

Crystallographic and Magnetic Properties of the Cd(OH)₂ Layer Structure Compound TiS₂ Containing Extra Iron

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The systems Fe_xTiS₂ were prepared by the reaction between Fe and TiS₂ in vacuum. Fe_xTiS₂ with $x = \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$ were found to have a monoclinic supercell with lattice parameters $a' = 2a$ and $c' = 2c$ in the pseudo-hexagonal description, where a and c are the lattice parameters for the TiS₂ cell. Fe_{1/4}TiS₂ had a trigonal supercell of $a' = \sqrt{3}a$ and $c' = 2c$. Magnetic measurements of these compounds were carried out between 78 and 340 K. The inverse susceptibility vs temperature curve for Fe_{1/4}TiS₂ followed the Curie-Weiss law, whereas that for Fe_{1/2}TiS₂ was non-linear. Fe_{1/4}TiS₂ and Fe_{3/4}TiS₂ were both ferromagnets with $T_c \sim 111$ K and 112 K and $\theta_p = 124$ K and 128 K, respectively.

Introduction

Recent studies (1-3) have revealed that the first-row transition-metal atoms can be inserted into the octahedral interstices between the prismatic chalcogen layers of the dichalcogenides NbX₂ and TaX₂, X = S and Se. Some compounds, e.g., MnNb₃S₆ and CrNb₃S₆, even become ferromagnetic. It should be of interest, therefore, to investigate the intercalation of 3d-transition metals into other layer-structure compounds. TiS₂ has the Cd(OH)₂ layer structure (space group $C\bar{3}m$) where every other metallic layer in the c direction of the hexagonal NiAs B8 structure is missing. It, therefore, is conceivable that 3d-transition metal atoms can be inserted into the interstices between neighboring sulfur layers in TiS₂. Indeed, the existence of such a compound, namely Fe_{1/4}TiS₂ (=FeTi₂S₄) has been known for some time (4-6). Hahn *et al.* prepared it from monosulfides and sulfur and reported that it has a trigonal $P\bar{3}m1$ structure in which vacancies are randomly distributed in alternate metal layers (4). More recently, Plovnick *et al.* prepared the sulfide from high-purity elements and found that it had the Cr₃S₄ $I2/m$ structure in which vacancies are ordered in alternate metal layers (5, 6). These conflicting results seem to indicate that the sulfide FeTi₂S₄ can adopt different crystal structures correspond-

ing to different degrees of ordering that in turn depend upon how the sulfide was prepared. In this respect, it is interesting to see what crystal structure will result when Fe_xTiS₂ is prepared from Fe metal and TiS₂. We therefore started an investigation of adding Fe to TiS₂.

Experimental

1. Sample Preparation

Fe_xTiS₂ ($x = \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$) were synthesized by firing stoichiometric mixtures of Fe metal powder (99.9%) and TiS₂ at 900°C in evacuated quartz ampoules. Repeated firings at 900°C were usually required for a complete reaction of the constituents. The TiS₂ used was synthesized from Ti metal (99.9% or better) either in the form of sponge or sheet, and elemental sulfur (99.9%), following the procedure described by Lotgering and van Stapele (7). The lattice parameters of TiS₂ thus synthesized agreed with those for the stoichiometric TiS_{2.00} within experimental error (8). The stoichiometry of the TiS₂ used was also checked by a weight-loss procedure after oxidation in dry oxygen at 700°C (Anal. Calcd. for Sulfur: 57.24%. Found: 57.25%) (5). The density of the TiS₂ was determined by weighing in toluene. The observed value of 3.21 ± 0.01 g/cm³ was in reasonable agreement with the

TABLE I
ANALYTICAL DATA FOR Fe_xTiS_2

Compound	% Fe		% S		Density (g/cm^3)	
	Calcd	Found	Calcd	Found	X ray	Measd
Fe_2TiS_2	11.08	11.20	50.90	49.97	3.61	3.56
Fe_4TiS_2	14.25	14.08	49.08	47.91	3.72	3.66
Fe_2TiS_2	19.96	19.98	45.81	45.14	3.95	3.87
Fe_3TiS_2	24.95	24.84	42.96	42.11	4.22	4.03

theoretical value of $3.245 \text{ g}/\text{cm}^3$ calculated by using the lattice parameters obtained (cf. Table II).

