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Temperature-dependent magnetic susceptibility behaviour of spinelloid and spinel solid solutions in the systems $\text{Fe}_2\text{SiO}_4\text{--Fe}_3\text{O}_4$ and $(\text{Fe,Mg})_2\text{SiO}_4\text{--Fe}_3\text{O}_4$

Received: 23 October 2002 / Accepted: 13 May 2003

Abstract The magnetic behaviour and Curie temperatures (T_C) of spinelloids and spinels in the $\text{Fe}_3\text{O}_4\text{--Fe}_2\text{SiO}_4$ and $\text{Fe}_3\text{O}_4\text{--}(\text{Mg,Fe})_2\text{SiO}_4$ systems have been determined from magnetic susceptibility (k) measurements in the temperature range -192 to 700 °C. Spinelloid II is ferrimagnetic at room temperature and the k measurements display a characteristic asymmetric hump before reaching a T_C at 190 °C. Spinelloid V from the Mg-free system is paramagnetic at room temperature and hysteresis loops at various low temperatures indicate a ferri- to superparamagnetic transition before reaching the T_C . The T_C shows a non-linear variation with composition between -50 and -183 °C with decreasing magnetite component ($X_{\text{Fe}_3\text{O}_4}$). The substitution of Mg in spinelloid V further decreases T_C . Spinelloid III is paramagnetic over nearly the total temperature range. Ferrimagnetic models for spinelloid II and spinelloid V are proposed. The T_C of $\text{Fe}_3\text{O}_4\text{--Fe}_2\text{SiO}_4$ spinel solid solutions gradually decrease with increasing Si content. Spinel is ferrimagnetic at least to a composition of $X_{\text{Fe}_3\text{O}_4} = 0.20$, constraining a ferrimagnetic to antiferromagnetic transition to occur at a composition of $X_{\text{Fe}_3\text{O}_4} < 0.20$. A contribution of the studied ferrimagnetic phases for crustal anomalies on the Earth can be excluded because they lose their magnetization at relatively low temperatures. However, their relevance for magnetic anomalies on other planets

(Mars?), where these high-pressure Fe-rich minerals could survive their exhumation or were formed by impacts, has to be considered.

Keywords Spinelloid · Spinel · Magnetic properties · Curie temperature

Introduction

Olivine and spinels are important minerals in the Earth's mantle, and extensive research has been done on their stabilities. Studies of their phase relations at high pressures and temperatures showed that additionally to wadsleyite (isostructural with spinelloid III) other polytypes of spinelloids occur (e.g. Akaogi et al. 1982; Canil et al. 1991; Woodland and Angel 1998, 2000). The possible incorporation of Fe^{3+} into oxide minerals, silicate spinels and spinelloids has implications for the redox state in the upper mantle and transition zone (e.g. O'Neill et al. 1993) and the physical properties of these phases are important to explain geoelectromagnetic phenomena.

Spinelloids are a family of structures that are polytypes of the basic spinel structure, and their structural relations were first described by Horiuchi et al. (1980). All spinelloids are based on an approximately cubic-close-packed oxygen sublattice and have an ideal stoichiometry of A_2BO_4 . However, they are orthorhombic (*Imma*), and two thirds of the cations occupy octahedral sites and one third is tetrahedrally coordinated. In the system $\text{Fe}_2\text{SiO}_4\text{--Fe}_3\text{O}_4$, spinelloid II, III and V are stable at high pressures and temperatures (Fig. 1; Woodland and Angel 2000). The structures of these three polytypes can be constructed by different stacking sequences of the (110) slabs of the spinel structure. The individual slabs are polar in character, which means a stack of one octahedron upon a tetrahedron. Each slab can be oriented "up" (\uparrow) or "down" (\downarrow). The stacking sequence along [110] in spinel can be represented by $\dots \uparrow\downarrow \dots$, and in spinelloid II by $\dots \uparrow\uparrow\downarrow\downarrow \dots$, in spinelloid III by

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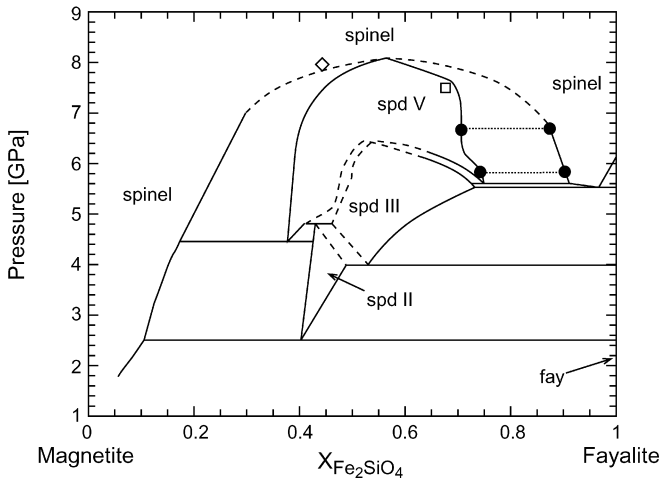


Fig. 1 Phase relations in the system $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{SiO}_4$ as a function of pressure at 1100 °C after Woodland and Angel (2000). Dots indicate spinelloid (*spd*) compositions in equilibrium with spinel. The open symbols denote single-phase samples; for sample numbers and phases see Table 1

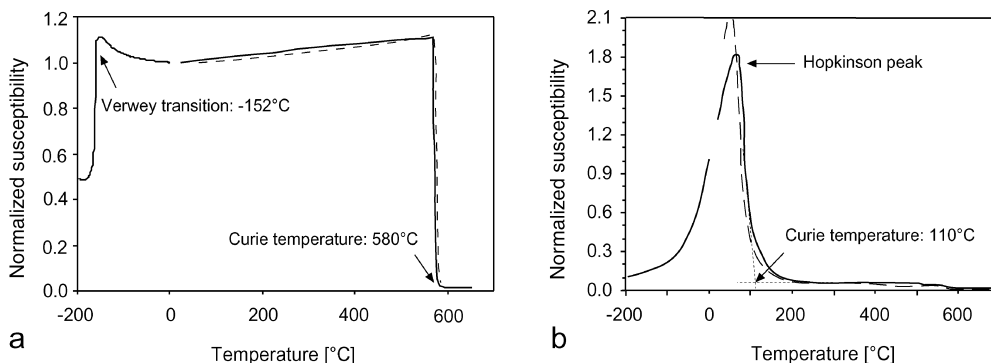
... $\uparrow\uparrow\downarrow\downarrow$... and in spinelloid V by ... $\uparrow\uparrow\downarrow$... (Angel and Woodland 1998). Thus, spinelloids III and V contain tetrahedral T_2O_7 groups (see Fig. 1 in Woodland and Angel 1998) while spinelloid II contains T_3O_{10} groups (see Fig. 1 in Angel and Woodland 1998). Two crystallographically distinct tetrahedral sites are present in the spinelloid II structure, with the T1 sites occupied preferentially by Fe^{3+} , and the T2 sites by Si. Spinelloid V also possesses TO_4 tetrahedra that are distinct from the T_2O_7 groups. Octahedral sites are filled mainly with Fe^{2+} (and Fe^{3+}). Such a cation distribution requires a coupled substitution of the type $^{\text{IV}}\text{Fe}^{3+} + ^{\text{VI}}\text{Fe}^{3+}$ for $^{\text{IV}}\text{Si}^{4+} + ^{\text{VI}}\text{Fe}^{2+}$, similar to many binary spinel systems.

