbauer effect. *Phys. Scr.* **15** (1977) 285–288.
- Herzenberg, C. L., Riley, D. L.: Oxidation states and site symmetries of iron in ilvaite using Mössbauer spectrometry. *Acta Crystallogr.* **A25** (1969) 389–391.
- International Tables for Crystallography*. Vol. IV. Kynoch Press, Birmingham (1974).
- Ito, T.: *X-ray Studies on Polymorphism*. Maruzen, Tokyo (1950).

- King, H. E., Finger, L. W.: Diffracted beam crystal centering and its application to high-pressure crystallography. *J. Appl. Crystallogr.* **12** (1979) 374–378.
- Litterst, F. J., Amthauer, G.: Electron delocalization in ilvaite, a reinterpretation of its ^{57}Fe Mössbauer spectrum. *Phys. Chem. Minerals* **10** (1984) 250–255.
- Megaw, H. D.: Notation for feldspar structures. *Acta Crystallogr.* **9** (1956) 56–60.
- Merrill, L., Bassett, W. A.: Miniature diamond anvil pressure cell for single crystal X-ray diffraction studies. *Rev. Sci. Instrum.* **45** (1974) 290–294.
- Nasland, H. R., Hughes, J. M., Birnie, R. W.: Ilvaite, an alteration product replacing olivine in the Skaergaard intrusion. *Am. Mineral.* **68** (1983) 1004–1008.
- Nolet, D. A., Burns, R. G.: Temperature dependent $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ electron delocalization in ilvaite. *Geophys. Res. Lett.* **5** (1978) 821–824.
- Nolet, D. A., Burns, R. G.: Ilvaite: a study of temperature dependent electron delocalization by the Mössbauer effect. *Phys. Chem. Minerals* **4** (1979) 221–234.
- Ralph, R. L., Finger, L. W.: A computer program for refinement of crystal orientation matrix and lattice constants from diffractometer data with lattice symmetry constraints. *J. Appl. Crystallogr.* **15** (1982) 537–539.
- Robinson, K., Gibbs, G. V., Ribbe, P. H.: Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science* **172** (1971) 567–570.
- Shannon, R. D.: Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32** (1976) 751–767.
- Takéuchi, Y.: The structure of ilvaite, $\text{HCaFe}_2^+ \text{Fe}^{3+} \text{Si}_2\text{O}_9$. *X-rays* **5** (1948) 8–14.
- Takéuchi, Y., Haga, N., Bunno, M.: X-ray study on polymorphism of ilvaite, $\text{HCaFe}_2^+ \text{Fe}^{3+} \text{O}_2[\text{Si}_2\text{O}_7]$. *Z. Kristallogr.* **163** (1983) 267–283.
- Thompson, A. B., Perkins, E. H.: Lambda transitions in minerals. In: *Thermodynamics of Minerals and Melts* (Eds. A. Navrotsky, R. C. Newton, B. J. Wood), Vol. 1, pp. 35–62. *Advances in Physical Geochemistry*. Springer-Verlag, New York (1981).
- Yamanaka, T., Takéuchi, Y.: Mössbauer spectra and magnetic features of ilvaite. *Phys. Chem. Minerals* **4** (1979) 149–159.