



Crystal structure, phase transitions and magnetic properties of pyrrhotite-type compounds $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$



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ABSTRACT

A series of $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds with Ti concentrations up to $x=4$ has been synthesized by solid state reactions. The substitution of Ti for Fe in pyrrhotite (Fe_7S_8) modifies its crystal structure from the initial monoclinic 4C superstructure of the NiAs-type to the hexagonal 3C superstructure at $x=1$ and then to the 2C monoclinic superstructure at $x \geq 2$. The structural phase transition associated with the disordering of vacancies in metallic layers is found to persist in all the compounds. The growth of the Ti content in $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ is accompanied by a gradual decrease of the magnetic ordering temperature from ~ 590 K at $x=0$ down to 145 K at $x=4$, by a substantial increase of the low-temperature coercive field (up to 24 kOe) and reduction of the effective magnetic moment from $\sim 5.8\mu_B$ to $4.3\mu_B$. Unlike ferrimagnetic order in Fe_7S_8 , the compound $\text{Fe}_6\text{Ti}_1\text{S}_8$ shows an antiferromagnetic behavior, while further growth of the Ti concentration above $x=2$ increases the resultant magnetization up to a value almost in twice higher than the value for non-substituted Fe_7S_8 . Such non-monotonous changes in magnetization behavior with increasing Ti concentration are ascribed to the preferential substitution of Ti for Fe in alternating metallic layers.

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1. Introduction

The iron sulfide with composition Fe_7S_8 has been studied for several decades by various experimental techniques on polycrystalline samples and single crystals of artificial or natural origin [1–8]. This compound belongs to a group of minerals pyrrhotite Fe_{1-x}S ($0.05 < x \leq 0.125$), which is of interest from different points of view, such as geomagnetism, physics of the Earth's core, meteoritics, metallurgy, physics and chemistry of solids. For $x=0.125$, the Fe_7S_8 compound (pyrrhotite) has a layered superstructure of the NiAs type with alternating layers of iron and sulfur. The planes containing sulfur atoms are full. One eighth of the iron sites are vacant; and superstructures arise from ordering of vacancies in some iron layers, in a way that there is a layer of iron atoms without vacancies followed by a layer containing vacancies. The type of superstructure depends on the type of vacancy ordering, which in turn depends on the condition of sample preparation and on the heat treatments performed. Fe_7S_8 was

reported to have monoclinic 4C [$(2\sqrt{3})a_0 \times 2a_0 \times 4c_0$] or hexagonal 3C ($2a_0 \times 2a_0 \times 3c_0$) superstructures, where a_0 and c_0 are the lattice parameters of the hexagonal NiAs unit cell. The 4C phase is stable at room temperature, and can be obtained by a slow cooling process or by low temperature heat treatment, while the 3C phase is a high temperature phase, that can be brought to room temperature by quenching from high temperature [1–4].

The results of neutron diffraction studies [6] showed that the magnetic structure of this compound also exhibits a layered character. The magnetic moments of iron atoms ($\mu_{\text{Fe}} \sim 3.2\mu_B$ [6]) are arranged ferromagnetically inside each layer, but coupled antiferromagnetically between adjacent layers. The presence of vacancies in every second iron layer leads to incomplete cancellation of magnetic moments, and hence to the appearance of ferrimagnetism in Fe_7S_8 with critical (Neel) temperatures of about 590 K [7,8]. The iron selenide Fe_7Se_8 having also a NiAs-type structure exhibits a ferrimagnetic order below 480 K [9]. The Co containing compounds Co_7S_8 and Co_7Se_8 with reduced interlayer distances (by about 10%) in comparison with Fe_7X_8 ($\text{X}=\text{S}, \text{Se}$) are reported to be Pauli paramagnets [10,11]. It was pointed out that the substitution of iron in Fe_7S_8 even by a small amount of other transition metal atoms (up to 10%) may affect the magnetic properties [12]; for example, the replacement of Fe by 10% Ti, V,

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Co or Ni atoms results in significant decrease of the effective magnetic moment (μ_{eff}) calculated per 3d atom, however, the substitution of Fe by Cr or Mn does not strongly influence μ_{eff} . As was shown for $(\text{Fe}_{1-x}\text{Co}_x)_7\text{S}_8$ and $(\text{Fe}_{1-x}\text{Co}_x)_7\text{Se}_8$ systems, the substitution of Co for Fe up to $x \sim 0.6$ leads to the disappearance of a long-range magnetic order and zeroing a magnetic moment on 3d atoms [13,14]. The collapse of a Fe magnetic moment in Fe_{1-x}S was detected also under application of hydrostatic pressure by the Mossbauer spectra measurements [15,16] and X-ray spectroscopy experiments [17]. As debated in the literature [17,18] this change in the Fe magnetic state may result from a high spin–low spin transition of Fe^{2+} or by delocalization of Fe 3d electrons owing to the reduction of interatomic distances.

