

Features of structural ordering and magnetic properties of the cobalt intercalates of titanium dichalcogenides

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Co_xTiS_2 ($x = 0.20, 0.30, 0.50, 0.75$) compounds have a layered crystal structure with Ti atoms surrounded by the S octahedrons in the S-Ti-S layers and Co ions which could be surrounded both by the S octahedrons and tetrahedrons. The features of the crystal structure and magnetic properties of the polycrystalline Co_xTiS_2 samples were studied as a function of the cobalt concentration using X-ray diffraction and magnetization measurements. The disordered state of the Co atoms ($x < 0.20$) changes to the ordered one ($x \geq 0.20$). The magnetic ordering arises at $x = 0.20$ with mostly antiferromagnetic interaction. For compound with $x = 0.30$ and 0.50 there is a weak ferromagnetic ordering. The ferromagnetic ordering is observed in $\text{Co}_{0.75}\text{TiS}_2$ below $T_c = 375$ K.

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1. Introduction

The layered transition metal dichalcogenides (LTMDs) intercalated with transition metals are the object of numerous studies [1–6]. The layered morphology of the compounds provides a relatively weak bonding between neighboring chalcogen layers [7, 8]. This makes it possible to invertibly introduce (intercalate) atoms, ions, or molecules into the interlayer space without losing the layered structure of the compound. Both the crystal and electronic structure of the intercalation compounds substantially depend on the dopant type and concentration. TiS_2 belongs to the TiCh_2 ($\text{Ch} = \text{S}, \text{Se}, \text{Te}$) LTMDs family with the highest ionic contribution to the chemical bonding within the Ch-Ti-Ch layers [9]. At the same time, TiS_2 possesses high electrical conductivity [10, 11] as well as high Li^+ diffusion rate [12, 13], which makes it good candidate for a battery cathode material. Indeed, TiS_2 is used as the host for Li/TiS_2 electrochemical system with excellent dynamic characteristics [14]. At the same time, the so-called “blocking effect” [12, 15] (when Li ions occupy all octa- and tetra-positions in the TiS_2 interlayer space) prevents high specific capacity values. To solve this problem, one can reduce the solubility of Li in Li_xTiS_2 . The first way is to use the substitutional host lattice, as it was done in Ref. [16]. The second way is to use intercalate Li into previously intercalated M_xTiS_2 ($\text{M} - 3d$ -transition metal). For example, it was found, that Cu intercalation into Ni_yTiSe_2 leads to the displacement of the Ni atoms from the octahedral to tetrahedral positions [17]. In the same manner we could modify M_xTiS_2 lattice by forcing the M atoms to displace from the octahedral sites during Li intercalation decreasing the Li solubility limit.

In the current work we prepared Co_xTiS_2 compounds for further Li intercalation. The electronic configuration of Co is $3d^7$, so, being displaced into the tetrahedral site, it should form the chemical bonding with four nearest neighbors and its configuration should be a high spin $3d^3$ one. Therefore, we can expect high values of the magnetic moment and possible magnetic ordering of the Co atoms. The Co_xTiS_2 system was extensively studied [18–22]. However, the data on both

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crystal and magnetic structure even for the compounds with the same composition are often inconsistent.

2. Experimental section

Polycrystalline samples of Co_xTiS_2 ($x = 0.20, 0.30, 0.50, 0.75$) were prepared using solid-state reaction method in two stages. At the first stage, polycrystalline TiS_2 was prepared. The stoichiometric amounts of elements (titanium (after iodine purification, 99.95%) and sulfur (OSCh16-5, 99.999%) (St. Petersburg Krasnij Khymik Plant) were placed into sealed quartz ampoules evacuated to 10^{-5} Torr. The sealed ampoules were placed into a furnace and heated at $650\text{ }^\circ\text{C}$ for 96 hours. The heating and cooling rates were set to $1\text{ }^\circ\text{C}/\text{min}$. The obtained material was grinded, pressed into pellets and homogenized for two times at the same conditions. At the second stage, the Co_xTiS_2 ($x = 0.20, 0.30, 0.50, 0.75$) compounds were prepared from previously obtained TiS_2 and powder Co (99.4%). The stoichiometric amounts of TiS_2 powder and Co powder were mixed, pressed into pellets and placed into sealed quartz ampoules evacuated to 10^{-5} Torr, and heated at $650\text{ }^\circ\text{C}$ for 48h. The homogenization procedure and the heating/cooling rates were set the same as for TiS_2 preparation. It is worth to mention that the use of the slow cooling rate is crucial for the sulfur containing LTMDs to allow sulfur re-enter into the compound without condensing on the ampoule wall.