Numerous studies report on the magnetic properties of oxide spinel solid solutions (e.g. $\text{Fe}_3\text{O}_4\text{-FeCr}_2\text{O}_4$, Robbins et al. 1971; $\text{Fe}_3\text{O}_4\text{-MgAl}_2\text{O}_4$, Harrison and Putnis 1995, 1996, 1997; MgFe_2O_4 , Harrison and Putnis 1999). Magnetite has a cubic inverse spinel crystal structure of $^{\text{IV}}\text{Fe}^{3+} (^{\text{VI}}\text{Fe}^{2+}, ^{\text{VI}}\text{Fe}^{3+})_2\text{O}_4$ with two magnetic sublattices on A and B sites giving the mineral a ferrimagnetic character. At the Curie temperature (T_C) of 580 °C (Fig. 2a) the ferrimagnetic ordering disappears and paramagnetism results. Below about -152 °C, there

is an ordered arrangement of Fe^{2+} and Fe^{3+} ions on the octahedral sublattice and the unit cell is slightly distorted from cubic to monoclinic symmetry. Above -152 °C, electron hopping from Fe^{2+} to neighbouring Fe^{3+} on the octahedral site converts the Fe^{2+} to Fe^{3+} and vice versa, and destroys the cation ordering. In this case, all [100] directions are equivalent and the lattice is cubic. Verwey (1939) first reported this structural transition in magnetite (Verwey transition), which can be monitored by temperature-dependent magnetic susceptibility measurements (Fig. 2a). This transition can be observed only in k -T curves from pure, multidomain and not in single domain magnetite grains (e.g. Muxworthy 1999 and own observations), indicating that its magnetic effect strongly depends on grain size. Furthermore, it is suppressed with only minor substitutions of other cations (e.g. Moskowitz et al. 1998). The incorporation of other cations modifies the magnetic properties of the pure magnetite. Curie temperatures are very sensitive to the intracrystalline cation distribution in the spinel crystal lattice and therefore the composition of magnetite-bearing spinel solid solutions can be monitored by the determination of the ferro- to paramagnetic transition. The relationship between the composition of the spinel solid solutions and the Curie temperature are either nearly linear (e.g. $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{TiO}_4$) or follow third-order polynomial functions (e.g. the $\text{Fe}_3\text{O}_4\text{-MgAl}_2\text{O}_4$ solid solution, Harrison and Putnis 1996).

Fe_2SiO_4 -ringwoodite has a normal spinel crystal structure $^{\text{IV}}\text{Si}^{4+} (^{\text{VI}}\text{Fe}^{2+})_2\text{O}_4$ and is paramagnetic above the Néel temperature of -261 °C and antiferromagnetic below this temperature (Suito et al. 1984). Magnetic properties of the $\text{Fe}_2\text{SiO}_4\text{-Fe}_3\text{O}_4$ spinel solid solutions were first reported by Yamanaka and Okita (2001) for samples synthesized at high pressures between 8 and 10 GPa and temperatures between 1150 and 1215 °C. The T_C of these phases decreases gradually, but

Fig. 2a, b Normalized magnetic susceptibility (k) as a function of temperature for **a** pure, multi-domain magnetite from a metamorphic basic dike (Kontny and de Wall 2000). The increase of k at the Verwey transition denotes the monoclinic to cubic transition. **b** Titanomagnetite (TM70) from basalt (Kontny et al. 2003) with a strong increase of k before reaching the Curie temperature. Dotted lines indicate the graphic construction for determining Curie temperatures. In both diagrams, solid lines are for the heating curve and dashed lines for the cooling curve



not linearly, with increasing Si^{4+} content. According to magnetic hysteresis measurements, a ferrimagnetic to antiferromagnetic transition is proposed between a composition $X_{\text{Fe}_3\text{O}_4} = 0.206$ and 0.643 .

Our present study addresses the magnetic properties of spinelloids II, III and V, which are stable at pressures between ~ 2.5 and 9 GPa in the Fe_2SiO_4 – Fe_3O_4 and $(\text{Mg,Fe})_2\text{SiO}_4$ – Fe_3O_4 systems (Woodland and Angel 2000; Koch et al. 2001). From Mössbauer studies it is known that at room temperature spinelloid II and spinelloid III are ferrimagnetic and paramagnetic, respectively (A. B. Woodland, personal communication 1998). Spinelloid V is dominantly paramagnetic with a small ferrimagnetic component apparent in the Mössbauer spectrum. The magnetic behaviour of such spinelloid solid solutions has not been determined until now. In addition, we have measured the properties of several Fe_2SiO_4 – Fe_3O_4 spinels, improving on the dataset of Yamanaka and Okita (2001) to further constrain the composition at which a magnetic transition occurs in these solid solutions.

Methods and materials

Samples used in this study were synthesized under varying high-pressure and -temperature conditions between 4 and 9 GPa and 900 and 1200 °C in a belt apparatus at the Institut für Mineralogie, Universität Frankfurt and in a multianvil press at the Bayerisches Geoinstitut, Bayreuth. Starting material of the experiments was stoichiometric mixtures of fayalite or olivine_{ss} of different composition and magnetite. Sample synthesis conditions and characterization by XRD and microprobe are given in Woodland and Angel (2000) for samples from the Fe_2SiO_4 – Fe_3O_4 system and in Koch et al. (2001) for samples from the $(\text{Fe,Mg})_2\text{SiO}_4$ – Fe_3O_4 system. The phase relations at 1100 °C in the Mg-free system, with samples used for this study, are illustrated in Fig. 1. Phase relations in the Mg-bearing system are analogous, with a shift of the spinelloid stability fields to higher pressures.

The alternating low field (300 A/m, 920 Hz) magnetic susceptibility (k) was measured in the temperature range between -192 and 700 °C using a KLY-2 Kappabridge, combined with a CS-2/CS-L furnace apparatus from AGICO (Hroudá 1994) at the Geologisch-Paläontologisches Institut, Universität Heidelberg. Temperatures and susceptibilities were recorded as the sample warmed from -192 to 0 °C after cooling with liquid nitrogen. Heating/cooling cycles from room temperature to 700 °C (heating rate 10 °C min^{-1}) were performed in a flowing argon atmosphere (110 ml min^{-1}) to avoid mineral reactions with atmospheric oxygen during the heating process. The raw data were corrected for the empty furnace and normalized to the susceptibility magnitude at 0 °C (low-temperature segment) and room temperature (high-temperature segment). The temperature uncertainty is approximately ± 5 °C. Pure magnetite-bearing samples always yield a T_C between 580 and 590 °C (Fig. 1a). A small thermal hysteresis of the furnace assembly occurs between Curie temperatures measured during heating and cooling. The cooling run usually displays a higher T_C of 1 – 5 °C. For one pure spinelloid V sample, magnetic susceptibility and remanence measurements were performed in the temperature range between -271 and 7 °C along with hysteresis loops (maximum field of 2.4 T) at -263 , -163 , -78 and 7 °C using a magnetic properties measurement system (MPMS XL-7). The sample was cooled in zero field and magnetized at -271 °C in a field of 5 T. The amplitude and magnetization were measured during warming up in zero field. Hysteresis loops at room temperature were done for spinelloid II and spinel samples using a PMC alternating gradient field magnetometer (AFM) with maxi-

imum fields of 1.4 T. MPMS and AFM measurements were done at the Institut für Marine Geophysik, Universität Bremen.

k describes the magnetization M (A/m) acquired by a material in a magnetic field H (A/m) according to $k = M/H$ (SI units). The temperature dependence of k can be used to determine the Curie temperature, which is indicative of magnetic phase transitions. Furthermore, changes in Curie temperature are reported to monitor cation order/disorder processes (Harrison and Putnis 1999). T_C was determined using the method described by Grommé et al. (1969), which is shown by dashed lines in Fig. 2b. Below T_C the temperature dependence of k depends on the relationship of $M_S(T)/K(T)$, where M_S is the spontaneous magnetization and K is the magnetic anisotropy. Both parameters decrease with increasing temperature. At low temperatures, these two effects cancel out and k remains nearly constant. If k decreases faster than M_S the thermal fluctuation at T close to T_C causes an increase in k which is called the Hopkinson effect (Dunlop and Özdemir 1997). It occurs in titanomagnetite for special compositions independent of grain size (Fig. 2b) or dependent on grain size, as has been shown for magnetite-bearing samples in Fig. 4a of Kontny and de Wall (2000).

Results and discussion

Temperature-dependent k of spinelloid II, III, V and spinel synthesized from the Fe_3O_4 – Fe_2SiO_4 and Mg-bearing, Fe_3O_4 – $(\text{Mg,Fe})_2\text{SiO}_4$ systems exhibit different magnetic behaviour in the temperature range -192 and 700 °C. The experimental conditions, mineral compositions and characteristic temperatures from the k – T curves are presented in Table 1 for the investigated samples. Spinel and spinelloid compositions are always given in terms of $X_{\text{Fe}_3\text{O}_4}$ along with the number of Mg cations per formula unit, where pertinent.