The present work aims to reveal the influence of Ti for Fe substitution on the crystal structure, phase transitions and magnetic order in a $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ system in a wide concentration range. As was shown recently [19], the compound $\text{Fe}_4\text{Ti}_3\text{S}_8$ with 7:8 composition exhibits an almost twice higher saturation magnetization per formula unit than that observed for Fe_7S_8 . Such a change of the resultant magnetization owing to the Fe–Ti substitution was suggested to result from the non-random distribution of Ti atoms in the two iron sublattices. Alternating layers of titanium, sulfur and iron were observed in compounds $\text{Fe}_x\text{Ti}_{2-x}\text{S}_2$ obtained by intercalation of iron atoms into TiS_2 matrix [20,21]. The parent TiS_2 compound has a CdI_2 -type layered structure in which every other metallic layer in the c direction of the NiAs structure is missing. Therefore, it could be expected that the growth of the Ti concentration in $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ will lead to the situation analogous to that observed in highly intercalated $\text{Fe}_x\text{Ti}_{2-x}\text{S}_2$. Together with X-ray diffraction and magnetization measurements we employed the thermal expansion measurements bearing in mind its high sensitivity to the structural changes, in particular, to the vacancy order–disorder. Another goal of this paper is to achieve a better understanding of mechanisms responsible for the formation of a magnetic moment, magnetic order and magnetic hysteresis in the compounds the magnetism of which is associated with the presence of iron atoms.

2. Experimental

Polycrystalline samples $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ ($x=0$ –5) were obtained by solid-state reactions in evacuated quartz tubes. The starting materials were small pieces of 99.95% pure titanium, sulfur (99.99%) and powder of iron (99.98%). The tubes with starting materials were gradually heated in a furnace from room temperature up to 950 °C (with one-day temperature steps at 200 °C, 400 °C and 600 °C), then the samples were kept for 2 weeks at temperature 950 °C followed by slow cooling to room temperature. The obtained samples were ground, compressed in tablets, sealed in quartz tubes under vacuum and then homogenized in a furnace for another week at 800 °C followed by slow cooling to room temperature. In order to examine the quality of the samples and the changes in the crystal structure upon substitution a powder X-ray diffractometer Bruker D8 ADVANCE with $\text{Cu K}\alpha$ radiation was used. The FULLPROF program (Le Bail fit) [22] was used for analysis of diffraction patterns. The variation of the coefficient of thermal expansion with temperature was measured using the dilatometer DL-1500 RHP/DL-1500-H (UCVAC/SINKU). The measurements of the magnetic susceptibility and magnetization were performed by means of a Quantum Design SQUID MPMS magnetometer in the temperature interval $2\text{ K} \leq T \leq 350\text{ K}$ and Vibrating sample magnetometer Lake Shore VSM 7407 in the temperature interval $300\text{ K} \leq T \leq 1000\text{ K}$. The samples for high-temperature measurements (above 300 K) were placed into evacuated quartz ampoules to prevent oxidation.

3. Results

3.1. X-ray diffraction

From the absence of extra lines on X-ray diffraction patterns the $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ samples with the titanium concentration up to $x=4$ were determined to be single phase, while the sample with $x=5$ was found to exhibit several reflections corresponding to pure non-reacted iron even after prolonged heat treatments. The X-ray diffraction patterns for $\text{Fe}_6\text{Ti}_1\text{S}_8$, $\text{Fe}_5\text{Ti}_2\text{S}_8$ and $\text{Fe}_3\text{Ti}_4\text{S}_8$ are shown in Fig. 1. The X-ray data for $\text{Fe}_4\text{Ti}_3\text{S}_8$ were presented in our previous work [19]. The crystal lattice characteristics derived from the X-ray analysis performed for all $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ samples are presented in Table 1. The crystal structure of our Fe_7S_8 sample

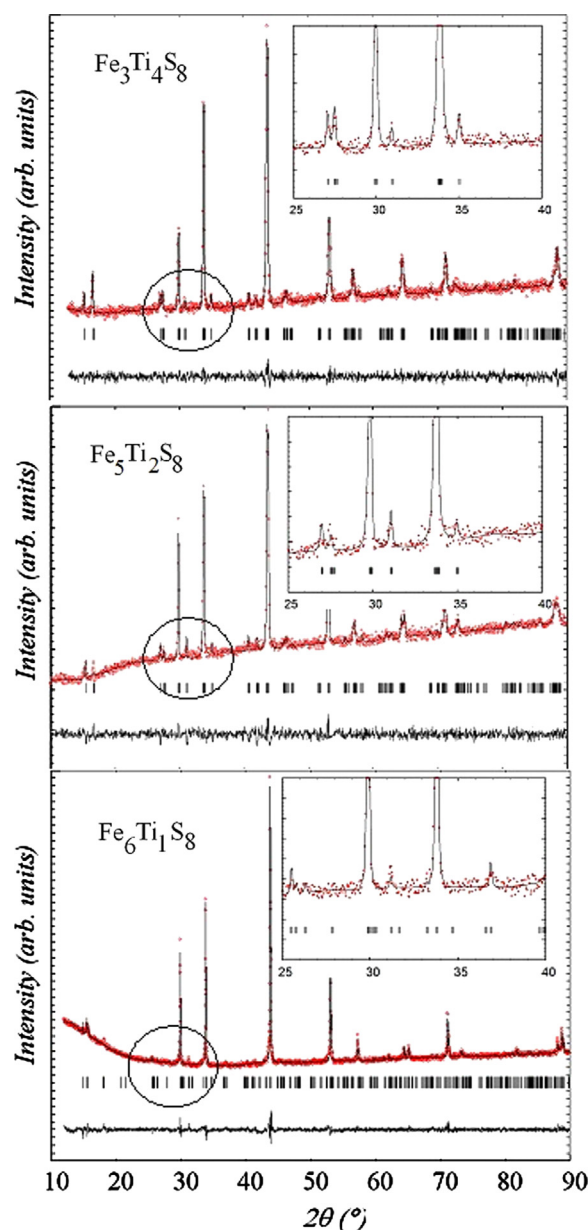


Fig. 1. Observed (symbols) and calculated (line) X-ray diffraction pattern for $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds with Ti concentrations $x=1, 2, 4$. Vertical bars indicate the Bragg peaks positions corresponding to the P3_12_1 space group in the case of $\text{Fe}_6\text{Ti}_1\text{S}_8$ and to I12/m1 space group for $\text{Fe}_5\text{Ti}_2\text{S}_8$ and $\text{Fe}_3\text{Ti}_4\text{S}_8$. The difference between calculated and observed intensities is shown in the bottom. Insets show the parts of the X-ray patterns in detail.