The morphology of the powder Co_xTiS_2 samples and their chemical composition were studied using scanning electron microscopy (SEM) and X-ray energy dispersive analysis (EDA) methods on a JEOL JSM 6390 microscope equipped with a JED 2300 detector.

The structure and phase composition of the samples were studied at room temperature using X-ray powder diffraction (XRD) method on a high-resolution Shimadzu XRD-7000 diffractometer ($\text{Cu}_{K\alpha}$ radiation, $2\theta = 5\text{--}70\text{ }^\circ$, Bragg-Brentano geometry). The crystal structure refinement was performed using Fullprof software package [23]. To visualize the refined crystal structure, VESTA software was used [24].

Magnetic measurements for Co_xTiS_2 ($x = 0.20, 0.30, 0.50, 0.75$) were performed with MPMS XL-7 EC SQUID-magnetometer in the temperature range of 2-300 K in zero-field cooled (ZFC) and field-cooled (FC) regimes under the applied magnetic field of 100 Oe.

3. Results and discussion

3.1. Morphology

According to SEM data, Co_xTiS_2 ($x = 0.20, 0.30, 0.50, 0.75$) samples contain homogeneous grains with an average size of 2 to $50\text{ }\mu\text{m}$ (Fig. 1). The shape of the grains strongly depends on the Co concentration. In pristine TiS_2 the grains have a form of thin plates [25], but as the Co concentration increases, the grains stick together into larger agglomerates of irregular shape. The analysis of EDX spectra confirms that all the samples contain only initial elements, and the deviation in Co content does not exceed 10 at. % as compared to the nominal concentration (see Table 1).

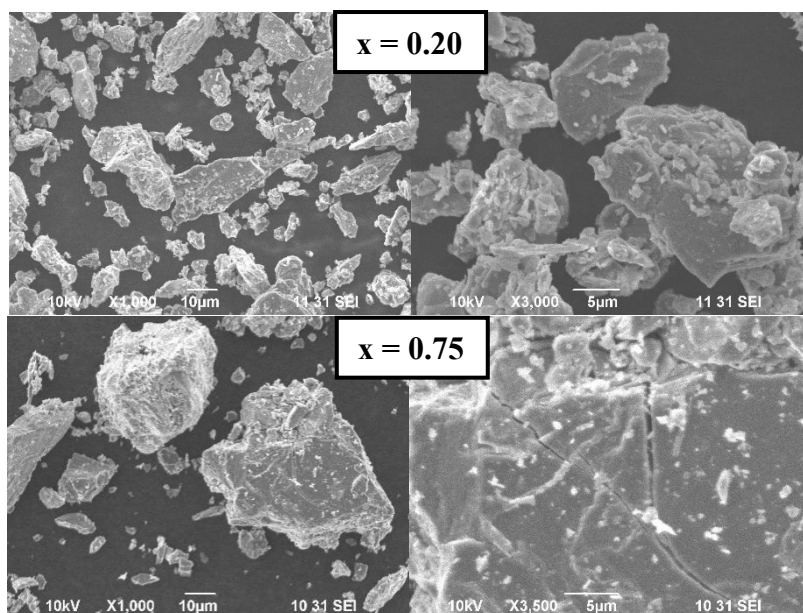


Fig. 1. SEM images of polycrystalline samples of Co_xTiS_2 ($x = 0.20, 0.75$)