Spinelloid II

Measurements were performed on three different ferrimagnetic spinelloid II samples; one being Mg-free (Fig. 3a) and two containing Mg (Fig. 3b,c). The Mg-free spinelloid II displays a distinct increase in k above about -50 °C until a peak at 185 °C (Hopkinson peak) is reached. The following sharp decrease of k indicates a Curie temperature (T_C) at 190 °C. The shape of the k curve is asymmetrical, pointing either to the pinning/unpinning of domain walls in multidomain material or the occurrence of more than one transition lying close together in temperature. Normally, a single transition would give a symmetric or near-symmetric peak, as shown for titanomagnetite in Fig. 2b. The excellent correspondence of the heating and cooling segment, especially the good reversibility of T_C at 190 °C, points to a high stability of the spinelloid II sample during the heating experiment. A second heating run of this sample attested the reversibility of the k curve shape and confirmed the stable behaviour of the spinelloid II phase and its characteristic asymmetric peak shape (Fig. 3a). The Mg-bearing spinelloid II also displays a T_C at 190 °C, with a second transition temperature clearly appearing at lower temperatures (Fig. 3b,c). Especially Fig. 3b shows a symmetric shape of the peak at ~ 60 °C,

Table 1 Chemical composition and characteristic magnetic transition temperatures for spinel and spinelloids. *spd* spinelloid; *sp* spinel; *cpx* clinopyroxene; *coe* coesite; *ol* olivine; *ski* “skiaite” garnet; *phases* in brackets minor; *numbers in brackets* one standard deviation; $X_{\text{Fe}_3\text{O}_4}$ magnetite component; *nMg* refers to cations on the basis of four oxygens; T_C Curie temperature

Sample	T [°C]	P [GPa]	Coexisting phases	Spinel $X_{\text{Fe}_3\text{O}_4}$	nMg	Spinelloid $X_{\text{Fe}_3\text{O}_4}$	nMg	Low T Peak [°C]	Tc low [°C]	Tc Spd II [°C]	Tc sp [°C]
Fe₂SiO₄-Fe₃O₄ system											
Mt55-Fr1058	1200	4.0	spd II	0.100 ^a		0.565 (3)		-70	-55	190	585
Mt45-Fr1061	900	5.5	spd V			0.466(2)		-183	-116/-45		
Mt25-Fr1084	1100	5.8	spd V + (sp)			0.269(6)					
Mt20-Fr1073	1200	6.0	spd III + opx			0.331(9)					
Mt45-Fr1044	1200	6.0	spd III			0.459(11)		-77	Paramagnetic		585
Mt70-Fr1073	1200	6.0	sp + spd V	0.804(2)		0.637(4)		-50	-35		530
Mt15-V51	1100	6.7	sp + spd V + cpx	0.124(10)		0.350(30)		-158	-45		16-330/580
Mt25-H1000	1100	7.5	spd V	0.195(56)		0.324(3)		-152	-116/-45		360/433/580
Mt25-S3034	1200	9.5	sp + ski + coe	0.463(50)							445/590
Mt40-S3034	1200	9.5	sp + ski + coe	0.558(8)							
Mt55-H843re	1100	8.0	sp + (coe)								
(Fe,Mg)₂SiO₄-Fe₃O₄ system											
4F8B271	1100	4.0	sp + spd II + ol	0.888(33)	0.04	0.580(9)				140/190	520
4F8V95	1100	6.0	sp + spd II + ol	0.843(16)	0.06	0.555(6)				100/190	540
8F5V81	1100	8.0	spd V + ol + (cpx)			0.478(16)		-120	-90		580
9F8V99	1100	9.0	spd V + (cpd + Si-sp)			0.331(27)		-200	-90		505/580
4F5V129	1100	9.0	sp + spd V + (cpx)	0.875(2)	0.13	0.480(4)		-145	-130		

^a Composition was determined from cell parameters

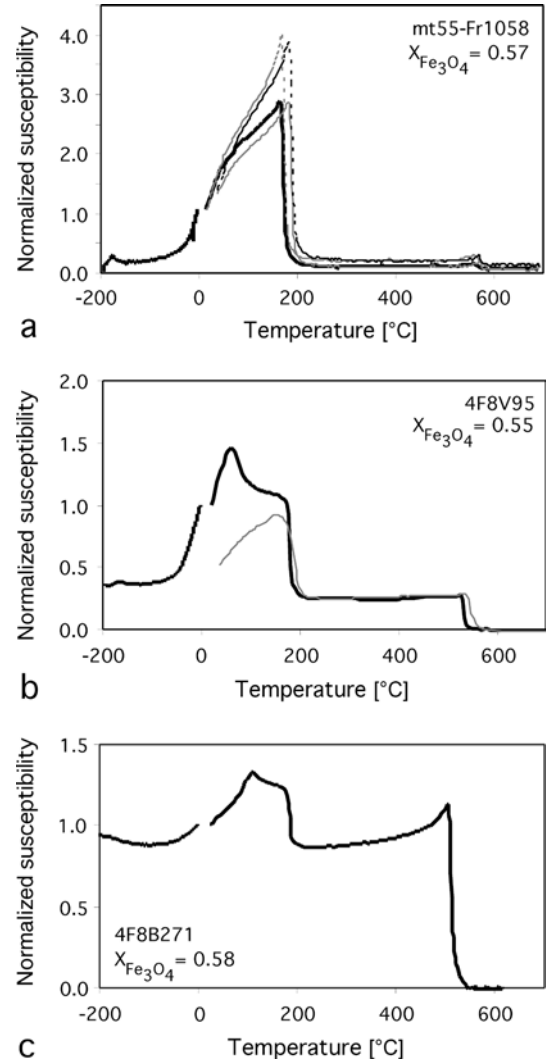


Fig. 3a-c Normalized susceptibility as a function of temperature for **a** Mg-free spinelloid II. *Black solid line* shows the first heating, *grey solid line* the first cooling experiment; *dashed lines* show the second heating and cooling run. **b, c** Mg-bearing spinelloid II with different compositions coexisting with spinel and olivine (see Table 1)

which grades into a shoulder at its high-temperature side. At 190 °C, *k* exhibits a sudden drop. While the T_C at 190 °C is again very stable and independent of composition and pressure (Table 1), the lower transition temperature seems to be variable and sensitive to composition: the 4 GPa sample with a higher $X_{\text{Fe}_3\text{O}_4}$ (0.58) exhibits this transition temperature at 140 °C and the 6 GPa sample with a lower $X_{\text{Fe}_3\text{O}_4}$ (0.55) has one at 100 °C. The cooling curve is not reversible with respect to the pronounced peak for these samples. This observation could indicate that upon cooling through T_C the domain walls form in more stable position. However, a similar behaviour has also been observed in natural titanomagnetite samples and was interpreted to reflect variable titanomagnetite compositions rather than the behaviour of quenched multidomain material (A. Konny, personal communication, 2000).

The compositional range where Mg-free and Mg-bearing spinelloid II solid solutions are stable is small: $0.5 < X_{\text{Fe}_3\text{O}_4} < 0.6$ (Fig. 1). Assuming that the asymmetric shape is not governed by domain processes but related to two different Curie temperatures, several explanations for this behaviour can be considered: (1) alteration or changes in cation order/disorder during the heating experiment, (2) microstructural intergrowth of spinelloid II with two different compositions (e.g. $X_{\text{Fe}_3\text{O}_4} = 0.4$ and $X_{\text{Fe}_3\text{O}_4} = 0.5$), (3) two magnetic sublattices in spinelloid II that behave independently of each other or (4) a structural transition, comparable to the Verwey transition in magnetite.

The excellent reversibility of the asymmetric shape of the k - T curve argues against alteration of the sample during the measurement at elevated temperature. For low-temperature oxidized titanomagnetite, alteration during heating experiments is described as moving T_C to higher temperatures (i.e. in the direction of the magnetite endmember), resulting in an irreversible heating and cooling run (e.g. Worm and Banerjee 1984). Such behaviour is also reported for other spinel systems like Fe_3O_4 - MgAl_2O_4 solid solutions (see Fig. 1b in Harrison and Putnis 1996). However, this is not the case for our Si-bearing spinelloid II samples, leading us to exclude in situ alteration of the sample during the measurement.