Table 1
Structural characteristics of $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds.

Compound	Superstructure	Space group	a (Å)	b (Å)	c (Å)	β (°)
Fe_7S_8	4C $[(2\sqrt{3})a_0 \times 2a_0 \times 4c_0]^*$	C2/c	11.9035(5) $a=(2\sqrt{3})a_0$	6.8515(2) $b=2a_0$	22.763(1) $c=4c_0$	117.95(3)
$\text{Fe}_6\text{Ti}_1\text{S}_8$	3C $[2a_0 \times 2a_0 \times 3c_0]$	P3_12_1	6.8972(4) $a=2a_0$	6.8972(4) $b=2a_0$	17.168(6) $c=3c_0$	90
$\text{Fe}_5\text{Ti}_2\text{S}_8$	2C $[a_0\sqrt{3} \times a_0 \times 2c_0]$	I12/m1	5.9854(4) $a=a_0\sqrt{3}$	3.4442(2) $b=a_0$	11.503(4) $c=2c_0$	90.23(5)
$\text{Fe}_4\text{Ti}_3\text{S}_8$	2C $[a_0\sqrt{3} \times a_0 \times 2c_0]$	I12/m1	5.9669(4) $a=a_0\sqrt{3}$	3.4396(3) $b=a_0$	11.561(5) $c=2c_0$	90.24(6)
$\text{Fe}_3\text{Ti}_4\text{S}_8$	2C $[a_0\sqrt{3} \times a_0 \times 2c_0]$	I12/m1	5.9680(7) $a=a_0\sqrt{3}$	3.4334(1) $b=a_0$	11.546(2) $c=2c_0$	90.28(4)

* a_0 and c_0 are the parameters of the NiAs-type hexagonal unit cell.

was identified as a monoclinic 4C superstructure in accordance with previous results [1–4], while the substitution of one Fe atom in the formula unit by titanium results in the transition to the hexagonal 3C superstructure (space group P3_12_1). Such a substitution apparently hampers the process of vacancy ordering, which leads to the 4C → 3C structural change. For the samples with higher Ti concentrations ($x=2-4$), a set of additional reflections were observed (see Fig. 1 and the insets therein). The diffraction patterns for these compounds correspond to the monoclinic 2C superstructure ($a_0\sqrt{3} \times a_0 \times 2c_0$) described by space group I12/m1 (a_0 and c_0 are the parameters of the NiAs-type hexagonal unit cell). The definitions of the supercell parameters are presented in Table 1 as well.

The formation of the 2C superstructure in $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ with $x \geq 2$ may be associated with stacking faults caused by the replacement of Fe by Ti or by preferential substitution of Ti for Fe in alternating cation layers. Unfortunately, the information about the partitioning of Fe and Ti over cation layers cannot be derived from these X-ray measurements owing to the similarity of X-ray scattering powers of iron and titanium.

In order to reveal the effect of the Ti for Fe substitution on the interatomic distances we plotted in Fig. 2 the concentration dependences of the parameters a_0 and c_0 by using the data presented in Table 1. As is seen from Fig. 2, the Ti for Fe substitution up to $x=2$ leads to the growth of both the a_0 and c_0 values which characterize the average intralayer and interlayer distances, respectively, while a further increase of the Ti concentration the does not affect substantially the crystal lattice.

3.2. Thermal expansion

Fig. 3 displays temperature dependences of the linear coefficient α of the thermal expansion for the polycrystalline samples of $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds. As is seen, for the non-substituted compound Fe_7S_8 , a sharp peak of α is observed at the critical temperature $T_t \sim 590$ K, which is in good agreement with the published data [6]. This anomaly is associated with a first-order structural transition from a superstructure with ordered vacancies to the NiAs-type structure with vacancy disorder above 590 K and accompanied by a sudden change in lattice parameters and unit cell volume [1,6]. It is worth to note that at the same temperature, pyrrhotite exhibits a phase transition from the magnetically ordered (ferrimagnetic) state to the paramagnetic state [1,6]. As follows from Fig. 3, the peak of α persists in the substituted compounds $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ as well; however, the peak value significantly decreases with increasing Ti concentration up to $x=2$, while further growth of the Ti content leads to the enhancement of a peak height. Moreover, the Ti for Fe substitution influences the critical temperature of the structural transition: at first, the T_t value slightly increases from 590 K up to ~ 620 K at $x=2$, while T_t reaches 720–740 K at high Ti concentrations ($x=3, 4$). Unlike the initial Fe_7S_8 in which the structural phase transition coincides with magnetic one ($T_t=T_N$), the T_N value, as could be expected, decreases with increasing Ti concentration (see below).

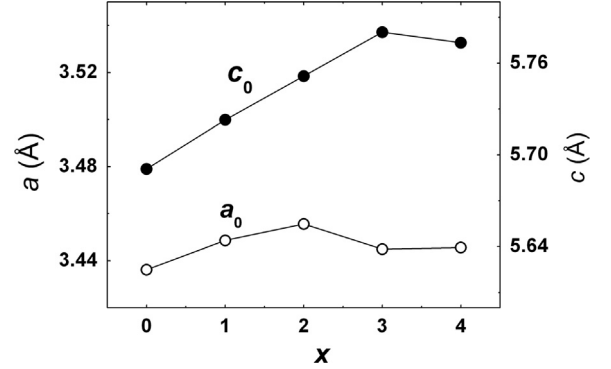


Fig. 2. The a_0 and c_0 values as a function of the Ti concentration in $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$.