3.2. Crystal structure

Figure 2 (a, b) shows the experimental, calculated, and difference X-ray patterns for the border $\text{Co}_{0.20}\text{TiS}_2$ and $\text{Co}_{0.75}\text{TiS}_2$ compounds. The phase analysis indicated that all the studied compounds Co_xTiS_2 ($x = 0.20, 0.30, 0.50, 0.75$) are the single-phase ones. The results of the refinement of the XRD patterns are listed in Table 1. We can distinguish two concentration regions of Co on the concentration dependence of the a_0 lattice parameter. The increase in Co content up to $x = 0.30$ significantly decreases the a_0 lattice parameter as compared to the undoped TiS_2 ($a_0 = 3.4073(2) \text{ \AA}$, $c_0 = 5.6953(2) \text{ \AA}$ [26]), and the increase of a_0 with x is observed above $x = 0.30$ (Fig. 2 (c)). At the same time, the c parameter slightly increases with x in the whole studied concentration region (Fig. 2d). Our data are in rather good agreement with ones reported in Refs. [19, 21] instead of the compound with $x = 0.50$, where the values obtained in our study are nearly 0.5% higher than that reported in Ref. [19]. As the Co concentration increases, the ordering of the Co atoms is observed. Even at $x = 0.20$ the Co atoms are ordered in the octahedral positions in the interlayer space. However, no traces of the Co ordering were reported for this compound previously [19, 22]. According to our data, $\text{Co}_{0.20}\text{TiS}_2$ crystallizes in the monoclinic structure with an $I2/m$ space group with $a = a_0\sqrt{3}$, $b = a_0$, $c = 2c_0$, where a_0 and c_0 are the lattice parameters of the initial trigonal unit cell (space group $P\bar{3}m1$). $\text{Co}_{0.50}\text{TiS}_2$ also crystallizes in the same monoclinic structure. $\text{Co}_{0.30}\text{TiS}_2$ crystallizes in trigonal structure with a $P\bar{3}1c$ space group with $a = a_0\sqrt{3}$, $b = a_0\sqrt{3}$, $c = 2c_0$. In this compound, the Co atoms are distributed over 3 types of octahedral positions: Co1 ($1/3, 2/3, 0.25$) ($2c$), Co2 ($0, 0, 0.25$) ($2b$) and Co3 ($2/3, 1/3, 0.25$) ($2b$); however, the occupation of Co3 positions is significantly lower than that of Co1 and Co2 (see Table 1). As the Co concentration increases to $x = 0.75$, the Co atoms become to be disordered in the octahedral and tetrahedral positions, and the space group returns to initial $P\bar{3}m1$, which, according to data reported by Guelou et al. [19], is also typical for Co_xTiS_2 compounds with low ($0.02 \leq x \leq 0.15$) Co content. The occupation of the tetrahedral position Co2 for $\text{Co}_{0.75}\text{TiS}_2$ is almost 20% of the total occupation number. For the composition $\text{Co}_{0.67}\text{TiS}_2$, Guelou et. al. [19] calculated the occupation of the tetrahedral position is almost 7%. With an increase in the cobalt concentration to $x = 0.75$, the occupation of the tetrahedral position sharply increases from 7% to 20%.