A microstructural intergrowth of spinelloid II, e.g. from spinodal decomposition during the quenching of the synthesis experiment, could form two distinct compositions ($X_{\text{Fe}_3\text{O}_4} = 0.4$ and $X_{\text{Fe}_3\text{O}_4} = 0.5$) and would be a possible explanation for the observed double T_C of spinelloid II. The high- $X_{\text{Fe}_3\text{O}_4}$ limit of spinelloid II stability is nearly independent of pressure (Fig. 1) and could be correlated with the stable T_C at 190 °C. The solid solution limit at the low- $X_{\text{Fe}_3\text{O}_4}$ side shifts towards lower $X_{\text{Fe}_3\text{O}_4}$ with increasing pressure (Fig. 1). This would be in agreement with a decrease in T_C as we observed in our measurements. However, no indication of two separate spinelloid II phases was found by either XRD or microprobe analysis.

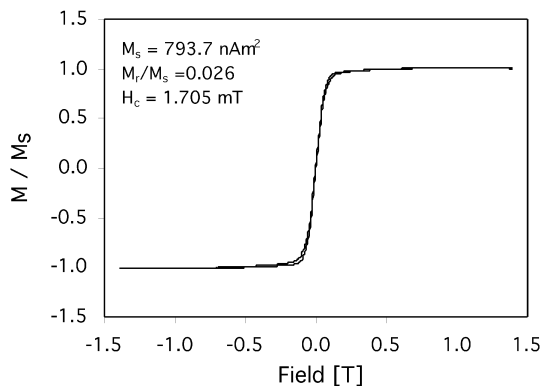


Fig. 4 Hysteresis loop of the spinelloid II sample mt55-Fr1058 showing magnetic moment normalized by saturation (M/M_s) versus applied field

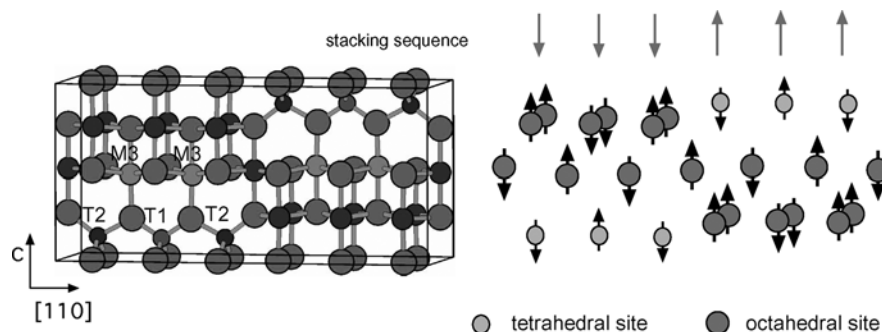
Hysteresis loops for the spinelloid II sample at room temperature show a ramp-like curve with rapid saturation, typical for one multidomain phase (Fig. 4), confirming the mineralogical results. Therefore, two different intimately intergrown magnetic phases can be excluded as an explanation for the two different Curie temperatures since such an intergrowth would lead to hysteresis loops with wasp-waisted shapes (e.g. Tauxe et al. 1996). Saturation magnetization of spinelloid II seems to be higher than for pure magnetite, although a mass-related value could not be obtained. Sensitivity problems of the alternating gradient field magnetometer required a repeated reduction of the sample size, which hindered a mass unit-related correction. The size of the measured samples was about 1 mm or less in diameter. Assuming a volume of 1 mm^3 , the saturation magnetization would be 794 emu cm^{-3} , which is significantly higher than that for magnetite (480 emu cm^{-3} ; e.g. Dunlop and Özdemir 1999).

In general, different magnetic sublattices of one mineral phase (e.g. A and B sublattice in magnetite) compensate each other, resulting in a net magnetic moment that provides a single Curie temperature (e.g. for magnetite $T_C = 580 \text{ °C}$). However, two different Curie temperatures are reported for the magnetic mineral ilvaite $[\text{Ca}(\text{Fe}^{2+}, \text{Fe}^{3+})\text{Fe}^{2+}\text{Si}_2\text{O}_7\text{O}(\text{OH})]$ (Ghose et al. 1984). One T_C at -157 °C occurs when magnetic ordering sets in along chains of edge-sharing octahedral, and the second T_C at -233 °C arises when spins in octahedra, attached to this chain, order at a lower temperature. Another example is gadolinium (Gd), where surface atoms lose their long-range magnetic order at a temperature 60 to 80 degrees higher than bulk atoms (Fadley et al. 1997). Here, the bonding of atoms seems to have an influence on the magnetic stability.

For the ferroelectric oxide BaTiO_3 more than one T_C is reported to be related to structural transitions (Abrahams and Nassau 1986). Below a T_C of 20 °C , the symmetry transforms from cubic to a tetragonal structure and the resulting displacement gives rise to a spontaneous polarization and further T_C s at 5 and -90 °C are described (Abrahams and Nassau 1986). Such a structural transition is also reported for pure magnetite at -152 °C (Verwey transition), reflecting the monoclinic to cubic structural transformation.

The structure of spinelloid II can be constructed by a stacking sequence of the (110) slabs from the spinel structure by $\dots \uparrow\uparrow\downarrow\downarrow \dots$. Two different types of tetrahedral and four different octahedral sites occur (Fig. 5; Angel and Woodland 1998). While the T1 sites preferentially are occupied with Fe^{3+} ($3/4 \text{ Fe}^{3+}$ and $1/4 \text{ Si}$), the somewhat smaller T2 sites are filled favourably by Si ($3/4 \text{ Si}$ and $1/4 \text{ Fe}^{3+}$). On octahedral sites, Fe^{2+} , Fe^{3+} (and Mg) occur, but the M3 site, which is the only one coordinated by the bridging O3 oxygen of the T_3O_{10} group, is exclusively populated by Fe^{2+} (Angel and Woodland 1998). The tetrahedral site occupancy is particularly sensitive to chemical composition, since Fe^{3+} replaces Si in the solid solution. In Fig. 5 the

Fig. 5 Structural (*left*) and magnetic (*right*) model of spinelloid II. According to this model the octahedral layer has an antiferromagnetic structure while the tetrahedral–octahedral layers have uncompensated magnetic spins resulting in a ferrimagnetic sublattice. The sketch for the structural model was kindly provided by R. Angel



crystal structure of spinelloid II and an interpretation of the magnetic structure are presented. The magnetic moment directions, illustrated in the magnetic model (Fig. 5), were arbitrarily chosen according to the assumption of antiferromagnetic spin coupling. Assuming that neighbouring sites of M3 are filled by Fe^{3+} , and all other octahedral sites by Fe^{2+} , the octahedral layer is antiferromagnetic with compensated magnetic moments. Assuming that the T1 sites are 1/4 filled by Si and 3/4 by Fe^{3+} and T2 sites are 3/4 filled by Si and 1/4 by Fe^{3+} , the mixed tetrahedral–octahedral layers should have a ferrimagnetic sublattice with a magnetic moment of $2.25 \mu_{\text{B}}$. Referenced to one unit cell, the magnetic moment is $4.5 \mu_{\text{B}}$, which is larger than that of magnetite ($4 \mu_{\text{B}}$). Such a ferrimagnetic structure should be uniquely related to spinelloid structures with unequal stacking sequences.

Since the spinelloid structure contains corner-sharing rather than isolated tetrahedra, their exchange interactions are probably more complex compared to spinel. Therefore, a magnetic behaviour similar to ilvaite with two different T_{C} s related to different magnetic ordering temperatures might be reasonable.