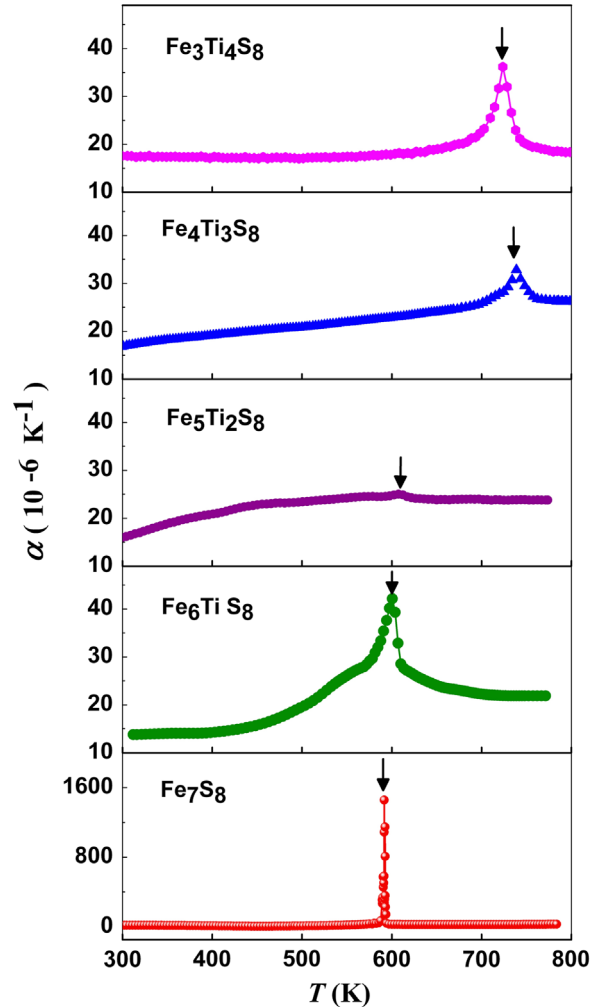


Fig. 3. Temperature dependences of the linear coefficient of thermal expansion for $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds with various Ti concentrations. The critical temperatures of the structural transition are marked by arrows.

3.3. Magnetization data

Fig. 4 represents the temperature dependences of the magnetization measured with decreasing temperature in an applied field of 1 kOe on the $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ polycrystalline samples. For the non-substituted Fe_7S_8 compound, the Neel temperature T_N was obtained to be equal 590 K, which coincides with the critical temperature T_t of the structural transition (see above). At temperature around 32 K, an anomalous change of the magnetization is observed (indicated by the arrow in Fig. 4). This anomaly is reported in the literature as a characteristic feature of the monoclinic 4C pyrrhotite [23,24]. The substitution of Ti for Fe decreases the critical temperature of the magnetic phase transition from the magnetically ordered state to the paramagnetic state, which is indicative of weakening the exchange interactions between iron atoms due to the Ti for Fe substitution.

Such a behavior seems to be quite expected bearing in mind that titanium ions usually do not possess an own magnetic moment in chalcogenide compounds [20]. For Fe_6TiS_8 , the change of the magnetization with temperature is found to depend on the cooling conditions. As is seen from the inset of Fig. 4, the rapidly-cooled sample exhibits a much lower magnetization value than the slow-cooled sample measured at the same field; and the shape of the $M(T)$ curves around the critical temperature is different in these cases as well. Small peak of the magnetization for the quenched sample instead of gradual decrease for the slow-cooled sample is observed at the critical temperature which does not depend markedly on the cooling rate.

Unlike monotonous decrease of T_C with substitution, the low-temperature magnetization of $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ shows an unusual behavior. As follows from Fig. 4, the substitution of one Ti atom for Fe in formula unit ($x=1$) results in a dramatic reduction of the magnetization in comparison with the non-substituted Fe_7S_8 , and then for $\text{Fe}_5\text{Ti}_2\text{S}_8$, the magnetization returns to a value close to that of Fe_7S_8 . Further increase of the Ti content up to $x=3$ and $x=4$ results in substantial growth of the low-temperature (~ 2 K) magnetization; the magnetization of these compounds is about two times higher than that of Fe_7S_8 . It should be also noted that unlike Fe_7S_8 , the anomaly on the temperature dependences of the magnetization around 32 K was not observed for all substituted $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds.

The temperature dependences of the reciprocal susceptibility (χ^{-1}) obtained as H/M for $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ at $H=10$ kOe from 300 K up

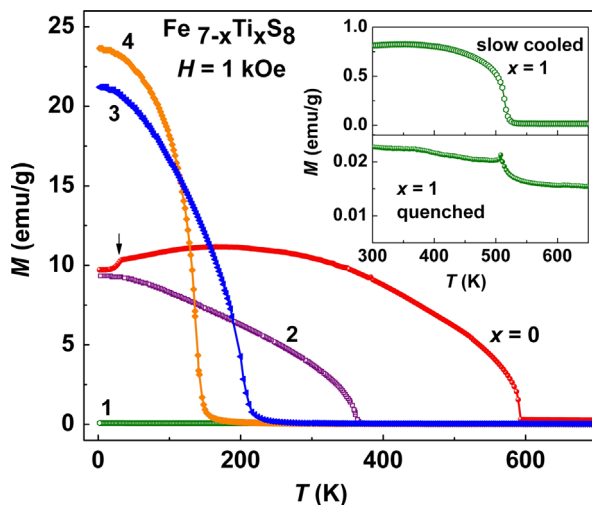


Fig. 4. Temperature dependences of the magnetization measured at $H=1$ kOe on the $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ samples with various Ti concentrations as labeled. Inset shows the $M(T)$ dependences for the Fe_6TiS_8 sample after slow cooling (full symbols) and quenching (open symbols).

