



# Table of contents

## 3 Fe oxides and Fe–Me–O compounds

(R. LEFEVER)

<b>3.0 Introduction</b>	1
3.0.1 General remarks	1
3.0.2 List of frequently used symbols and abbreviations	1
<b>3.1 Fe oxides</b>	2
3.1.1 Wüstite $\text{Fe}_x\text{O}$ and wüstite with substitutions	2
3.1.1.1 Data	2
3.1.1.2 References for 3.1.1	6
3.1.2 Hematite $\alpha\text{-Fe}_2\text{O}_3$ and hematite with substitutions	7
3.1.2.1 Data	7
3.1.2.2 References for 3.1.2	19
3.1.3 Maghemite $\gamma\text{-Fe}_2\text{O}_3$	21
3.1.3.1 Data	21
3.1.3.2 References for 3.1.3	26
<b>3.2 Fe–Me–O compounds</b>	27
3.2.1 Data	27
3.2.2 References for 3.2	51

## 4 Spinels

<b>4.0 Structure table of spinels</b> (H. VON PHILIPSBORN, L. TREITINGER)	54
<b>4.1 <math>\text{Fe}^{3+}</math> spinels</b>	55
4.1.1 $\text{Fe}^{2+} - \text{Fe}^{3+}$ spinels (magnetite) and $\text{Fe}^{2+} - \text{Fe}^{3+}$ spinels with substitutions (R. LEFEVER)	55
4.1.1.0 Introduction	55
4.1.1.0.1 Special remarks	55
4.1.1.0.2 List of frequently used symbols and abbreviations	55
4.1.1.1 Summary of physical and magnetic properties	58
4.1.1.2 Magnetic order and magnetization	59
4.1.1.3 Magnetocrystalline anisotropy	61
4.1.1.4 Magnetostriction and elastic constants	62
4.1.1.5 Nuclear magnetic resonance	64
4.1.1.6 Mössbauer data	65
4.1.1.7 Optical and thermal properties	74
4.1.1.8 Electrical properties	77
4.1.1.9 Phase diagrams	84
4.1.1.10 References for 4.1.1.0–4.1.1.9	84
4.1.2 Ni– $\text{Fe}^{3+}$ spinels (Ni ferrite) and Ni– $\text{Fe}^{3+}$ spinels with substitutions (T.R. MCGUIRE)	88
4.1.2.0 List of frequently used symbols and abbreviations	88
4.1.2.1 Ni ferrite $\text{NiFe}_2\text{O}_4$	89
4.1.2.2 Ni ferrite with Zn substitutions	99
4.1.2.3 Ni ferrite with Co substitutions	111
4.1.2.4 Ni ferrite and Ni ferrite aluminate with dilute Mn and Co substitutions (see Vol. III/4b, p. 91)	
4.1.2.5 Ni ferrite with Ge substitutions (see Vol. III/4b, p. 96)	
4.1.2.6 Ni ferrite chromite	113