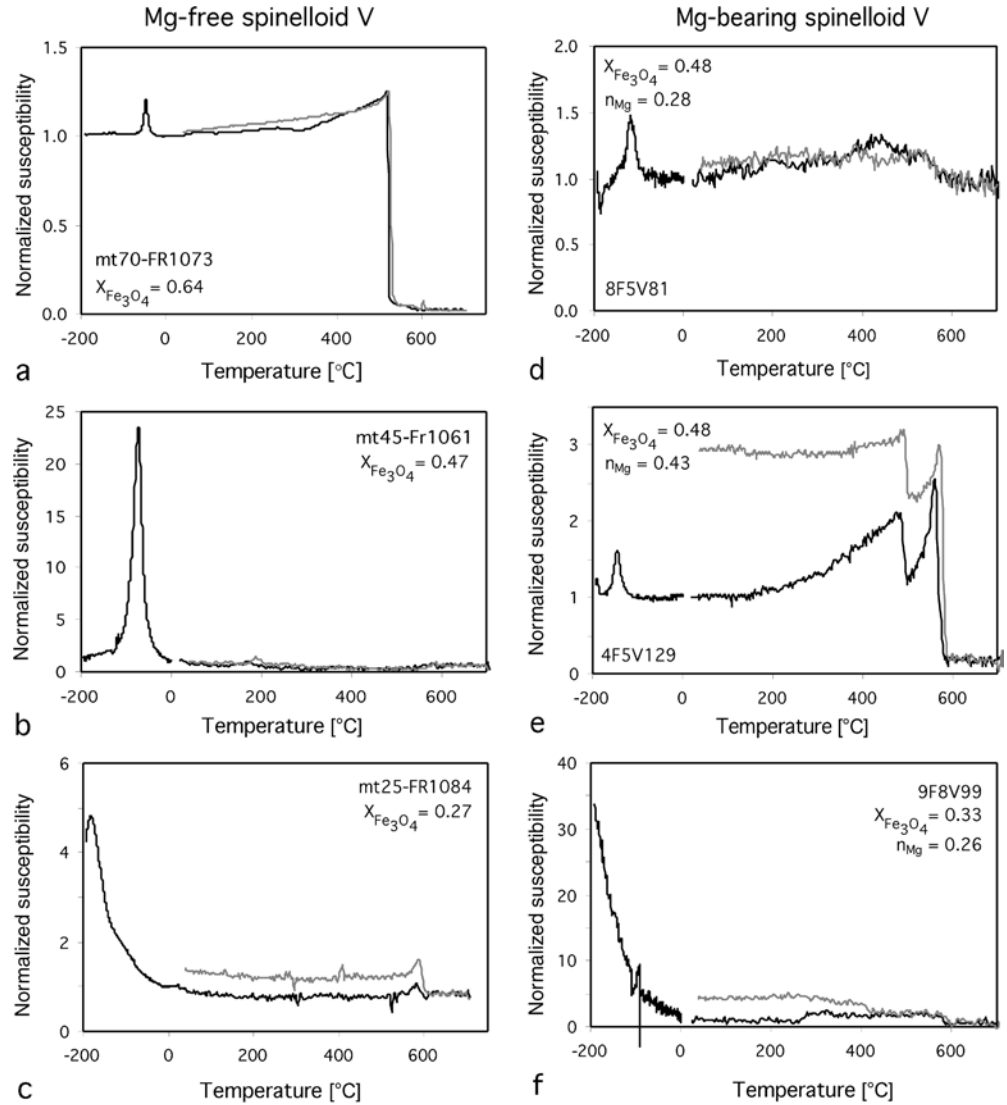
Another possibility to explain the asymmetric k - T behaviour of spinelloid II is that the lower transition temperatures illustrated in Figures 3a–c may be related to a structural transition occurring between ~ 100 and 190 °C from the orthorhombic to another modification of spinelloid II (cubic?), with a T_{C} at 190 °C for the latter phase, similar to that described for BaTiO_3 and magnetite. The lower T_{C} between 100 and 140 °C would then be related to the orthorhombic modification, which is ferrimagnetic at room temperature (Fig. 4). This transition may depend on composition as it is described for the Verwey temperature of magnetite, for example. The Mg-free spinelloid II sample also displays a subordinate T_{C} at 585 °C, characteristic for pure magnetite, indicating that not all of the starting material reacted during the experiment. The presence of relict magnetite grains surrounded by spinelloid was also observed during microprobe characterization. The Mg-bearing spinelloid II samples record a second T_{C} at 520 and 540 °C, respectively, indicating that the minor relict magnetite starting material incorporated some Si during the course of the high-pressure experiment (Koch et al. 2001).

Spinelloid V

Compared to spinelloid II and III, the stability field for spinelloid V is significantly larger with respect to composition ($0.64 > X_{\text{Fe}_3\text{O}_4} > 0.27$; Fig. 1 in Woodland and Angel 2000). The k - T curves of Mg-free spinelloid V samples reveal a magnetic transition at low temperature, the actual temperature being composition-dependent (Fig. 6a–c). Sample mt70-Fr1073 with $X_{\text{Fe}_3\text{O}_4} = 0.64$ displays a k peak at -50 °C and is interpreted as a characteristic temperature of the spinelloid V based upon comparison with the k - T curve obtained for sample mt45-Fr1061, which is single-phase spinelloid (cf. Fig. 6a and b). The observed sharp decrease in k at 530 °C is attributable to the T_{C} of the coexisting magnetite-rich spinel in this sample ($X_{\text{Fe}_3\text{O}_4} = 0.80$; Table 1). Yamanaka and Okita (2001) obtained a similar T_{C} for a spinel of comparable composition. The characteristic peak for a sample with $X_{\text{Fe}_3\text{O}_4}$ of 0.47 is shifted to -70 °C (Fig. 6b). The peak is much better resolved in this case since the sample is single-phase and the k - T curve is not dominated by the stronger signal from any magnetite-rich spinel. The transition shifts to still lower temperatures for compositions poorer in Fe_3O_4 content; at $X_{\text{Fe}_3\text{O}_4} = 0.27$, the characteristic peak lies at -183 °C (Fig. 6c). Only the high-temperature portion of the peak is observed because we were only able to cool down the sample to liquid N_2 temperature with the Kappabridge. The shape of the visible slope is not symmetrical and two kinks are present, one at -116 °C and a second at -45 °C (Fig. 6c). These two kinks can be related to spinelloid V and the coexisting magnetite-poor spinel in this sample, respectively. Such a T_{C} for a spinel with $X_{\text{Fe}_3\text{O}_4} = 0.12$ is consistent with the measurements of Yamanaka and Okita (2001; cf. Fig. 12). The small k heterogeneity at 580 °C indicates minor relics of the magnetite starting material in the sample. The reversibility of the heating and cooling runs indicates that no other phases nucleated during heating. Only sample mt25-Fr1084 exhibits a small irreversibility between the heating and cooling run, probably due to a small enhancement of the relict magnetite or to cation order/disorder processes.

Mg-bearing spinelloid V also has a characteristic transition at low temperatures (Fig. 6d–f), with the peak

Fig. 6a–f Normalized susceptibility as a function of temperature for **a, b, c** Mg-free spinelloid V and **d, e, f** Mg-bearing spinelloid V of different compositions. *Black solid lines* show the heating, *grey lines* the cooling segment



temperatures being significantly lower than for the Mg-free samples (Table 1). In sample 4F5V129 (Fig. 6e), spinelloid V coexists with a magnetite-rich spinel that is represented by the observed transition temperature of 505 °C (Table 1). The T_C at 580 °C indicates a significant amount of the magnetite starting material in this sample. The pronounced increase in k just before reaching the T_C at 505 and 580 °C (Hopkinson peak) probably indicates small magnetic domain sizes for both of the ferrimagnetic phases. This observation clearly shows that k - T curves are a rapid and precise tool to detect the reaction progress in experiments.

From the magnetic structure model presented in Fig. 7, weak ferrimagnetism is proposed for spinelloid V. As for the spinelloid II structure, the octahedral layer is antiferromagnetic, assuming that the octahedral sites are exclusively occupied with equally distributed Fe^{2+} and Fe^{3+} . The site preference for Fe^{3+} is different for the two crystallographically distinct tetrahedral sites. For example, a crystal refinement on a sample with composition $X_{\text{Fe}_3\text{O}_4} = 0.60$ by Ross II et al.

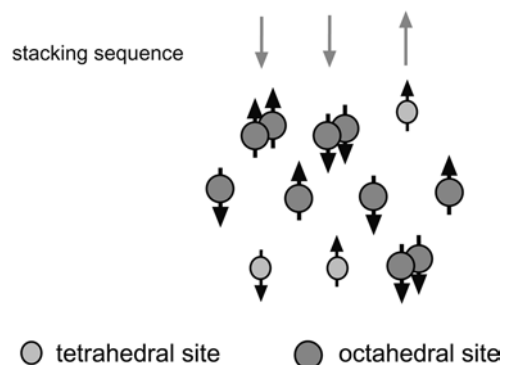


Fig. 7 Magnetic model of spinelloid V. Assuming that 1/3 of the tetrahedral sites are filled with Si, Fe^{3+} must also occur on octahedral sites (Ross II et al. 1992). This arrangement suggests an antiferromagnetic structure of octahedral layers and a weak ferrimagnetic moment for mixed octahedral–tetrahedral layers

(1992) yielded $X_{\text{Fe}} = 0.84$ for the isolated T1 sites and $X_{\text{Fe}} = 0.60$ for the T2 sites (T_2O_7 groups). For this site occupancy, magnetic spins are not fully compensated,

giving rise to a net magnetic moment within the mixed tetrahedral-octahedral layer of $0.2 \mu_B$. However, with decreasing Fe_3O_4 content in the solid solution, anti-ferromagnetic behaviour should develop when the T1 sites have $X_{\text{Fe}} = 0.8$. A further decrease of Fe^{3+} on T1 leads to a net magnetic moment but in the opposite direction. For example, when the T1 site has $X_{\text{Fe}} = 0.4$, the magnetic moment should be $2 \mu_B$.

