# Magnetic properties of Cr-intercalated TiSe$_2$

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## Abstract

Using the measurements of the susceptibility and magnetization in steady and pulsed magnetic fields and under applied hydrostatic pressure we have investigated the magnetic properties of Cr-intercalated Cr$_x$TiSe$_2$ compounds having a hexagonal crystal structure of a quasi-two-dimensional type. It has been found that the effective magnetic moment $\mu_{eff}$ of Cr changes nonmonotonously with Cr-content. The $\mu_{eff}(x)$ dependence correlates with the change in the interlayer distance at the intercalation which is attributed to the change of the localization degree of the chromium 3d-electrons. The intercalation leads to changes of the magnetic state of Cr$_x$TiSe$_2$ from the Pauli paramagnetism at $x=0$ to the claster-glass behavior at $0.25 \leq x \leq 0.33$ and then to the antiferromagnetic order in Cr$_{0.5}$TiSe$_2$. The last compound exhibits a field-induced spin-flip transition below the Néel temperature $T_N = 38$ K due to the very low ratio between the interlayer and intralayer exchange interaction ($w_2/w_1 \approx 5.4 \times 10^{-3}$). The applied hydrostatic pressure decreases the Néel temperature with a rate $dT_N/dp = -0.19$ K/kbar. The interlayer exchange interaction was found to be more sensitive to the Cr–Cr distance than the intralayer one.   © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The titanium dichalcogenide TiX$_2$ (X=S, Se, Te) compounds have a hexagonal crystal structure of the CdI$_2$ type. The triple X–Ti–X layers in these compounds are bound by weak van der Waals (vdW) forces. Because of their layer structure the compounds TiX$_2$ reveal a high anisotropy of physical properties [1]. By intercalation of different M atoms in the octahedral positions between the X–Ti–X layers a wide class of M$_x$TiSe$_2$ compounds with unusual electronic and magnetic properties can be obtained. Metal–semiconductor phase transitions and the appearance of charge density waves were observed in some of the intercalated compounds as well as in the parent TiSe$_2$ compound [2–4]. The existence of different magnetic states ranging from spin-glass like behavior up to states with three-dimensional magnetic order was established in TiS$_2$ intercalated by 3d-transition metals. The magnetic state of these compounds was found to be dependent on the type and concentration of the 3d-element intercalated between the S–Ti–S layers [5–7].

The intercalated compounds based on titanium diselenide are much less investigated. There are some indications [5,6] that the compounds Fe$_x$TiSe$_2$ ($x=0.25$; 0.33; 0.5) have an antiferromagnetic order below the corresponding Néel temperatures of 62, 95 and 129 K [8,9]. One can expect that the ratio between the intralayer and interlayer exchange interaction depends on the distance between the X–Ti–X blocks. Since the vdW gap in TiSe$_2$ is greater (0.3004 nm) than in TiS$_2$ (0.2847 nm) the M$_x$TiSe$_2$ compounds may be more preferable to reveal two-dimensional effects.

The aim of the present paper is to study the influence of Cr intercalation on the magnetic properties of the titanium diselenide by means of magnetic susceptibility and magnetization measurements for the compounds with different Cr-contents in steady and pulsed magnetic fields and under hydrostatic pressure.

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## 2. Experimental

Polycrystalline samples of $Cr_xTiSe_2$ ($0 < x \leq 0.5$) were prepared in two stages. At first the parent compound $TiSe_2$ was synthesized by heat treatment of a mixture of the starting materials Ti (99.9) and Se (99.99) at 800°C during 150 h. In the second stage the mixtures of Cr- and $TiSe_2$-powders were sealed in evacuated quartz tubes and annealed under the same conditions. The obtained specimens were milled, compacted into pellets and then homogenized for 1 week at 800°C followed by cooling down to room temperature during about 10 min. Powder X-ray diffraction investigations have shown that all samples have the $CdI_2$ structure. Lattice parameters were measured by X-ray diffraction with an error of $3 \times 10^{-4}$ nm.

The static magnetization and magnetic susceptibility at ambient pressure were measured by means of a Quantum Design SQUID magnetometer in the temperature interval from 2 up to 300 K in magnetic fields up to 5 T. The measurements under hydrostatic pressures of up to 12 kbar were made by using an extraction-type magnetometer with a superconducting magnet with a field of up to 7 T. The high field magnetization measurement was carried out at 4.2 K in a pulsed magnetic field up to 40 T by an induction method using a wire-wound pulse magnet with a duration time of about 10 ms.