4.1.2.7	Ni ferrite vanadate (see Vol. III/4b, p. 99)	
4.1.2.8	Ni ferrite aluminate . . . . .	115
4.1.2.9	Ni ferrite gallate (see Vol. III/4b, p. 103)	
4.1.2.10	Ni ferrite with Cu substitutions . . . . .	116
4.1.2.11	Ni ferrite with Ti substitutions . . . . .	116
4.1.2.12	Ni ferrite with Sn substitutions . . . . .	117
4.1.2.13	Ni indate ferrite . . . . .	118
4.1.2.14	Ni ferrite with Mn substitutions . . . . .	118
4.1.2.15	Ni ferrite with Ru substitutions . . . . .	119
4.1.2.16	Ni ferrite scandate . . . . .	119
4.1.2.17	References for 4.1.2 . . . . .	119
4.1.3	Mn–Fe <sup>3+</sup> spinels (Mn ferrites) and Mn–Fe <sup>3+</sup> spinels with substitutions (M. PAULUS, R. VAUTIER)	
4.1.3.0	List of frequently used symbols and abbreviations . . . . .	122
4.1.3.1	Phase equilibria and structure . . . . .	123
4.1.3.1.1	Phase equilibria . . . . .	123
4.1.3.1.2	Equilibrium oxygen partial pressure . . . . .	126
4.1.3.1.3	Lattice constants . . . . .	129
4.1.3.1.4	Ionic distribution . . . . .	132
4.1.3.1.5	Mössbauer data or spin arrangements . . . . .	132
4.1.3.2	Thermal properties . . . . .	133
4.1.3.2.6	Solid state crystal growth . . . . .	134
4.1.3.2.7	Reactivity and sintering . . . . .	135
4.1.3.3	Mechanical properties. . . . .	135
4.1.3.3.1	Elastic properties . . . . .	136
4.1.3.3.2	Hardness . . . . .	136
4.1.3.4	Electrical properties. . . . .	136
4.1.3.4.1	Electrical resistivity . . . . .	137
4.1.3.4.4	Seebeck effect . . . . .	140
4.1.3.5	Spontaneous magnetization . . . . .	140
4.1.3.5.1	Saturation moment at 0 K . . . . .	141
4.1.3.5.2	Magnetization as a function of temperature . . . . .	142
4.1.3.5.4	Curie temperatures . . . . .	142
4.1.3.5.5	Exchange interaction . . . . .	144
4.1.3.6	Magnetocrystalline anisotropy . . . . .	144
4.1.3.6.2	Magnetocrystalline anisotropy in Mn ferrites with substitutions . . . . .	145
4.1.3.6.4	Magnetic annealing . . . . .	146
4.1.3.7	Domain and domain walls (see Vol. III/4b, p. 176)	
4.1.3.8	Response of magnetization to a field. . . . .	147
4.1.3.8.3	Permeability variation with composition, impurities, irradiation and grain size	148
4.1.3.8.4	Permeability vs. temperature . . . . .	149
4.1.3.8.7	After-effect, disaccommodation, and viscosity . . . . .	150
4.1.3.8.8	Coercive force . . . . .	153
4.1.3.8.9	Losses . . . . .	154
4.1.3.9	Microwave properties . . . . .	155
4.1.3.9.1	Resonance linewidth . . . . .	155
4.1.3.10	Optical properties . . . . .	156
4.1.3.11	References for 4.1.3 . . . . .	158
4.1.4	Mg–Fe <sup>3+</sup> spinels (Mg ferrites) and Mg–Fe <sup>3+</sup> spinels with substitutions (M. SUGIMOTO) .	160, 774
4.1.4.0	List of frequently used symbols and abbreviations . . . . .	160
4.1.4.1	Mg ferrite MgFe <sub>2</sub> O <sub>4</sub> . . . . .	162
4.1.4.2	Mg ferrite and Mg–Fe mixed oxides . . . . .	166
4.1.4.3	Other ferrite systems containing Mg . . . . .	167, 744
4.1.4.3.1	Systems containing Mn <sup>2+</sup> . . . . .	167
4.1.4.3.2	Systems containing Zn <sup>2+</sup> and Cd <sup>2+</sup> . . . . .	168
4.1.4.3.3	Systems containing Cu <sup>2+</sup> . . . . .	170
4.1.4.3.4	Systems containing Ni <sup>2+</sup> . . . . .	170