The compositional dependence of the peak temperature for the Mg-free and Mg-bearing spinelloid V samples is plotted in Fig. 8. Curie temperatures decrease non-linearly with decreasing $X_{\text{Fe}_3\text{O}_4}$ in the Mg-free spinelloid V samples. The dashed line is a least-squares fit to the data with a third-order polynomial function $T_C = -1187x^2 + 922x - 227$. The Mg-bearing samples clearly deviate from this curve which implies that Mg substitution produces a decrease in T_C through the dilution effect of Mg substituting Fe^{2+} on octahedral sites.

In order to understand the magnetic behaviour below T_C , frequency-dependent, low-temperature susceptibility and magnetic remanence measurements, as well as hysteresis loops (Fig. 9) for the pure spinelloid sample mt45-Fr1061 were performed using an MPMS in the temperature range between -271 and 7 °C. Susceptibility measurements confirm the susceptibility peak at -73 °C. Below about -100 °C, magnetic remanence increases continuously, indicating ferrimagnetic behaviour. Hysteresis loops indicate a change in magnetic domain state that occurs as a function of microstructure and temperature. At -263 °C the hysteresis loop reveals high coercivities suggesting single-domain magnetic behaviour. With increasing temperature, coercivity decreases, indicating a growth of magnetic domains. However, at the susceptibility peak temperature of -73 °C, superparamagnetic behaviour occurs just before reaching the T_C at -57 °C. This is confirmed by the frequency-dependent, strong increase in susceptibility

just before reaching the T_C and the decay of remanence before the susceptibility increases to form the peak. Superparamagnetic domains are in the range between 0.03 and $0.09 \mu\text{m}$ (e.g. Dunlop and Özdemir 1999) and preserve no remanence. The hysteresis measurement at 7 °C has a very small loop, indicating a minor ferrimagnetic contribution to the magnetization. This agrees with room-temperature Mössbauer data that also revealed a minor ferrimagnetic component in the spectrum (A. B. Woodland, personal communication, 1998). The magnetic behaviour of spinelloid V seems to be typical for spinel and spinel-like phases with intermediate to low magnetite contents, which display a pronounced susceptibility peak as is shown for titanomagnetite in Fig. 2b. The rapid drop in coercivity and the superparamagnetic curves before reaching T_C are evidence for thermal fluctuations in the crystal lattice (Özdemir and O'Reilly 1981).

Spinelloid III

k - T curves for two Mg-free spinelloid III samples are presented in Fig. 10. Sample mt20-Fr1073 has a depression at low temperatures (Fig. 10a), which could indicate a transition temperature at about -160 °C. This sample contains spinelloid III together with paramagnetic orthopyroxene and, therefore, the transition temperature could be related to either of these phases. Sample mt45-Fr1044 shows a more complex behaviour. A dominantly paramagnetic behaviour is apparent between -192 and 300 °C, with an exponential decrease in susceptibility. A very small peak is observable at -77 °C (Fig. 10b). Above about 300 °C an increase in k occurs and may indicate either changes in cation ordering or the formation of a new phase with a slightly higher k . A subordinate T_C at 585 °C attests to the presence of minor amounts of relict magnetite starting material. The cooling curve also records the magnetite T_C , but no decrease occurs at ~ 300 °C, indicating a non-reversibility of the k due to heating. A second heating experiment (Fig. 10b) exhibited behaviour similar to that of sample mt20-Fr1073 with a depression in k . This sample contains only spinelloid III and therefore it seems most probable that the low-temperature behaviour with the depression in susceptibility is related to the spinelloid III. This could represent the Néel temperature. However, the temperature is similar for the two different compositions, which is unusual, since substitution of non-magnetic cations is expected to change the magnetic properties. Therefore, we consider that the Néel temperature of spinelloid III occurs below -200 °C, outside the temperature range of our measurements. Based upon the $\dots \uparrow\uparrow\downarrow\downarrow \dots$ stacking of the basic structural units, we would expect spinelloid III to exhibit perfect anti-ferromagnetic ordering below the Néel temperature. The magnetic signal of our spinelloid III samples is generally very weak, and further studies on other compositions, such as $(\text{Mg,Fe})_2\text{SiO}_4$ -wadsleyites are

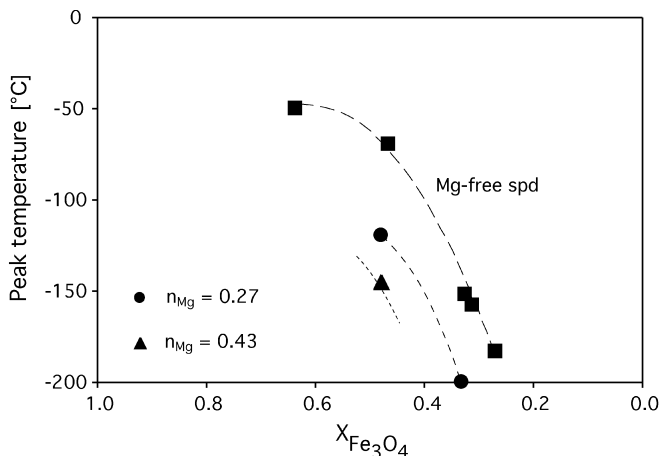
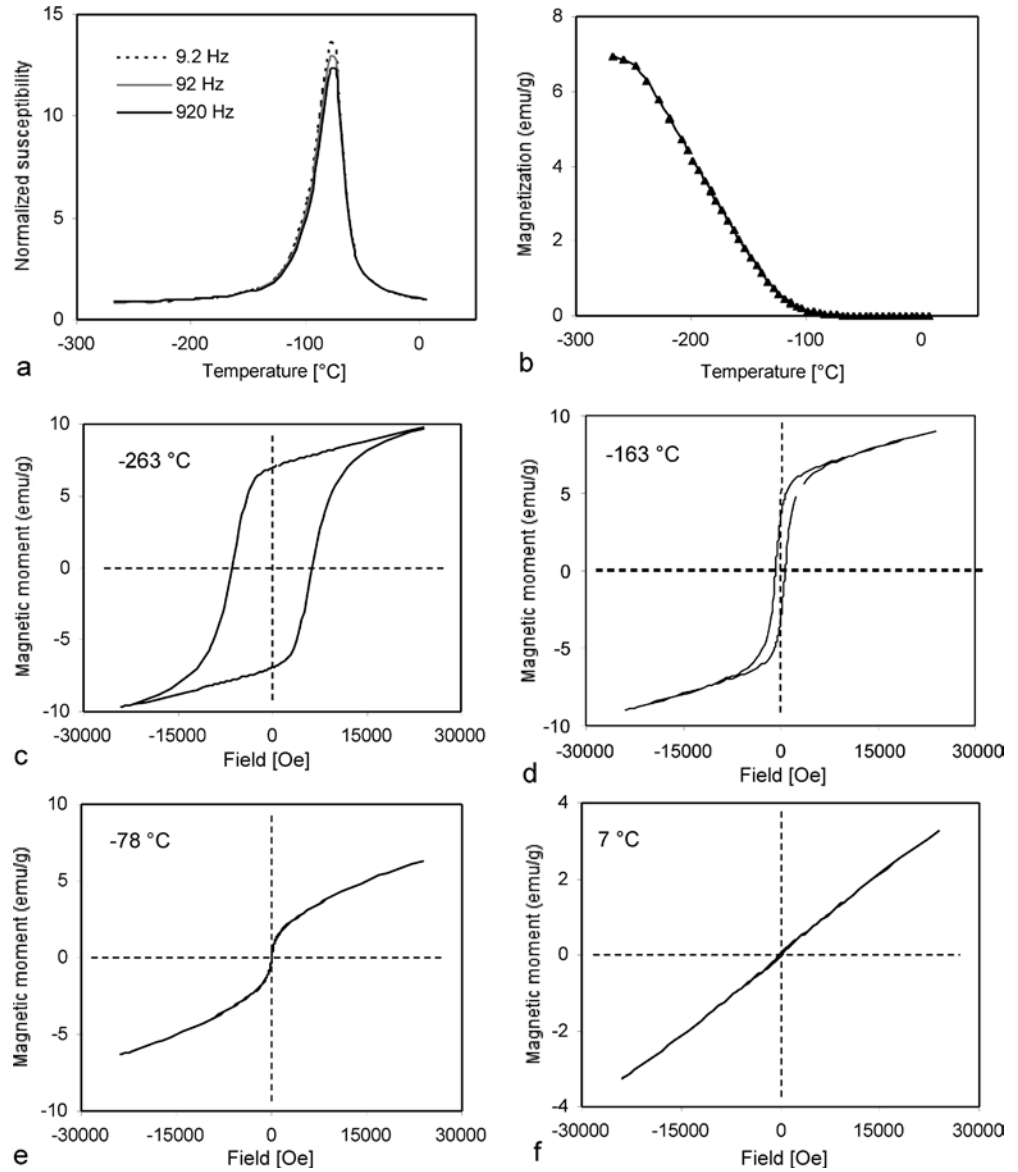