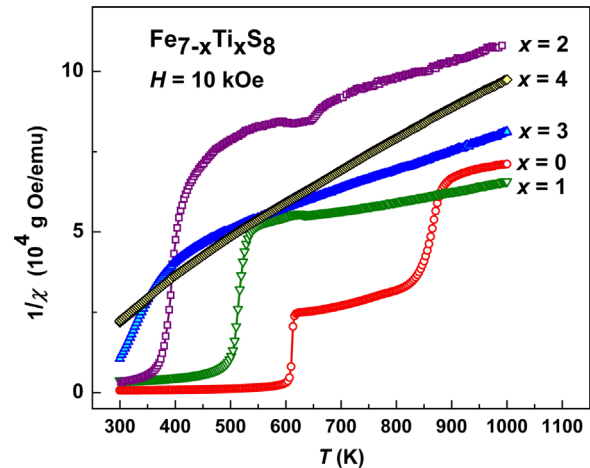


Fig. 5. Temperature dependences of the reciprocal susceptibility for $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds measured at $H=10$ kOe.

to 1000 K are shown in Fig. 5. Together with the sharp susceptibility change associated with the ferrimagnetic to paramagnetic phase transition, the χ^{-1} versus T curve for the parent Fe_7S_8 compound is found to exhibit another anomaly in the vicinity 850–880 K, which is in good agreement with earlier data for Fe_7S_8 (see Ref. [25], for instance). This high-temperature anomaly can be associated with the magnetic phase transition in a small amount of the ferromagnetic impurity phase Fe_3O_4 (magnetite with $T_N \sim 856$ K, see Ref. [26]) which exists perhaps in our sample, but is not detected by conventional X-ray powder diffraction. Note, that in the vicinity of the critical temperatures corresponding to the structural transition T_t in Fe_6TiS_8 and $\text{Fe}_5\text{Ti}_2\text{S}_8$, an anomaly on $\chi^{-1}(T)$ curves is observed, which agrees with thermal expansion data (see above). However, no visible anomalies of χ^{-1} were detected around T_t for the compounds with higher Ti contents ($x=3, 4$). From the susceptibility data obtained at high temperatures, the effective magnetic moment of iron can be estimated using the Curie–Weiss law $\chi(T) = C/(T - \theta_p)$, where C is the Curie constant, θ_p is the paramagnetic Curie temperature, and assuming that titanium atoms do not possess a magnetic moment. The value of the effective magnetic moment (μ_{eff}) of iron atoms is found to decrease monotonously with substitution from $5.8\mu_B$ for $x=0$ down to $4.3\mu_B$ for $x=4$. The paramagnetic Curie temperatures θ_p are determined to be negative for all $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$, while the absolute value $|\theta_p|$ decreases with growing Ti concentration from ~ 2600 K for $x=0$ down to 95 K for $x=4$. These results show that the negative exchange interaction dominates in this system.

A dramatic impact of the Ti for Fe substitution on the magnetic behavior of $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ is clear seen from Fig. 6, which displays the field dependences of the magnetization measured at 2 K after zero field-cooling.

Unlike initial Fe_7S_8 , which shows the $M(H)$ dependence typical for ferrimagnetic or ferromagnetic materials, the Fe_6TiS_8 is found to exhibit a substantially reduced magnetization values and the magnetization curve which can be rather associated with the presence of an antiferromagnetic order. As was shown above, this compound enters a magnetic order with decreasing temperature below ~ 510 K. Further increase of the Ti concentration in $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ up to $x=2$ leads to recovery of the hysteresis loop similar to that observed for the non-substituted pyrrhotite. The $\text{Fe}_3\text{Ti}_4\text{S}_8$ compound with the maximal Ti content shows an unexpectedly high value of the coercive field $H_c \sim 24$ kOe at $T=2$ K and magnetization jumps around H_c (Fig. 6). Such a step-like behavior of the magnetization was observed in $\text{Fe}_3\text{Ti}_4\text{S}_8$ up to 15 K. It is worth to note, that the compounds with the Ti concentrations above $x=2$ show increased magnetization values under