4.1.4.3.5	Systems containing $\text{Co}^{2+}$	172
4.1.4.3.6	Other systems containing trivalent and higher valency cations	173, 744
4.1.4.4	References for 4.1.4.1...4.1.4.3	175
4.1.5	Zn- $\text{Fe}^{3+}$ spinels (Zn ferrites) and Zn- $\text{Fe}^{3+}$ spinels with substitutions	176, 745
4.1.5.1	Zn ferrite $\text{ZnFe}_2\text{O}_4$	176, 745
4.1.5.2	Zn ferrite and Zn-Fe mixed oxides	179, 745
4.1.5.3	Zn-Ni, Zn-Ni-Co, Zn-Co, Zn-Ni-Cu and Zn-Ti ferrites	181, 745
4.1.5.4	References for 4.1.5.1...4.1.5.3	185
4.1.6	Li- $\text{Fe}^{3+}$ spinels (Li ferrites) and Li- $\text{Fe}^{3+}$ spinels with substitutions	186, 748
4.1.6.1	Tables and figures	186, 748
4.1.6.2	References for 4.1.6.1	189
4.1.7	Cu- $\text{Fe}^{3+}$ spinels (Cu ferrites) and Cu- $\text{Fe}^{3+}$ spinels with substitutions	190, 751
4.1.7.0	General remarks	190, 751
4.1.7.1	Cu ferrite $\text{CuFe}_2\text{O}_4$	190
4.1.7.2	Cu-Zn and Cu-Cd ferrites	208
4.1.7.3	Cu-Mn ferrites and those containing other oxides	210
4.1.7.4	Cu-Ni ferrites and those containing other oxides	222
4.1.7.5	Cu-Li ferrites and those containing other oxides	225
4.1.7.6	Other ferrites systems containing Cu	228, 755
4.1.7.7	References for 4.1.7.1...4.1.7.6	230
4.1.8	Co- $\text{Fe}^{3+}$ spinels (Co ferrites) and Co- $\text{Fe}^{3+}$ spinels with substitutions	232, 755
4.1.8.1	Co ferrite $\text{CoFe}_2\text{O}_4$	232, 755
4.1.8.2	Co ferrite and Co-Fe mixed oxides	245
4.1.8.3	Co-Zn, Co-Cd ferrites	251
4.1.8.4	Co-Mn, Co-Ni, Co-Ti and other ferrites	265, 756
4.1.8.5	References for 4.1.8.1...4.1.8.4	282
<b>4.2</b>	<b>Chromium spinels (H. VON PHILIPSBORN, M. RUBINSTEIN, L. TREITINGER)</b>	<b>285</b>
4.2.0	Introduction and comparative data (H. VON PHILIPSBORN, L. TREITINGER)	285
4.2.0.1	List of frequently used symbols and abbreviations	285
4.2.0.2	Comments on data	288
4.2.0.2.1	Data acquisition and processing	288
4.2.0.2.2	Data arraying and retrieval	289
4.2.0.3	Comments on material	289
4.2.0.3.1	Occurrence of chromium spinels	289
4.2.0.3.2	Versatile properties in science and technology	289
4.2.0.3.3	Crystal chemistry	290
4.2.0.3.4	Materials preparation and characterization	291
4.2.0.4	$\text{ACr}_2\text{X}_4$ data, compared	294
4.2.0.5	References for 4.2.0.4	316
4.2.1	Chromium oxide spinels of Li, Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd. (H. VON PHILIPSBORN, L. TREITINGER)	318
4.2.1.0	Locating of the data	318
4.2.1.0.1	Survey of contents	318
4.2.1.0.2	Quotation tables	321
4.2.1.1	$\text{ACr}_2\text{O}_4$ data, compared	322
4.2.1.2	(Li, A)(Cr, B) $_2\text{O}_4$	324
4.2.1.3	Mg-Cr spinels	330
4.2.1.3.1	$\text{MgCr}_2\text{O}_4$	330
4.2.1.3.2	Mg-Cr spinels with substitutions	337
4.2.1.4	Mn-Cr spinels	344
4.2.1.4.1	$\text{MnCr}_2\text{O}_4$	344
4.2.1.4.2	Mn-Cr spinels with substitutions	347
4.2.1.5	Fe-Cr spinels	354
4.2.1.5.1	Crystallographic and thermodynamic properties (including neutron diffraction)	354
4.2.1.5.1.1	$\text{FeCr}_2\text{O}_4$	354