Fig. 8 Peak temperature plotted as a function of Fe_3O_4 content in spinelloid V. Filled squares denote Mg-free spinelloid V, filled circles and triangle are Mg-bearing spinelloid V. n_{Mg} refers to Mg cations based on four oxygens

Fig. 9a–f Susceptibility **a** and isothermal remanent magnetization **b** in the temperature range -271 and 7 °C for the pure spinelloid V sample mt45-Fr1061. **c, d, e, f** Hysteresis loops at various temperatures. Note the different scale for the magnetic moment in **f**



necessary to better understand the magnetic behaviour of this polytype.

Spinel

A range of spinel-solid solution compositions are stable in the Mg-free and Mg-bearing systems depending on temperature, pressure and bulk composition (Fig. 1; Woodland and Angel 2000; Koch et al. 2001). In this study, the T_C s of spinels, including some coexisting with a variety of other phases, were investigated (Table 1). Spinel with $X_{\text{Fe}_3\text{O}_4} = 0.20$ and 0.46 were additionally synthesized for this study to provide information on compositions lying within the compositional gap in the dataset of Yamanaka and Okita (2001). k - T curves of the single-phase spinel samples are presented in Fig. 11. For a spinel with $X_{\text{Fe}_3\text{O}_4} = 0.56$ (mt55-H843) there is a

sharp decrease in k at $T_C = 445$ °C and a weak second T_C at 580 °C. This latter value corresponds to relict magnetite in the sample while the lower T_C is attributable to the spinel (Fig. 11a). At low temperatures, constant k values occur and indicate a suppression of the Verwey transition. Spinel with lower $X_{\text{Fe}_3\text{O}_4}$ contents exhibit more complex susceptibility behaviour. In contrast to the spinel in sample mt55-H843, k - T curves from the samples with lower $X_{\text{Fe}_3\text{O}_4}$ have a third transition temperature located on the flank of the k slope that is related to the spinel phase (cf Fig. 11a with 11b and c). This behaviour is interpreted as reflecting two separate spinel compositions, one with a lower and one with a higher $X_{\text{Fe}_3\text{O}_4}$. The good reversibility illustrated in Fig. 11b suggests that both phases were originally present in the sample and were not formed during the heating experiment. If cation ordering or exsolution were the reason for the two different spinel Curie tem-

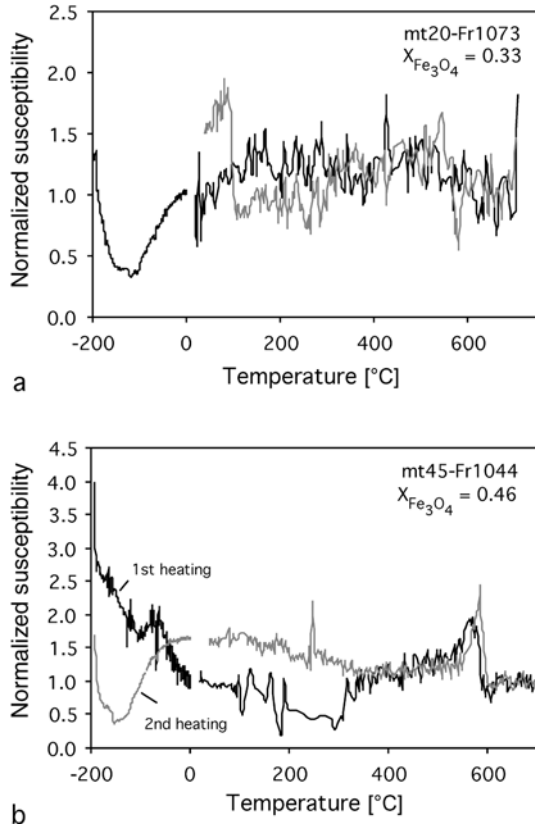


Fig. 10a, b Normalized susceptibility as a function of temperature for Mg-free spineloid III of two different compositions. *Black solid lines* show the heating, *grey lines* the cooling segment

peratures, then the lower T_C would be strongly depressed or would no longer appear in the cooling segment of the measurement.

The shape of the k - T curve for the sample with $X_{\text{Fe}_3\text{O}_4} = 0.20$ is distinctly different in comparison to the signal from spinels with higher $X_{\text{Fe}_3\text{O}_4}$ contents. This low- $X_{\text{Fe}_3\text{O}_4}$ sample has a broader slope in the susceptibility curve, indicating an even larger range in composition (Fig. 11c) compared to the samples with $X_{\text{Fe}_3\text{O}_4} = 0.56$ and 0.46 which display a sharp decrease in susceptibility (Figs. 11a,b). The wider FWHM (full width at half maximum) of peaks in the powder diffraction pattern for this low- $X_{\text{Fe}_3\text{O}_4}$ sample supports this interpretation of the k - T curves. The low-temperature k segment for the low- $X_{\text{Fe}_3\text{O}_4}$ spinel displays a gradual increase in susceptibility up to about 0 °C followed by a gentle decrease. The difference in curve shape probably relates to a change of the magnetic interactions between A and B sublattices with composition.

The variation in T_C with composition is listed in Table 1 and is illustrated in Fig. 12 along with the data of Yamanaka and Okita (2001). T_C decreases with increasing nonmagnetic Si^{4+} ions in the spinel structure. This is in agreement with the magnetic concept of magnetite-bearing spinel systems where dilution with

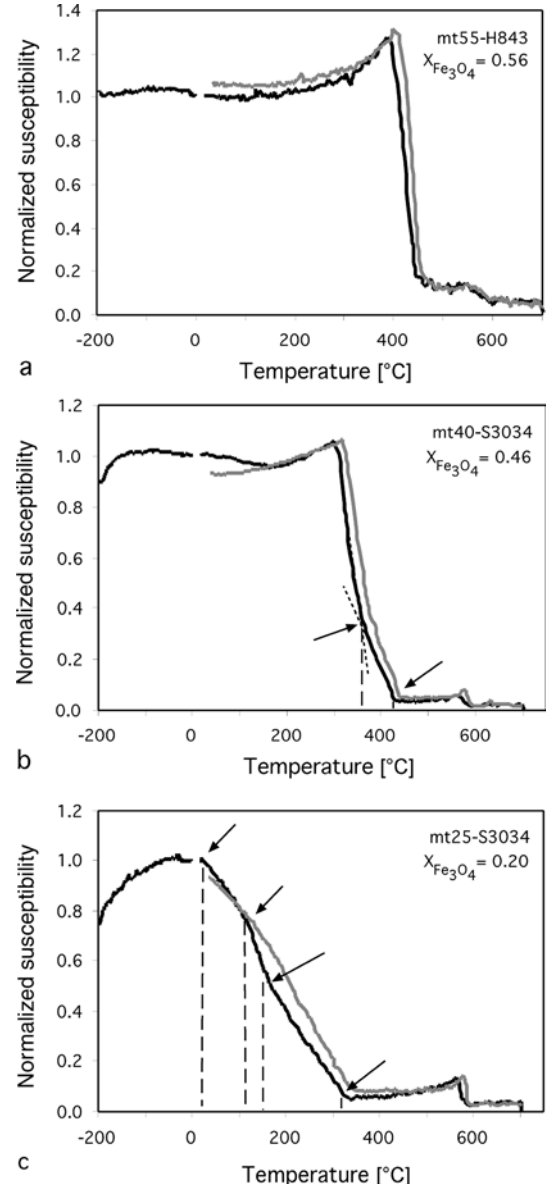


Fig. 11a–c Normalized susceptibility as a function of temperature for three different spinel compositions in the system Fe_3O_4 - Fe_2SiO_4 . **a** A spinel T_C at 445 °C and a subordinate T_C for relict magnetite occur. **b** In contrast to **a**, two different T_C s for spinel solid solutions and some magnetite are seen. **c** Wide peak with several kinks at the high-temperature slope results from a heterogeneous composition of the spinel phase. *Black solid lines* show the heating, *grey lines* the cooling segment. *Arrows* in **b** and **c** indicate different T_C s