2. Analytical Work

Analyses of all compounds for iron and sulfur were performed by atomic absorption spectroscopy using a Hitachi 208 Atomic Absorption Spectrometer.

Details of analytical procedures will be found elsewhere (9). Densities were determined by weighing in 1,1,2,2-tetrachloroethane. The results of the chemical analyses and density measurements are summarized in Table I.

3. X-ray Measurements

Powder samples were examined by a JEOL¹ X-ray diffractometer with $\text{CuK}\alpha$ radiation. Lattice parameters were determined from films taken by a Debye-Scherrer camera using Cu - or $\text{FeK}\alpha$ radiation. The lattice parameters were refined using the $\sin^2\theta$ extrapolation.

¹ Japan Electron Optics Laboratory.

4. Magnetic Measurements

Magnetic properties were measured between 78 and 340 K using a Princeton Applied Research vibrating sample magnetometer. Magnetic susceptibilities were calculated from the data in the paramagnetic region assuming $M = \chi H$.

Results and Discussion

1. Crystallographic Properties

The X-ray data for the compounds Fe_xTiS_2 as well as TiS_2 used for the present experiment are listed in Table II. The lattice parameters for Fe_4TiS_2 (= FeTi_2S_4) prepared by other workers from different raw materials are also listed for comparison. The inclusion of iron led to the increase in the c parameter of the $\text{Cd}(\text{OH})_2$ cell in all the compounds. No single-phase materials were obtained for Fe_xTiS_2 with $x > \frac{3}{2}$. Ordering took place in all the Fe_xTiS_2 compounds. Fe_2TiS_2 , Fe_4TiS_2 and Fe_3TiS_2 were found to have a supercell of $a' = 2a$ and $c' = 2c$, whereas Fe_2TiS_2 was found to have a supercell of $a' = \sqrt{3}a$ and $c' = 2c$, where a and c are the lattice parameters for the original TiS_2 cell. These supercells, projected along the c axis, are schematically illustrated in Fig. 1. In Fig. 1(a), the $\sqrt{3}a$ supercell as well as the original $\text{Cd}(\text{OH})_2$ cell are illustrated. Identifying Fe atoms by letters, the cation stacking sequence for Fe_4TiS_2 will be O-B-O-C-O where O denotes the layer without Fe atoms, i.e., Ti layers. In Fig. 1(b), the $2a$ cell is illustrated. The probable stacking sequence for Fe_4TiS_2 will be O-A-O-D-O while that for Fe_3TiS_2 will be O-(A+D)-O-(B+C)-O. Therefore, the true crystal symmetry for the $\sqrt{3}a$ cell is

TABLE II
X-RAY DATA FOR Fe_xTiS_2

Compound	Space group	Lattice parameters for $\text{Cd}(\text{OH})_2$ cell	
		a (\AA)	c (\AA)
TiS_2	$C\bar{3}m$	3.408 ± 0.005	5.698 ± 0.005
Fe_4TiS_2	$C2/m$	3.422 ± 0.005	5.712 ± 0.005
Fe_4TiS_2	$P\bar{3}1c$	3.428 ± 0.005	5.733 ± 0.005
Fe_2TiS_2	$I2/m$	3.437 ± 0.005	5.749 ± 0.005
Fe_3TiS_2	$I2/m?$	3.429 ± 0.005	5.764 ± 0.005
$\text{Fe}_{0.50}\text{Ti}_{1.00}\text{S}_2^a$	$P\bar{3}m1$	3.416 ± 0.005	5.699 ± 0.005
$\text{FeTi}_2\text{S}_4^b$	$I2/m$	3.426 ± 0.005	5.730 ± 0.005

^a Synthesized from monosulfides and sulfur by Hahn *et al.* (4).

^b Synthesized from elements by Plovnick *et al.* (5) ($\beta = 90.10^\circ$).