4.2.1.5.1.2	Fe–Cr spinels with Ni substitutions . . . . .	356
4.2.1.5.1.3	Chromite-magnetite solid solutions. . . . .	357
4.2.1.5.1.4	Fe(Cr, B) <sub>2</sub> O <sub>4</sub> with B = Al or Ti. . . . .	362
4.2.1.5.2	Magnetic and related properties. . . . .	364
4.2.1.5.3	Electrical properties. . . . .	370
4.2.1.6	Co–Cr spinels. . . . .	373
4.2.1.6.1	Crystallographic and thermodynamic properties. . . . .	373
4.2.1.6.2	Magnetic properties. . . . .	375
4.2.1.6.3	Electrical properties. . . . .	379
4.2.1.7	Ni–Cr spinels . . . . .	379
4.2.1.7.1	Crystallographic, elastic and thermodynamic properties . . . . .	379
4.2.1.7.2	Magnetic and related properties. . . . .	387
4.2.1.8	Cu–Cr spinels. . . . .	391
4.2.1.8.1	Crystallographic properties. . . . .	391
4.2.1.8.2	Other properties . . . . .	394
4.2.1.9	Zn–Cr spinels . . . . .	396
4.2.1.9.1	Crystallographic and elastic properties (including neutron diffraction) . . . . .	396
4.2.1.9.2	Magnetic and optical properties. . . . .	398
4.2.1.10	References for 4.2.1.0–4.2.1.9 . . . . .	401
4.2.2	Chromium sulfide, selenide and telluride spinels of Mn, Fe, Co, Cu, Zn (H. VON PHILIPSBORN, L. TREITINGER). . . . .	405
4.2.2.0	Locating of the data . . . . .	405
4.2.2.0.1	Survey of contents . . . . .	405
4.2.2.0.2	Quotation tables . . . . .	408
4.2.2.1	(A, B)Cr <sub>2</sub> X <sub>4</sub> spinels, compared . . . . .	409
4.2.2.1.1	Crystal synthesis and thermodynamics . . . . .	409
4.2.2.1.2	Lattice parameters, magnetic and electrical properties . . . . .	413
4.2.2.1.3	Comparison of some properties of A-site ordered spinels . . . . .	417
4.2.2.2	Cu–Cr spinels. . . . .	419
4.2.2.2.1	Crystallographic and thermodynamic properties (magnetic structures included)	
4.2.2.2.1.1	Pure compounds CuCr <sub>2</sub> X <sub>4</sub> . . . . .	419
4.2.2.2.1.2	Cu–Cr spinels with anion substitutions . . . . .	421
4.2.2.2.1.3	Cu–Cr spinels with cation substitutions . . . . .	424
4.2.2.2.2	Magnetic properties (magnetic structures, see 4.2.2.2.1) . . . . .	427
4.2.2.2.2.1	Pure compounds CuCr <sub>2</sub> X <sub>4</sub> . . . . .	427
4.2.2.2.2.2	Cu–Cr spinels with anion substitutions . . . . .	432
4.2.2.2.2.3	Cu–Cr spinels with A-cation substitutions . . . . .	435
4.2.2.2.2.4	Cu–Cr spinels with B-cation substitutions . . . . .	436
4.2.2.2.2.5	NMR and Mössbauer spectroscopy . . . . .	439
4.2.2.2.3	Optical properties . . . . .	442
4.2.2.2.4	Electrical properties. . . . .	443
4.2.2.2.4.1	Pure compounds CuCr <sub>2</sub> X <sub>4</sub> . . . . .	443
4.2.2.2.4.2	Cu–Cr spinels with anion substitutions . . . . .	444
4.2.2.2.4.3	Cu–Cr spinels with cation substitutions . . . . .	445
4.2.2.3	Mn-, Fe-, Co–Cr spinels . . . . .	448
4.2.2.3.1	Crystallographic and thermodynamic properties (magnetic structures included) . . . . .	448
4.2.2.3.2	Magnetic properties (magnetic structures, see 4.2.2.3.1) . . . . .	453
4.2.2.3.2.1	Pure compounds Mn-, Fe-, Co–Cr <sub>2</sub> S <sub>4</sub> . . . . .	453
4.2.2.3.2.2	Mn-, Fe-, Co–Cr spinels with anion substitutions . . . . .	455
4.2.2.3.2.3	Mn-, Fe-, Co–Cr spinels with cation substitutions . . . . .	456
4.2.2.3.2.4	NMR and Mössbauer spectroscopy . . . . .	463
4.2.2.3.3	Optical properties . . . . .	469
4.2.2.3.3.1	Pure compounds Mn-, Fe-, Co–Cr <sub>2</sub> S <sub>4</sub> . . . . .	469
4.2.2.3.3.2	Mn-, Fe-, Co–Cr spinels with cation substitutions . . . . .	472
4.2.2.3.4	Electrical properties. . . . .	475
4.2.2.3.4.1	Pure compounds Mn-, Fe-, Co–Cr <sub>2</sub> S <sub>4</sub> . . . . .	475
4.2.2.3.4.2	Mn-, Fe-, Co–Cr spinels with cation substitutions . . . . .	480