non-magnetic ions generally lowers T_C . The variation over the complete compositional range is not linear but can be described in terms of a third-order polynomial function $T_C = -889.36x^2 + 73.86x + 568.37$. The data of Yamanaka and Okita (2001) are in reasonable agreement with ours, but show systematically lower T_C s (Fig. 12). This is probably related to the different methods used for the determination of T_C . Yamanaka and Okita (2001) derived T_C from temperature-dependent magnetization measurements using a vibrating sample

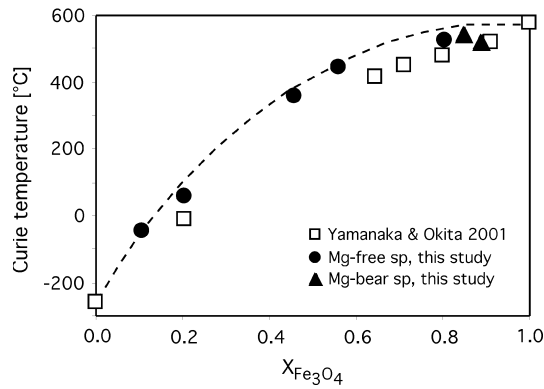


Fig. 12 Variation of Curie temperature of Mg-free and Mg-bearing spinel solid solutions with composition. *Open squares* are from Yamanaka and Okita (2001)

magnetometer, and we measured the temperature dependence of k with a Kappabridge. A shift due to differences in cation order can be ruled out, since samples from both studies were prepared under similar experimental conditions.

The low-temperature behaviour of single spinel phases from this study shows a change in curve shape with decreasing $X_{\text{Fe}_3\text{O}_4}$ from nearly constant k values (Fig. 11a) to an increase of k with temperature (Fig. 11c). This may be related to the occupancy of Si^{4+} , which becomes increasingly ordered with increasing Si content (Yamanaka and Okita 2001). Along with this cation ordering, a transition from ferri- to antiferromagnetic ordering occurs, which influences magnetic properties like the k - T behaviour. The non-linear trend between T_C and composition across the binary join (Fig. 12) may reflect this transition. Yamanaka and Okita (2001) found that a spinel with $X_{\text{Fe}_3\text{O}_4} = 0.21$ does not approach saturation during a hysteresis measurement at -271 °C, even at high magnetic fields of 7 T. They reported this spinel to be antiferromagnetic with a Néel temperature of -13 °C. Our k -data for a spinel of comparable composition (sample mt25-S3034) revealed a first T_C at 16 °C (Table 1). Room-temperature hysteresis measurements on this sample indicated ferrimagnetic behaviour. In fact, the hysteresis measurements for this sample are no different to those of sample mt40-S3034 with $X_{\text{Fe}_3\text{O}_4} = 0.46$. Both samples show ferrimagnetic behaviour, albeit with a different k - T curve shape. It should be noted that our hysteresis loops were determined on the same sample material that was previously heated during the k - T measurements. As the signal from sample mt25-S3034 is not exactly reversible (Fig. 11c), a small shift in composition prior to the hysteresis measurements cannot be definitely excluded. However, this possibility does not affect our interpretation that the change from ferrimagnetic to antiferromagnetic behaviour in these spinels is transitional rather than abrupt. Our data constrain the ferrimagnetic–antiferromagnetic transition to occur at a composition $\leq X_{\text{Fe}_3\text{O}_4} = 0.20$.

Conclusions

This study has demonstrated that spinelloid polytypes display magnetic ordering temperatures generally below 190 °C. Spinels, which may coexist with these spinelloid phases, have Curie temperatures between -261 and 580 °C depending on their composition. Spinelloid II probably exhibits an additional transition between about 100 and 140 °C, either indicating two different T_C s or a structural transition. However, this has yet to be confirmed by high-temperature neutron diffraction or XRD measurements. Depending on the Fe_3O_4 content in spinelloid V, a ferrimagnetic to paramagnetic transition occurs between -50 and -183 °C. Increasing Mg substitution depresses this transition temperature. The effect is relatively strong and implies that Mg substitution on the octahedral sublattice disturbs the ordering of Fe^{2+} on these sites. In contrast, spinelloid III predominantly behaves paramagnetically over the measured temperature range of -192 and 700 °C, and from structural considerations we expect perfect antiferromagnetic ordering below the Néel temperature. We have also demonstrated that spinel solid solutions exhibit predominantly ferrimagnetic behaviour. The ferri- to antiferromagnetic transition seems to be transitional and occurs at or below $X_{\text{Fe}_3\text{O}_4} = 0.20$.

In contrast to magnetite-rich spinel (i.e. titanomagnetite), the different spinelloid polytypes cannot contribute to deep magnetic anomalies in the Earth's lithosphere because they lose their magnetization at relatively low temperatures. It is generally considered that $(\text{Mg,Fe})_2\text{SiO}_4$ -wadsleyite, which is isostructural to spinelloid III, is a dominant phase in the upper portions of the transition zone of the Earth's mantle and would most likely contain at least some Fe^{3+} (e.g. O'Neill et al. 1993). Wadsleyite has also been reported from meteorites with impact-induced assemblages (Putnis and Price 1979; Price et al. 1983). However, considering our observations of the magnetic properties of Fe^{3+} -rich “wadsleyite”, it is unlikely that this phase could contribute to magnetic anomalies in the Earth or even on extraterrestrial bodies, where wadsleyite formed from meteorite impact and was subsequently cooled to ambient temperatures in space.

Nevertheless, the possibility that spinelloids II or V could contribute to magnetic anomalies of other planetary systems where these high-pressure minerals survive their exhumation or form from impacts cannot be ruled out. Unlike the magnetic anomalies on Earth, the crustal anomalies on Mars can only be due to remanent magnetization because no magnetic field currently exists that contributes an induced component. Local magnetic anomalies have been observed in the heavily cratered areas of Mars' southern hemisphere and are very strong, requiring the presence of magnetic minerals with significant remanence (e.g. Weitz and Rutherford 1999). The petrological carriers for these anomalies are heavily debated and none of the proposed minerals including

magnetite, titanomagnetite, hematite and pyrrhotite satisfies all the preconditions for an unequivocal interpretation (e.g. Kletetschka et al. 2000; Rochette et al. 2002). The larger magnetization of the Martian crust compared to the Earth is attributed to the former's higher Fe content. Since spinelloids II and V are stabilized in high-Fe bulk compositions (Koch et al. 2001), we can speculate that spinelloid II, with its very strong saturation magnetization, may produce very large magnetic signatures, and even spinelloid V could make a contribution at low surface temperatures, such as the range of -130 to 30 °C reported for Mars (Kieffer et al. 1992). Further investigations are necessary to test if spinelloids could indeed contribute to planetary magnetic anomalies.

Acknowledgements The samples investigated in this study were mostly synthesized or investigated under projects supported by the Deutsche Forschungsgemeinschaft (grants Ko 1514/1, Wo 652/1–2, Wo 652/4–1, AL 166/14–2). G. Brey (Universität Frankfurt) and D. Rubie (Bayerisches Geoinstitut) are thanked for access to their high-pressure facilities. R. Angel kindly provided the structural model of Fig. 4. R. Angel and C. McCammon are thanked for fruitful discussions pertaining to this work and T. Frederichs is thanked for his support and discussions during the stay of A. K. at the Institut für Marine Geophysik, Universität Bremen. We are grateful to an anonymous reviewer for his constructive comments.

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