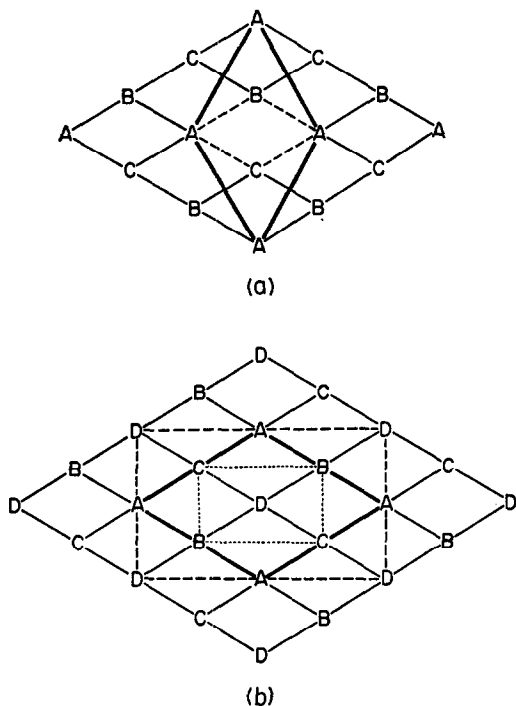
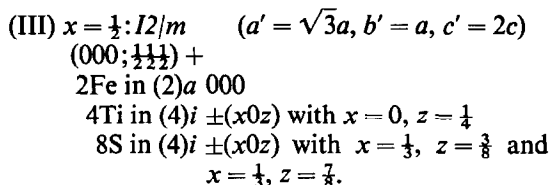
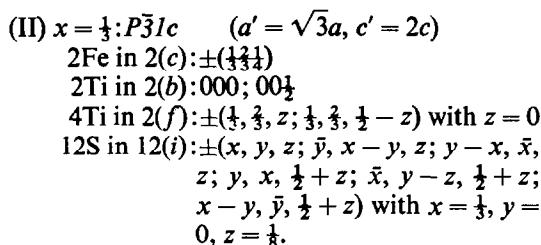
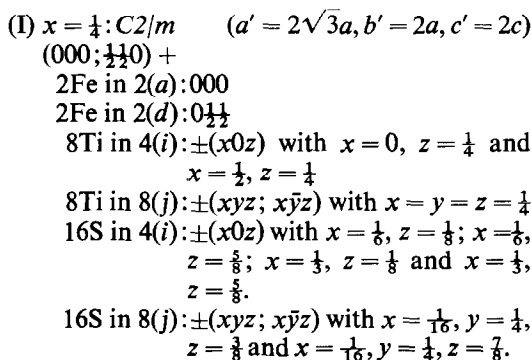


FIG. 1(a). Schematic projection of the structures of TiS₂ and trigonal Fe₃TiS₂ on the *c* plane. The hexagonal unit cell of TiS₂ is indicated by broken lines. The trigonal $\sqrt{3}a$ supercell of Fe₃TiS₂ is indicated by full lines. (b) Schematic projection of the structures of Fe₄TiS₂ and Fe₃TiS₂ on the *c* plane. The pseudo-hexagonal $2a$ supercell is indicated by full lines. The monoclinic supercell of Fe₄TiS₂ is indicated by broken lines and that of Fe₃TiS₂ is indicated by dotted lines.

trigonal (space group $P\bar{3}1c$) whereas that for the $2a$ cell is monoclinic (space group; $C2/m$ for $x = \frac{1}{4}$ and $I2/m$ for $x = \frac{1}{2}$). Those monoclinic cells are also indicated in Fig. 1(b). In terms of the proposed space groups, the ordered structures Fe_{*x*}TiS₂ ($x = \frac{1}{4}, \frac{1}{3},$ and $\frac{1}{2}$) are described as follows:



Special mention must be made of the Fe₃TiS₂ supercell. Usually, the $\sqrt{3}a$ cell will be the more likely to occur for this stoichiometry. If one wants to maintain the rigid $2a$ supercell for this stoichiometry, extra Fe atoms exceeding Fe₃TiS₂ stoichiometry (i.e., $\frac{1}{6}$ Fe) cannot be accommodated in the octahedral interstices. As one possibility, these extra Fe atoms may occupy either tetrahedral or bipyramidal interstices. However, we cannot prove explicitly the existence of such interstitial Fe atoms at present. The low-angle reflection data for the four compounds are summarized in Table III. For the $2a$ cell compounds, X-ray reflections are also indexed in terms of a monoclinic cell.

In the monoclinic indexing, the reflections appeared in accordance with the nonextinction conditions for the proposed space groups, i.e., $h + k = 2n$ for $x = \frac{1}{4}$ and $h + k + l = 2n$ for $x = \frac{1}{2}$, respectively.