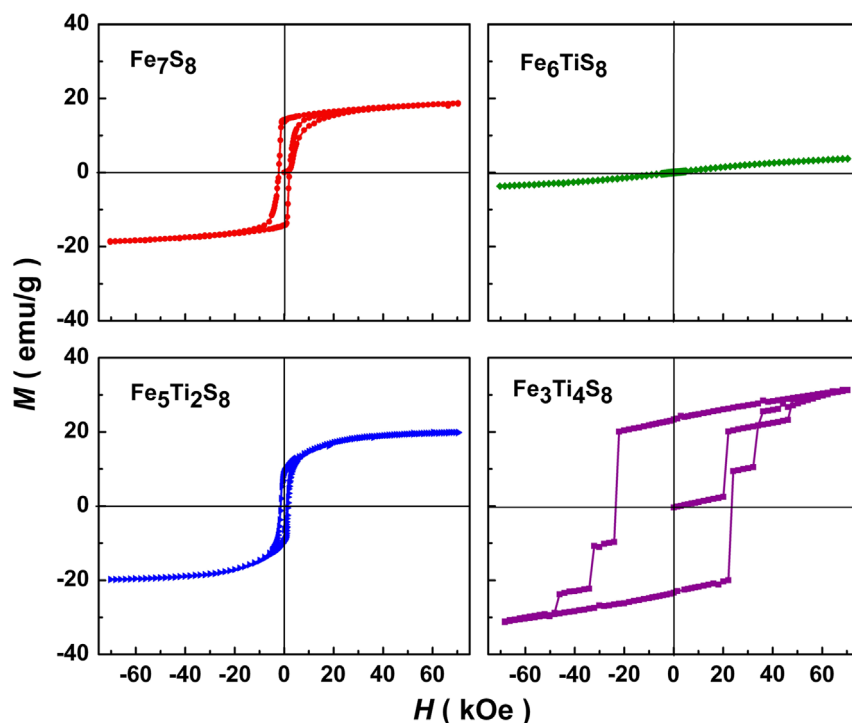


Fig. 6. Field dependences of the magnetization (M) measured at $T=2$ K on the $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ samples with various Ti concentrations.

application of a magnetic field in comparison with the parent Fe_7S_8 , which can hardly be explained in the suggestion about a statistical substitution of Ti for Fe in all metallic layers.

4. Discussion and conclusions

By using a solid state reaction method the single-phase pyrrhotite-type compounds $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ with Ti concentrations up to $x=4$ have been synthesized for the first time. The results of the crystal structure, thermal expansion and magnetization studies performed for the synthesized samples have shown that the substitution of Ti for Fe in pyrrhotite modifies its crystal structure and structural phase transitions, and leads to substantial changes in magnetic properties. With increasing Ti concentration, the crystal structure changes from the initial monoclinic 4C superstructure in Fe_7S_8 to the hexagonal 3C superstructure at $x=1$ and then to the 2C monoclinic superstructure at $x \geq 2$, however, in general, the crystal lattice of $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds remains of the layered NiAs-type. The substitution up to $x=2$ is observed to expand the lattice, while the changes in the interatomic distances become less pronounced with further growth of the Ti content. The structural phase transition associated with order–disorder within the subsystem of vacancies is found to persist in all $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds despite the substitution.

The changes in the main magnetic characteristics of $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ caused by substitution as well as the concentration dependence of the critical temperature of the structural transition are displayed in Fig. 7. The Neel temperature decreases with increasing Ti concentration (Fig. 7a), which is indicative of the reduction of exchange interactions between iron atoms apparently because of the absence or a low value of a magnetic moment on titanium atoms.

The most intriguing results are the cardinal changes in the magnetization behavior under application of the magnetic field around the Ti concentration $x=1$ (Fig. 6) and non-monotonous change of the low-temperature magnetization with the substitution (Fig. 7b). Such a behavior can be understood as a result of the

preferential substitution of Fe by Ti atoms in alternating metal layers. As was mentioned above, the iron layers in Fe_7S_8 can be divided into two sublattices; one sublattice contains ordered vacancies and the other sublattice does not contain vacancies [1]. According to previous studies [6], the Fe magnetic moments are arranged ferromagnetically inside each sublattice, but the coupling between two sublattices is antiferromagnetic, and the presence of ordered vacancies in one sublattice results in a net magnetization and ferrimagnetism. If the substitution of Ti for Fe occurs randomly in both sublattices, a ferrimagnetic behavior for all samples and monotonous reduction of the net magnetization with increasing Ti concentration should be observed, which is not consistent with our experiment. On the other hand, the preferential substitution of one iron atom by non-magnetic titanium in the sublattice without vacancies may result in the compensation of magnetizations of two iron sublattices, and, therefore, in antiferromagnetism which is observed in Fe_6TiS_8 . Further growth of the Ti concentration and the substitution of iron in fully occupied metal layers will lead to the growth of the resultant magnetization and to the situation analogous to that realized in the non-substituted Fe_7S_8 . This is because the vacancy and the titanium atom from the magnetic point of view may be roughly considered to be equivalent. Such a growth of the magnetization is observed in $\text{Fe}_5\text{Ti}_2\text{S}_8$ and then in $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds with higher Ti concentrations. As a result, the compounds $\text{Fe}_4\text{Ti}_3\text{S}_8$ and $\text{Fe}_3\text{Ti}_4\text{S}_8$ exhibit a nearly in twice increased magnetization value in comparison with non-substituted Fe_7S_8 (Fig. 7b). A lower value of the magnetization obtained at 50 kOe for $\text{Fe}_3\text{Ti}_4\text{S}_8$ in comparison with $\text{Fe}_4\text{Ti}_3\text{S}_8$ may result from the enhancement of the magnetocrystalline anisotropy with increasing Ti concentration.