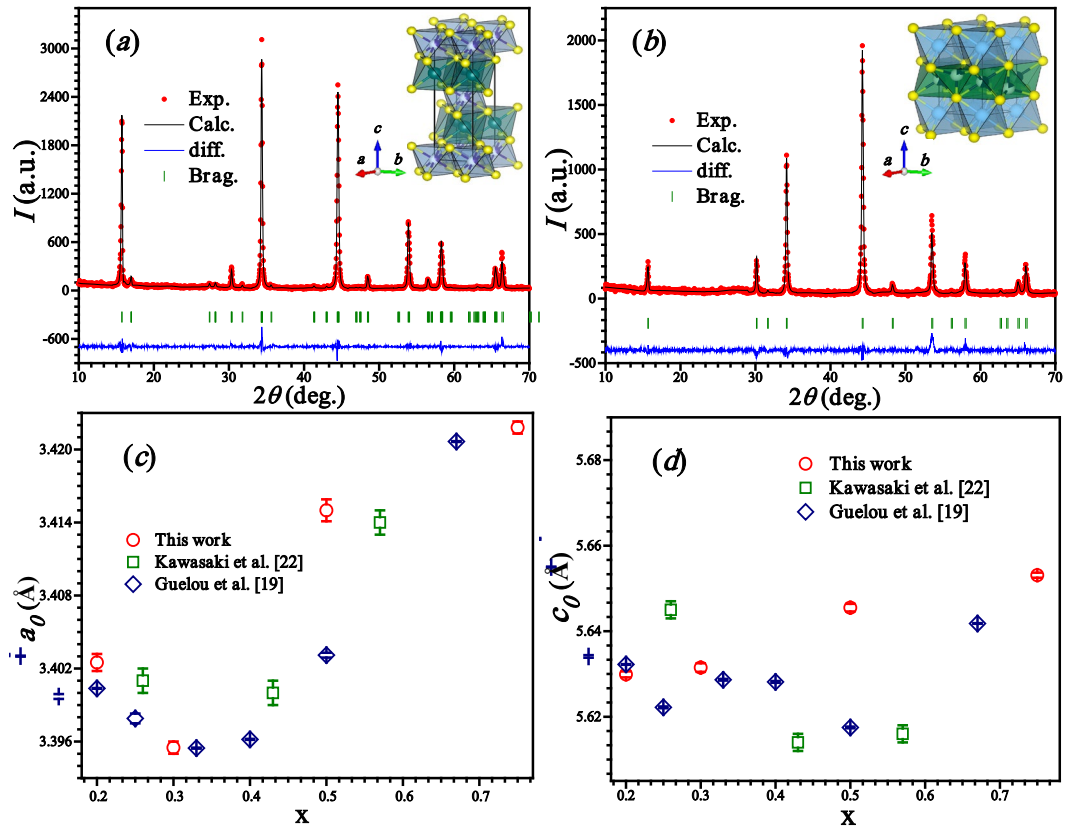


Fig. 2. Upper panels: experimental (red dots), calculated (black line), and difference (blue line) XRD patterns for $\text{Co}_{0.20}\text{TiS}_2$ (a) and $\text{Co}_{0.75}\text{TiS}_2$ (b). The insets show the crystal structures of the corresponding compounds according to the Rietveld refinement. Lower panels: Co concentration dependence of the a (c) and c (d) lattice parameters for Co_xTiS_2 . Our data (red circles) are compared to the previously reported by Kawasaki et al. [22] (green squares) and Guelou et al. [19] (blue diamonds).

Therefore, our data suggest the following transformation of the crystal structure: MS_2 ($P\bar{3}m1$) ($x < 0.20$), M_3S_4 ($I2/m$) ($x = 0.20$), M_2S_3 ($P\bar{3}1c$) ($x = 0.30$), M_3S_4 ($I2/m$) ($x = 0.50$), MS_2 ($P\bar{3}m1$) ($x = 0.75$). Guelou et al. [19] report on the following transformations: MS_2 ($P\bar{3}m1$) ($x < 0.20$), M_5S_8 ($F2/m$) ($x = 0.25$), M_2S_3 ($P\bar{3}1c$) ($x = 0.33, 0.40$), M_3S_4 ($I2/m$) ($x = 0.50$), MS_2 ($P\bar{3}m1$) ($x = 0.67$). We can see a good agreement in this “phase diagrams” suggesting the disorder in Co sublattice at high ($x > 0.60$) concentrations and redistribution of Co atoms between octahedral and tetrahedral positions. Kawasaki et al., however, reported on the trigonal $P\bar{3}m1$ structure for $\text{Co}_{0.26}\text{TiS}_2$ and $\text{Co}_{0.57}\text{TiS}_2$ and trigonal $P\bar{3}1c$ structure for $\text{Co}_{0.43}\text{TiS}_2$ single crystals [22], which meant no ordering in the Co sublattice. At the same time, a lot of authors [19, 22, 27, 28] report on the ordering in the Co_xTiS_2 compounds only above $x = 0.25$, while our data reveal the ordering of Co atoms even at $x = 0.20$.

Considering our results and the data obtained in Refs. [29, 30], we can conclude that taking Co_xTiS_2 with $0.20 \leq x \leq 0.50$ (Co atoms are only in octahedral positions) as a host lattice for Li intercalation, we could reduce the “blocking effect” in $\text{Li}_y\text{Co}_x\text{TiS}_2$. This is because Co atoms, which occupy part of the octahedral positions near the lateral faces of the crystallites TiS_2 , will prevent the gathering of the Li atoms in the near-surface regions of the lateral faces during intercalation. In addition to this, the intercalation of cobalt ions in the S-Ti-S layers slides apart the crystal lattice in the direction of c axis, which supports the advancement of the first lithium ions deep into the interlayer space.

Table 1. Crystallographic parameters of Co_xTiS_2 ($x = 0.20; 0.30; 0.50, 0.75$).