As we have pointed out in the introduction, the problem of the crystal structure of Fe₄TiS₂ (=FeTi₂S₄) has not been quite settled yet. Our lattice parameter data for Fe₄TiS₂ are indeed considerably different from those for the same sulfides prepared from different raw materials (cf. Table II). Our sample has the largest lattice parameters. This significant difference in lattice parameters may arise from the difference in metallic ion distribution as well as that in vacancy distribution. Both Hahn *et al.* (4) and Plovnick *et al.* (5, 6) assumed equivocally that Fe and Ti atoms are distributed in the alternate metal layers along the *c* axis. However, in order to bring about the proposed trigonal or monoclinic cell, it is only necessary to have vacancy ordering along the *c* axis. That is, one would have obtained almost the same X-ray reflection diagrams even

TABLE III
LOW-ANGLE REFLECTIONS FROM POWDER DIFFRACTOGRAMS (CuK α ; $2\theta = 10 \sim 50^\circ$)

		Fe ₄ TiS ₂ :C2/m			Fe ₄ TiS ₂ :P3c1			
Hexagonal ^a hkl	Monoclinic hkl	10 ⁴ sin ² θ obsd.	10 ⁴ sin ² θ calcd.	I obsd.	hkl ^b	10 ⁴ sin ² θ obsd.	10 ⁴ sin ² θ calcd.	I obsd.
002	002	184	184	vs	002	181	182	vs
101	201	216	216	vw	101	272	271	vw
111	021	555	556	vw	103	635	635	vw
103	203	582	583	vw	110	678	678	vw
200	(220)	680	680	w	004	726	726	vwv
	(400)				112	858	860	M
004	004	732	734	vw	200	910	906	vwv
202	(222)	865	864	s	105	1361	1361	vw
	(402)				114	1399	1404	s
113	023	918	923	vw	204	1630	1632	w
211	421	1238	1236	vw				
105	205	1319	1317	vw				
212	422	1373	1374	vw				
204	(224)	1414	1414	s				
	(404)							
115	025	1645	1657	w				
006	006		1651					

		Fe ₄ TiS ₂ :I2/m			Fe ₄ TiS ₂ :I2/m?				
Hexagonal ^a hkl	Monoclinic hkl	10 ⁴ sin ² θ obsd.	10 ⁴ sin ² θ calcd.	I obsd.	Hexagonal ^a hkl	Monoclinic hkl	10 ⁴ sin ² θ obsd.	10 ⁴ sin ² θ calcd.	I obsd.
002	002	179	176	s	002	002	180	180	M
101	101	212	212	w	101	101	213	213	w
111	011	553	549	vw	111	011	551	550	vw
103	103	571	564	w	200	(200)	673	674	w
200	(200)	673	673	w		(110)			
	(110)				202	(202)	851	853	s
004	004	717	704	vw		(112)			
202	(202)	851	849	M	113	013	910	911	vw
	(112)				114	211	1222	1227	vw
113	013	913	901	w	105	105	1296	1296	vw
211	211	1221	1223	vw	204	(204)	1392	1395	s
105	105	1288	1268	vw		(114)			
204	(204)	1391	1377	s	106	106	1771	1791	vwv
	(114)								
213	213	1577	1574	vw					
115	015	1615	1605	vw					

^a Indexed on the 2a supercell.

if Fe and Ti atoms are randomly distributed in the (000) and (00 $\frac{1}{2}$) sites, provided vacancies are confined to the (00 $\frac{1}{2}$) sites in the Cd(OH)₂ cell. This type of disordering of metallic ions seems to have been overlooked so far. Since we prepared our Fe $\frac{1}{2}$ TiS₂ from TiS₂ and Fe, such disordering may be kept to a minimum in our sample. This is the probable explanation of the observed difference in lattice parameters.

2. Magnetic Properties

The inverse magnetic susceptibilities $1/\chi$ for Fe $_x$ TiS₂ are plotted against temperature in Fig. 2. It is evident that the $1/\chi$ vs T curves for Fe $\frac{1}{2}$ TiS₂, Fe $\frac{2}{3}$ TiS₂ and Fe $\frac{3}{4}$ TiS₂ obey the Curie-Weiss law quite well in the high-temperature region. However, they all become non-linear near the Curie point. This nonlinear behavior is considered to be due to the short range magnetic ordering. A similar nonlinearity of $1/\chi$ near the Curie point has been observed in ferromagnetic chalcogenide spinels (10). In the same figure, the asymptotic lines used for the determination of the paramagnetic Curie temperature θ_p and the effective paramagnetic moment per Fe atom P_{eff} of these compounds are also drawn. In the calculation of P_{eff} , we implicitly neglected the contribution from Ti ions. This is justifiable because no localized moments are found in compounds containing Ti ions (11, 12).