The results obtained allow us to suggest that the titanium atoms substituting iron atoms tend to form in $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ the layers fully occupied by Ti atoms with growing x . In particular, the compound $\text{Fe}_3\text{Ti}_4\text{S}_8$ seems to be analogous to the titanium disulfide $\text{Fe}_{0.75}\text{TiS}_2$, intercalated with iron atoms [20]. The crystal structure of $\text{Fe}_{0.75}\text{TiS}_2$ consists of full S–Ti–S tri-layers with iron atoms located between them. According to a magnetic phase

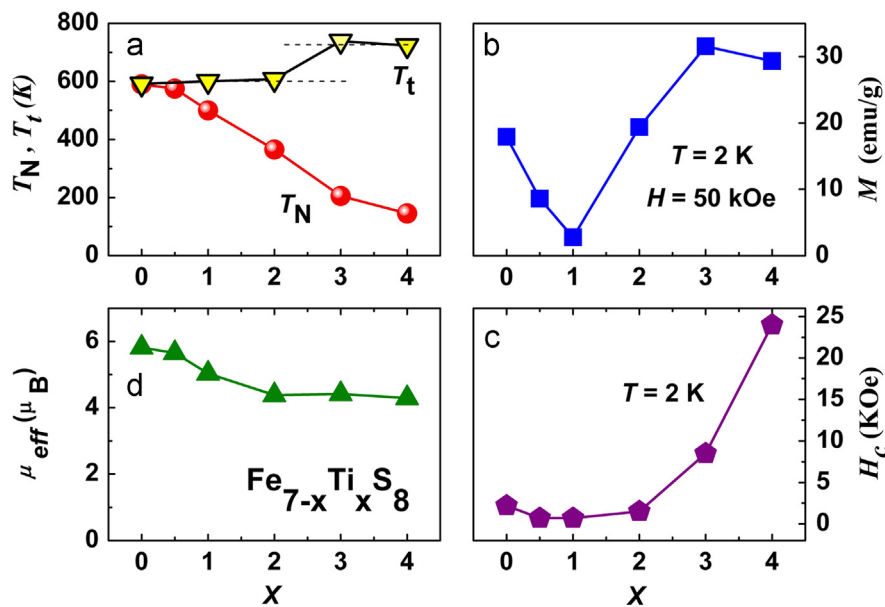


Fig. 7. Concentration dependences of the critical temperature of the structural (T_t) and magnetic phase transitions T_N (a), magnetization value M at temperature 2 K and $H=50$ kOe (b), effective magnetic moment μ_{eff} (c), and coercive field H_c at $T=2$ K (d) for $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds.

diagram proposed in Ref. [20] the $\text{Fe}_{0.75}\text{TiS}_2$ compound exhibits a long-range ferromagnetic order. However, bearing in mind a negative value of the asymptotic (paramagnetic) Curie temperature ($\theta_p = -95$ K) derived from high-temperature susceptibility data (Fig. 5) for $\text{Fe}_3\text{Ti}_4\text{S}_8$, it seems that the magnetic state of this compound is needed to be examined by neutron diffraction measurements.

It should be noted that a non-random distribution of 3d metal atoms having less or more than half-filled 3d shell was revealed in some other pseudobinary transition metal sulfides with the NiAs-related structures (see Ref. [27], for instance). Our assumption about a non-random Ti for Fe substitution in $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ allows explaining the presence of the structural “order–disorder” transition (see above) in the whole concentration range ($x=0$ –4) and an increase of the critical temperature T_t (shown in Fig. 7a) from $\sim(590\text{--}620)$ K at $x \leq 2$ up to $(725\text{--}740)$ K at $x > 2$. It can be suggested that such a transition persists in the whole concentration range since the Ti for Fe substitution predominantly occurs in fully occupied metallic layers, while the vacancy redistribution determining the structural transition takes place within the metal deficient layers. Assuming such a preferential substitution of Ti for Fe, the higher T_t values observed in $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ at $x > 2$ may be ascribed to an enhanced stiffness of the crystal lattice when more than half iron ions in full metallic layer are replaced by titanium.

A value of the effective magnetic moment of iron for the compositions with $x > 2$ is obtained to be about $4.3\text{--}4.4\mu_B$ (see Fig. 7c), which is lower than the expected spin-only values for high-spin Fe ions ($4.89\mu_B$ for Fe^{+2} and $5.91\mu_B$ for Fe^{+3}). According to recent X-ray MCD [28,29] studies the Fe_7S_8 compound contains only Fe^{2+} ions, which implies that a simple ionic model is not applicable for this material. The reduced values of μ_{eff} in the substituted compounds can be associated with the participation of 3d electrons of iron in bonds with sulfur and with the hybridization of Fe 3d and Ti 3d electronic states as well. The presence of a strong Fe–S hybridization in Fe_7S_8 has been revealed by X-ray MCD experimental studies [28] and theoretical consideration [29].

The substitution of Ti for Fe in pyrrhotite is observed to substantially enhance the coercive field at low temperatures (shown in Fig. 7d); a value of H_c reaches 24 kOe in the case of $\text{Fe}_3\text{Ti}_4\text{S}_8$. This value is a quite rare case for the Fe-based magnetic materials which usually demonstrate soft-magnetic properties.

However, there are several examples, like Lu_2FeO_4 [30], $\text{Fe}_{0.25}\text{TaS}_2$ [31], and $\text{Fe}_{0.5}\text{TiS}_2$ [20,21] exhibiting giant values of the coercive field (from 40 kOe up to 90 kOe) at low temperatures. Crystal structure of all these compounds is of a layered type; and, as evidenced by X-ray MCD measurements, Fe ions in these compounds exhibit a substantial orbital moment [32,33]. Since an unquenched orbital moment was also detected in Fe_7S_8 [28], the increased magnetic hardness of $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ compounds with high Ti concentrations ($x > 2$) may originate in the enhancement of orbital moment at the Fe sites in the layer with vacancies when Fe ions in full cation layers are replaced by Ti.