Compound	$\text{Co}_{0.20}\text{TiS}_2$	$\text{Co}_{0.30}\text{TiS}_2$	$\text{Co}_{0.50}\text{TiS}_2$	$\text{Co}_{0.75}\text{TiS}_2$
x(Co) (nominal concentration)	0.20	0.30	0.50	0.75
x(Co) (on EDX)	0.18	0.27	0.46	0.69
Space group	$I2/m$	$P\bar{3}1c$	$I2/m$	$P\bar{3}m1$
a , Å	5.8929(7)	5.8810(5)	5.915(1)	3.4211(6)
b , Å	3.3987(4)	-	3.4125(7)	-
c , Å	11.2599(6)	11.262(1)	11.291(1)	5.6522(7)
V , Å ³	225.52(4)	337.33(5)	227.93(7)	57.29(2)
Ti1, x,y,z	-0.003(3), 0, 0.2503(4)	0, 0, 0	-0.005(3), 0, 0.2544(4)	0,0,0
Ti2, x,y,z	-	1/3, 2/3, - 0.0029(3)	-	-
S1, x,y,z	0.325(2), 0, 0.3762(6)	0.334(1), - 0.0008(8), 0.3705(3)	0.334(5), 0, 0.3774(5)	1/3, 2/3, 0.271(1)
S2, x,y,z	0.329(2), 0, 0.8816(6)	-	0.332(6), 0, 0.8824(6)	-
Co1, x,y,z	0, 0, 0	1/3, 2/3, 0.25	0, 0, 0	0, 0, 0.5
Occ	0.182(1)	0.228(1)	0.350(1)	0.413(1)
Co2, x,y,z	-	0, 0, 0.25	0.5, 0.5, 0	2/3, 1/3, 0.390(2)
Occ	-	0.045(1)	0.105(2)	0.150(1)
Co3, x,y,z	-	2/3, 1/3, 0.25	-	-
Occ	-	0.006(1)	-	-
R_p , %	4.49	3.94	3.30	6.05
χ^2	2.03	1.96	2.81	3.07

3.3. Magnetic properties

Figure 3 shows the $\chi_m(T)$ dependences obtained in ZFC and FC regimes. The FC curve was measured in the magnetic field of 0.01 T. For the $\text{Co}_{0.20}\text{TiS}_2$ compound, the ZFC and FC curves become to split below $T = 12$ K, which can indicate transition to a spin glass state. The transition to the spin glass state was reported in Ref. [31] at $x \leq 0.20$, however, in other works there was reported about the transition to the ferromagnetic state in these compounds below $T_c = 130$ K [19, 32]. At the same time, Guelou et al. [19] claim that neutron powder diffraction didn't reveal any traces of the ferromagnetic ordering below $T_c = 130$ K. Therefore, the type of the magnetic ordering in Co_xTiS_2 with $x \leq 0.20$ remains controversial. At $x \geq 0.3$, a ferromagnetic contribution appears (see Fig. 2). For $x = 0.30$ and $x = 0.50$ the temperatures of the magnetic ordering are $T_c = 218$ K and $T_c = 180$ K, respectively. A weak ferromagnetism has been found below $T_c \approx 120 - 140$ K for Co_xTiS_2 with $0.075 \leq x \leq 0.33$ [32], but, at the same time, in [19] no magnetic transitions was observed for Co_xTiS_2 with $0.25 \leq x \leq 0.66$ in the temperature range of 2 – 300 K at all.

$\text{Co}_{0.75}\text{TiS}_2$ substantially differs from other Co_xTiS_2 compounds. Its magnetic susceptibility increases with temperature at least up to 370 K. Below $T_c = 370$ K ZFC and FC curves split, and we associate this temperature with the ferromagnetic transition. As for the value of the magnetic susceptibility, it increases with x . However, the entirely opposite behavior of the magnetic susceptibility, which decreased with increased x , has been observed by Guelou et al. [19].