The $1/\chi$ vs T curve for Fe $\frac{3}{4}$ TiS₂ can not be approximated by a single straight line and seems to be typical of a ferrimagnet. However, it cannot be concluded at present that Fe $\frac{3}{4}$ TiS₂ is a ferrimagnet, since no spontaneous magnetization was observed down to 78 K for this compound.

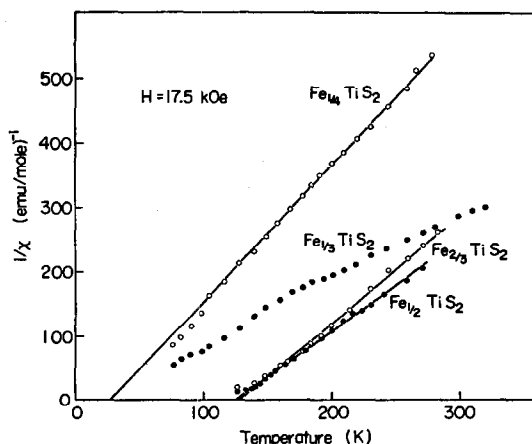


FIG. 2. Inverse susceptibility vs temperature for Fe $_x$ TiS₂; $x = \frac{1}{4}, \frac{1}{3}, \frac{1}{2}$ and $\frac{3}{4}$.

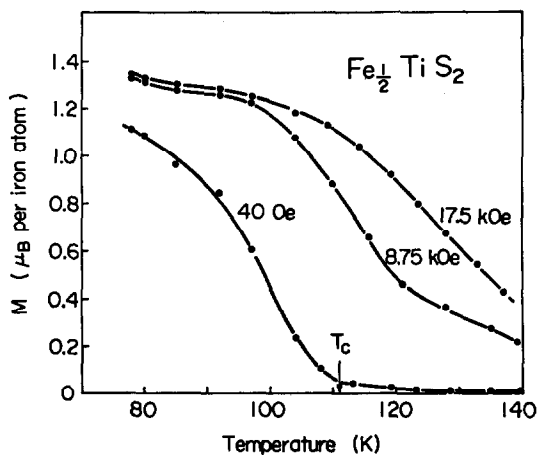


FIG. 3. Magnetic moment per iron atom vs temperature for Fe $\frac{1}{2}$ TiS₂.

The magnetization vs temperature curves for Fe $\frac{1}{2}$ TiS₂ and Fe $\frac{3}{4}$ TiS₂ are shown in Figs. 3 and 4, respectively. The ferromagnetic Curie temperature was arbitrarily determined by the kink point of the magnetization curve in the remnant magnetic field of 40 Oe. The θ_p , P_{eff} and T_c data are summarized in Table IV. Judging from the P_{eff} values, Fe atoms are effectively trivalent (Fe³⁺) in Fe $\frac{1}{2}$ TiS₂ and divalent (Fe²⁺) in Fe $\frac{3}{4}$ TiS₂. The anomalously low P_{eff} value for Fe $\frac{3}{4}$ TiS₂ can not be explained if d electrons in Fe ions are assumed to be completely localized. Delocalization of d electrons may be induced if interstitial Fe atoms bridge between neighboring Fe atoms in octahedral interstices.

The magnetic properties of our Fe $\frac{3}{4}$ TiS₂ sample are quite different from those reported

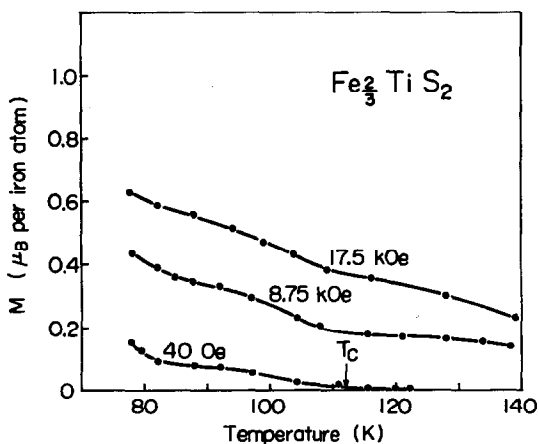


FIG. 4. Magnetic moment per iron atom vs temperature for Fe $\frac{3}{4}$ TiS₂.