In conclusion, in the present work it was shown how the substitution of Ti for Fe affects the crystal structure, structural phase transitions and magnetic properties of the pyrrhotite-type compounds $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ having the layered structures of the NiAs type. The changes from the ferrimagnetic to antiferromagnetic and then presumably to ferromagnetic state are suggested to occur with increasing Ti concentration in this system owing to the non-random distributions of Fe and Ti in cation layers. Further studies are needed to confirm this assumption as well to answer the question about the origins of increased magnetic hardness and reduced Fe magnetic moments observed in the $\text{Fe}_{7-x}\text{Ti}_x\text{S}_8$ system at high Ti concentrations.

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References

- [1] H. Wang, I. Salveson, *Ph. Transit.* 78 (2005) 547.
- [2] E.F. Bertaut, *Acta Crystallogr.* 6 (1953) 557.
- [3] F. Li, H.F. Franzen, M.J. Kramer, *J. Solid State Chem.* 126 (1996) 108.
- [4] J.R. Gosselin, M.G. Townsend, R.J. Tremblay, A.H. Webster, *Mater. Res. Bull.* 10 (1975) 41.
- [5] M.J. Dekkers, *Phys. Earth Planet. Inter.* 52 (1988) 376.

- [6] A.V. Powell, P. Vaqueiro, K.S. Knight, L.C. Chapon, R.D. Sanchez, *Phys. Rev. B* 70 (2004) 014415.
- [7] W. O'Reilly, V. Hoffmann, A.C. Chouker, H.C. Soffel, A. Menyeh, *Geophys. J. Int.* 142 (2000) 669.
- [8] A. Menyeh, W. O'Reilly, *Geophys. J. Int.* 104 (1991) 387.
- [9] A.F. Andresen, J. Iciejewicz, *J. Phys.* 25 (1964) 574.
- [10] V.L. Miller, W.L. Lee, G. Lawes, N.P. Ong, R.J. Cava, *J. Solid State Chem.* 178 (2005) 1508.
- [11] H. Ikeda, M. Shirai, N. Suzuki, K. Motizuki, *J. Magn. Magn. Mater.* 140–144 (1995) 159.
- [12] P. Terzieff, *J. Phys. Chem. Solids* 43 (3) (1982) 305.
- [13] M. Sato, T. Kamimura, T. Iwata, *J. Appl. Phys.* 57 (1985) 3244.
- [14] M. Sato, T. Kamimura, T. Shinohara, T. Sato, *J. Magn. Magn. Mater.* 90–91 (1990) 179.
- [15] H. Kobayashi, T. Kamimura, M. Sakai, H. Onodera, N. Kurodo, Y. Yamaguchi, *J. Phys.: Condens. Matter* 9 (1997) 515.
- [16] S. Takele, G.R. Hearne, *J. Phys.: Condens. Matter* 13 (2001) 10077.
- [17] J.P. Rueff, C.C. Kao, V.V. Struzhkin, J. Badro, J. Shu, R.J. Hemley, H.K. Mao, *Phys. Rev. Lett.* 82 (1999) 3284.
- [18] T. Kamimura, *J. Phys.* 49 (1988) 191.
- [19] P.N.G. Ibrahim, N.V. Selezneva, A.F. Gubkin, N.V. Baranov, *Solid State Sci.* 24 (2013) 26.
- [20] M. Inoue, H.P. Hughs, A.D. Yoffe, *Adv. Phys.* 38 (1989) 565.
- [21] N.V. Baranov, E.M. Sherokalova, N.V. Selezneva, A.V. Proshkin, L. Keller, A.S. Volegov, E.P. Proskurina, *J. Phys.: Condens. Matter* 25 (2013) 066004.
- [22] J. Rodriguez-Carvalay, *Physica B* 192 (1993) 55.
- [23] G. Fillion, P. Rochett, *Le Journal de Physique Colloques* 49 (1988) C8-907.
- [24] P. Rochette, G. Fillion, J.L. Mattei, M.J. Dekkers, *Earth Planet. Sci. Lett.* 98 (1990) 319.
- [25] L. Néel, *Rev. Mod. Phys.* 25 (1953) 58.
- [26] J.M.D. Coey, *Magnetism and Magnetic Materials*, Cambridge university press, Cambridge, 2010 (Chapter 6).
- [27] J.M. Newsam, Y. Endo, I. Kawada, *J. Phys. Chem. Solids* 48 (1987) 607.
- [28] I. Letard, P. Saintavit, C. Deudon, *Phys. Chem. Miner.* 34 (2007) 113.
- [29] V.N. Antonov, L.V. Bekenov, P. Shpak, L.P. Germash, A.N. Yaresko, O. Jepsen, *J. Appl. Phys.* 106 (2009) 123907.
- [30] W. Wu, V. Kiryukhin, H.J. Noh, K.T. Ko, J.H. Park, W. Ratcliff, P.A. Sharma, N. Harrison, Y.J. Choi, Y. Horibe, S. Lee, S. Park, H.T. Yi, C.L. Zhang, S-W. Cheong, *Phys. Rev. Lett.* 101 (2008) 137203.
- [31] Y.J. Choi, S.B. Kim, T. Asada, S. Park, W. Wu, Y. Horibe, S.W. Cheong, *Europhys. Lett.* 86 (2009) 37012.
- [32] K.T. Ko, H.J. Noh, J.Y. Kim, B.G. Park, J.H. Park, A. Tanaka, S.B. Kim, C.L. Zhang, S.W. Cheong, *Phys. Rev. Lett.* 103 (2009) 207202.
- [33] K.T. Ko, K. Kim, S.B. Kim, H.D. Kim, J.Y. Kim, B.I. Min, J.H. Park, F.H. Chang, H.J. Lin, A. Tanaka, S.W. Cheong, *Phys. Rev. Lett.* 107 (2011) 247201.