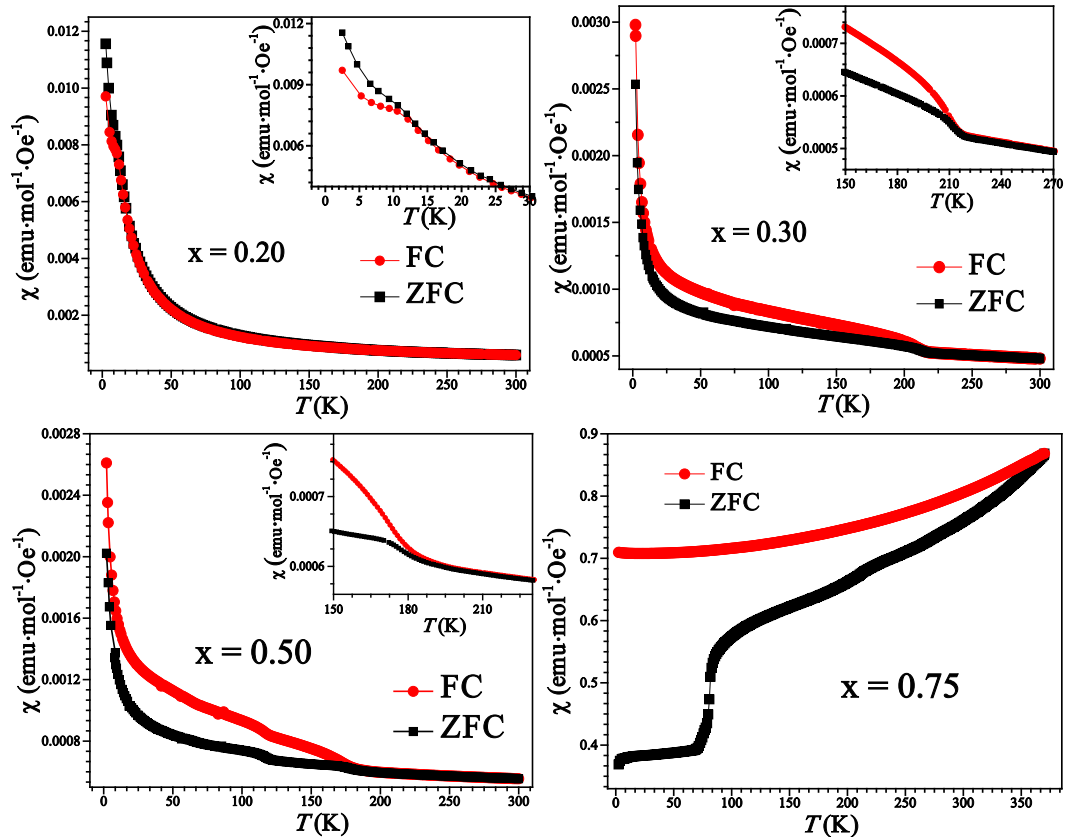


Fig. 3. Temperature dependences of the molar magnetic susceptibility χ_m measured in the ZFC and FC regimes in an external magnetic field of 0.01 T for Co_xTiS_2 ($x = 0.20, 0.30, 0.50, 0.75$).

The field dependences of the magnetization for $\text{Co}_{0.20}\text{TiS}_2$ measured at $T = 40$ K have a linear form, which is typical for materials with antiferromagnetic ordering. However, they revealed a small ferromagnetic contribution with coercive force of $H_c = 7$ Oe and residual magnetization of $M_r = 0.04$ emu/g (Fig. 4, left panel). $M(H)$ become to be linear at $T = 210$ and 290 K, which means no magnetic ordering at these temperatures. The right panel of the Fig. 4 shows the $M(H)$ loops for $\text{Co}_{0.75}\text{TiS}_2$ measured at $T = 40, 210, 290, 360$ K. A pronounced hysteresis with $H_c = 100$ Oe and $M_r = 2.7$ emu/g is well observed for all temperatures. This is the first data on the ferromagnetic ordering in Co_xTiS_2 with large Co content ($x = 0.75$) up to $T_c = 370$ K.

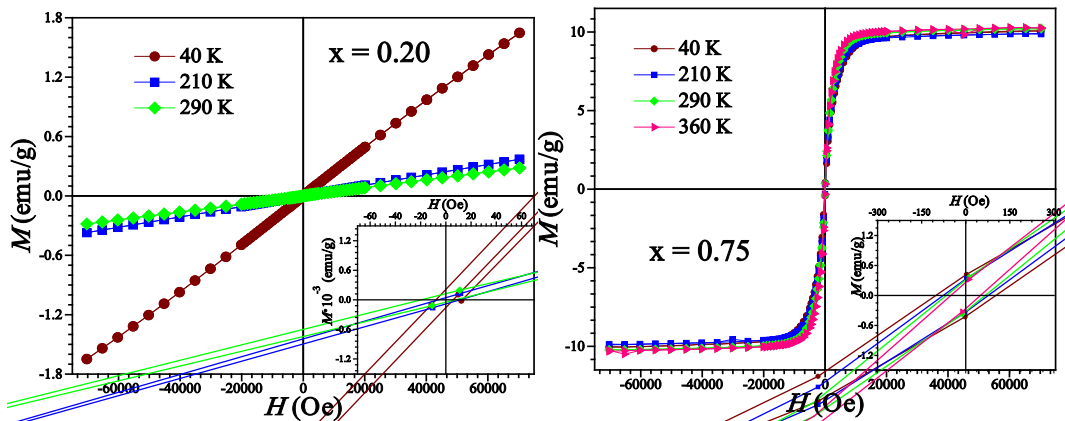


Fig. 4. Hysteresis loops $M(H)$ for Co_xTiS_2 with $x = 0.20$ (left panel) and $x = 0.75$ (right panel).