TABLE IV

FERROMAGNETIC CURIE TEMPERATURE T_c , PARAMAGNETIC CURIE TEMPERATURE θ_p AND EFFECTIVE PARAMAGNETIC MOMENT P_{eff} FOR Fe_xTiS_2 : $x = \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$.

Compound	T_c (°)	θ_p (°)	P_{eff} (μ_B)	(P_{eff}) cald. (μ_B)
$\text{Fe}_{\frac{1}{4}}\text{TiS}_2$	—	27	6.1	5.92 ^a
$\text{Fe}_{\frac{1}{2}}\text{TiS}_2$	111	124	4.8	4.90 ^b
$\text{Fe}_{\frac{3}{4}}\text{TiS}_2$	112	128	3.2	

^a The spin only moment calculated for Fe^{3+}

^b The spin only moment calculated for Fe^{2+}

by Morris *et al.* (13). They obtained a low T_c (60.2 K) and a smaller P_{eff} (3.54 for their sample 1). This difference may again be accounted for by the differences in both metallic ion and vacancy orderings as we have suggested in the preceding section.

The temperature dependence of the magnetization for $\text{Fe}_{\frac{1}{4}}\text{TiS}_2$ or $\text{Fe}_{\frac{3}{4}}\text{TiS}_2$ does not seem to be described by the ordinary Brillouin function (cf. Figs. 3 and 4). The magnetic properties of these compounds at $T \leq T_c$ should be highly anisotropic because of their layer structures. Magnetization measurements at lower temperatures, preferably on the single crystals, are desirable to study further the magnetic properties of these compounds.

Summary and Conclusions

The iron-containing $\text{Cd}(\text{OH})_2$ structure compounds, Fe_xTiS_2 ($x = \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ and $\frac{3}{4}$) have been prepared. $\text{Fe}_{\frac{1}{4}}\text{TiS}_2$, $\text{Fe}_{\frac{1}{2}}\text{TiS}_2$ and $\text{Fe}_{\frac{3}{4}}\text{TiS}_2$ form a pseudo-hexagonal supercell (crystal symmetry: monoclinic) of $a' = 2a$ and $c' = 2c$, while $\text{Fe}_{\frac{3}{4}}\text{TiS}_2$ forms a trigonal supercell (space group $P\bar{3}m1$) of $a' = \sqrt{3}a$ and $c' = 2c$. In these compounds, except for $\text{Fe}_{\frac{3}{4}}\text{TiS}_2$, all the Fe atoms occupy octahedral interstices between neighboring sulfur layers. In $\text{Fe}_{\frac{3}{4}}\text{TiS}_2$, there may be interstitial Fe atoms. Magnetic measurements indicate that $\text{Fe}_{\frac{1}{2}}\text{TiS}_2$ and $\text{Fe}_{\frac{3}{4}}\text{TiS}_2$ are ferromagnets, with $\theta_p = 124$ and 128 K and $T_c = 111$ and 112 K, respectively. The $1/\chi$ vs temperature plot for $\text{Fe}_{\frac{1}{2}}\text{TiS}_2$ follows the Curie-Weiss law at higher tempera-

tures giving $\theta_p = 26$ K, while that for $\text{Fe}_{\frac{3}{4}}\text{TiS}_2$ is typical of a ferromagnet. No spontaneous magnetization was observed for these two compounds down to 78 K. The effective paramagnetic moment per Fe atom, P_{eff} , calculated from the susceptibility data, indicated that iron atoms are in an effective trivalent Fe^{3+} state in $\text{Fe}_{\frac{1}{4}}\text{TiS}_2$ and in an effective divalent Fe^{2+} state in $\text{Fe}_{\frac{1}{2}}\text{TiS}_2$. An anomalously small P_{eff} value for $\text{Fe}_{\frac{3}{4}}\text{TiS}_2$ seems to indicate that d electrons in Fe ions are only partly localized in this compound.

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