4.2.2.4	Zn–Cr spinels . . . . .	483
4.2.2.4.1	Crystallographic properties (magnetic structures included) . . . . .	483
4.2.2.4.1.1	Lattice parameters . . . . .	483
4.2.2.4.1.2	Neutron diffraction . . . . .	484
4.2.2.4.2	Magnetic properties . . . . .	487
4.2.2.4.2.1	Pure compounds $\text{ZnCr}_2\text{X}_4$ . . . . .	487
4.2.2.4.2.2	Zn–Cr spinels with substitutions . . . . .	490
4.2.2.4.3	Optical properties . . . . .	494
4.2.2.4.4	Electrical properties . . . . .	498
4.2.2.5	References for 4.2.2.0–4.2.2.4 . . . . .	501
4.2.3	Chromium sulfide and selenide spinels of Cd and Hg (H. VON PHILIPSBORN, M. RUBINSTEIN, L. TREITINGER) . . . . .	505
4.2.3.0	Locating of the data . . . . .	505
4.2.3.0.1	Survey of contents . . . . .	505
4.2.3.0.2	Quotation tables . . . . .	506
4.2.3.1	Crystallographic and thermal properties . . . . .	507
4.2.3.1.1	Preparation . . . . .	507
4.2.3.1.2	Phase diagrams and thermodynamic properties . . . . .	510
4.2.3.1.3	Lattice parameter, anion parameter, R-value . . . . .	514
4.2.3.1.4	Lattice dynamics . . . . .	518
4.2.3.2	Magnetic properties . . . . .	520
4.2.3.2.1	Ordering temperatures and exchange interaction . . . . .	520
4.2.3.2.2	Magnetization . . . . .	523
4.2.3.2.3	Susceptibilities (photoferromagnetism included) . . . . .	527
4.2.3.2.4	Magnetostriction . . . . .	530
4.2.3.2.5	Magnetic resonance and torque measurements . . . . .	531
4.2.3.2.6	Mössbauer spectroscopy . . . . .	539
4.2.3.3	Optical properties . . . . .	540
4.2.3.3.1	Refractive index . . . . .	540
4.2.3.3.2	Transmission and absorption spectra in the band gap region . . . . .	540
4.2.3.3.3	Band gap and level schemes . . . . .	549
4.2.3.3.4	Luminescence and other photoinduced effects . . . . .	554
4.2.3.3.5	Magneto-optical effects (Faraday, Kerr, magnetocircular dichroism, reflectance circular dichroism) . . . . .	556
4.2.3.3.6	Reflectance and thermorefectance spectra . . . . .	561
4.2.3.3.7	Raman and IR phonon spectra . . . . .	565
4.2.3.4	Electrical properties . . . . .	578
4.2.3.4.1	Conductivity . . . . .	578
4.2.3.4.2	Hall effect . . . . .	585
4.2.3.4.3	Seebeck effect . . . . .	587
4.2.3.4.4	Photoconductivity . . . . .	588
4.2.3.4.5	Band structure . . . . .	593
4.2.3.4.6	ac conductivity . . . . .	593
4.2.3.4.7	Magnetoresistance . . . . .	594
4.2.3.4.8	Junctions . . . . .	602
4.2.3.4.9	Switching . . . . .	609
4.2.3.5	References for 4.2.3.0–4.2.3.4 . . . . .	610
4.3	Further spinels (D. BONNENBERG, K. A. HEMPEL) . . . . .	614
4.3.0	List of symbols and abbreviations . . . . .	614
4.3.1	V spinels and V spinels with substitutions . . . . .	615
4.3.1.1	V spinels containing $\text{V}^{3+}$ . . . . .	615
4.3.1.2	V spinels containing $\text{V}^{4+}$ . . . . .	625
4.3.1.3	V spinels containing $\text{V}^{5+}$ . . . . .	626
4.3.1.4	V spinels containing both $\text{V}^{3+}$ and $\text{V}^{4+}$ ions . . . . .	627
4.3.2	Ge spinels and Ge spinels with substitutions . . . . .	634
4.3.3	Rh spinels and Rh spinels with substitutions . . . . .	641

4.3.4	References for 4.3.1...4.3.3 . . . . .	650
4.3.5	Al spinels and Al spinels with substitutions . . . . .	654
4.3.6	Ga spinels and Ga spinels with substitutions . . . . .	673
4.3.7	In spinels and In spinels with substitutions . . . . .	680
4.3.8	References for 4.3.5...4.3.7 . . . . .	683
4.3.9	Co spinels and Co spinels with substitutions . . . . .	691
4.3.10	Ni spinels and Ni spinels with substitutions (see also Vol. III/4b, p. 488) . . . . .	695
4.3.11	Te spinels and Te spinels with substitutions (see also Vol. III/4b, p. 488) . . . . .	695
4.3.12	Mn spinels and Mn spinels with substitutions . . . . .	695
4.3.13	Ti spinels and Ti spinels with substitutions . . . . .	712
4.3.14	References for 4.3.9...4.3.13 . . . . .	720
4.3.15	Mo spinels and Mo spinels with substitutions . . . . .	725
4.3.16	W spinels . . . . .	727
4.3.17	Nb spinels and Nb spinels with substitutions; Ta spinels and Ta spinels with substitutions . . . . .	728
4.3.18	Zr spinels and Zr spinels with substitutions; Hf spinels and Hf spinels with substitutions . . . . .	728
4.3.19	Sb spinels and Sb spinels with substitutions; Te spinels and Te spinels with substitutions . . . . .	729
4.3.20	Sn spinels and Sn spinels with substitutions . . . . .	730
4.3.21	Si spinels and Si spinels with substitutions . . . . .	735
4.3.22	Rare earth spinels and rare earth spinels with substitutions . . . . .	738
4.3.23	References for 4.3.15...4.3.22 . . . . .	741