For the analysis of temperature dependences of the magnetic susceptibility in the paramagnetic region we used the modified Curie-Weiss law $\chi = \chi_0 + \frac{C}{T - \theta_p}$, where χ_0 is a temperature-independent term, C – Curie constant, θ_p – paramagnetic Weiss temperature. The results of the approximation are listed in Table 2. A negative θ_p is observed for $x = 0.20$ indicating the prevalence of the antiferromagnetic exchange interaction. In contrast, for compounds with $x = 0.30$ and $x = 0.50$, θ_p is positive indicating the prevalence of the ferromagnetic exchange interaction. The effective magnetic moment μ_{eff} for all the studied Co_xTiS_2 compounds ($x = 0.20, 0.30, 0.50$) is close to the spin-only value for the low-spin state Co^{2+} ($\mu_{eff}/\mu_B = 1.73$) and does not depend on the Co concentration. In contrast to our data, Guelou et al. [19] reported on the decrease in the effective magnetic moment with increased Co concentration, which might be associated with an increase in the degree of delocalization of electrons with increasing cobalt concentration in the interlayer space [19, 32] or with antiferromagnetic correlations in the material.

Table 2. Magnetic parameters of Co_xTiS_2 ($x = 0.20; 0.30; 0.50, 0.75$).

Compound	$\text{Co}_{0.20}\text{TiS}_2$	$\text{Co}_{0.30}\text{TiS}_2$	$\text{Co}_{0.50}\text{TiS}_2$
Temp. range (K)	125-300	224-300	200-300
χ_0 (emu mol ⁻¹)	2.65×10^{-4}	2.17×10^{-4}	4.38×10^{-4}
θ_p (K)	-8(2)	291(22)	99(7)
μ_{eff}/μ_B per Co	2.00(2)	2.04(5)	1.94(4)

The measurements for the $\text{Co}_{0.20}\text{TiS}_2$ compound allow to assume the antiferromagnetic ordering with weak ferromagnetism; however, the most volume of the sample remains paramagnetic. Opposite, for the Co_xTiS_2 samples with intermediate compositions ($x = 0.30, 0.50$) a weak ferromagnetic ordering is observed. The $\text{Co}_{0.75}\text{TiS}_2$ compound is entirely ferromagnetic in the temperature range of 2 – 370 K.

4. Conclusions

Polycrystalline Co_xTiS_2 compounds ($x = 0.20, 0.30, 0.50, 0.75$) were synthesized using solid-state-reaction method and studied using XRD, SEM and magnetization measurements to choose the best compounds for further Li intercalation. The increase in Co concentration changes the shape of grains changed from the thin plates to the agglomerates of irregular shape. The crystal structure of Co_xTiS_2 evolves with x from trigonal $P\bar{3}m1$ structure with disordered Co atoms in the octahedral positions ($x < 0.20$) through monoclinic $I2/m$ ($x = 0.20$), trigonal $P\bar{3}1c$ ($x = 0.30$) and monoclinic $I2/m$ ($x = 0.50$) structures with ordered Co atoms back to trigonal $P\bar{3}m1$ ($x = 0.75$) structure with disordered Co atoms both in the octahedral and tetrahedral positions. The first ordering of Co atoms occurs even at $x = 0.20$. The magnetic ordering also depends on the Co concentration and is, apparently, concerned with the ordering of Co atoms. For Co_xTiS_2 with $x = 0.20$ there is an antiferromagnetic ordering with a weak ferromagnetism, while the most volume of the samples remains paramagnetic. For Co_xTiS_2 with $x = 0.30$ and 0.50 there is a weak ferromagnetic ordering. $\text{Co}_{0.75}\text{TiS}_2$ is a ferromagnetic with $T_c = 370$ K. Most suitable for the further Li intercalation is Co_xTiS_2 with $0.20 \leq x \leq 0.50$.

Acknowledgements

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