## 3. Results and discussion

As was shown in Ref. [2], the pure $TiSe_2$ compound is a Pauli paramagnet. An intercalation of this compound by chromium changes dramatically its magnetic state. At $x < 0.25$ the $Cr_xTiSe_2$ compounds show paramagnetic behavior with a nonlinear temperature dependence of the reciprocal susceptibility (Fig. 1). A further increase of the Cr content
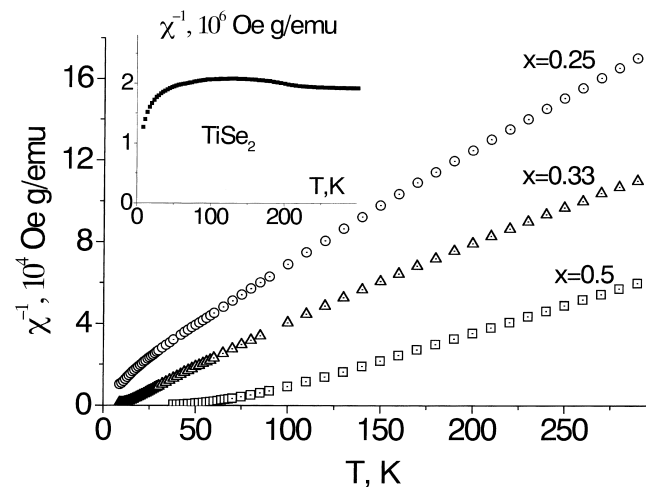


Fig. 1. Temperature dependencies of the inverse magnetic susceptibility of $Cr_xTiSe_2$ at various Cr content. Inset: $\chi^{-1}$ versus $T$ dependence for pure $TiSe_2$.
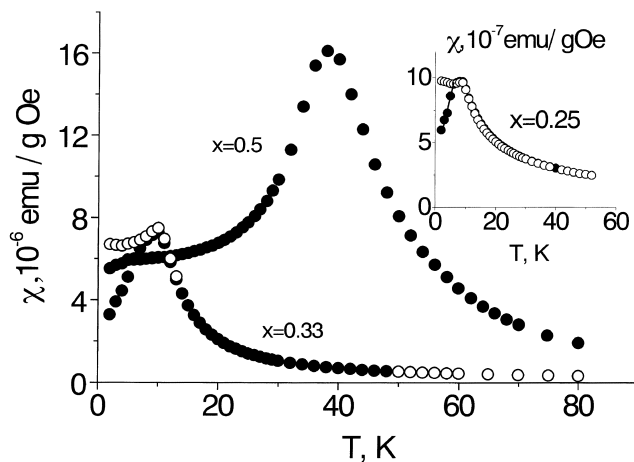


Fig. 2. Temperature dependencies of the magnetic susceptibility of $Cr_xTiSe_2$ measured on ZFC (full symbols) and on FC (open symbols) samples.

leads to the appearance of anomalies in the temperature dependencies of the susceptibility. As can be seen in Fig. 2, the $\chi(T)$ dependencies of $Cr_xTiSe_2$ compounds with $x = 0.25$; 0.33; 0.5 show maximums at temperatures of 8, 10 and 38 K. The temperature dependencies of the magnetic susceptibility of these compounds at high temperatures ($T > 80$ K) can be well described by the expression

$$\chi(T) = \chi_0 + \frac{C}{T - \Theta_p} \qquad (1)$$

Here $\chi_0$ is a temperature independent term which includes the diamagnetic contribution ($\chi_d$) and paramagnetic contribution from the delocalized electrons ($\chi_p$). The second term in (1) describes the Curie–Weiss contribution. $C$ is the Curie constant. The diamagnetic susceptibility can be estimated from the following expression [10]:

$$\chi_d = 0.79 \times 10^{-6} \sum_i Z_i (r_i/a_0)^2 \qquad (2)$$

Here $Z_i$ is the number of electrons in the full electron shells of the ion $i$, $r_i$ is the average radius of $i$th ion and $a_0 = 0.529$ Å is the Bohr radius. Such an estimation has given the value $\chi_d = -0.52$ emu/g Oe for all the compounds under investigation. Using this value of $\chi_d$ the Pauli paramagnetic contribution $\chi_p$ as well as the effective magnetic moment ($\mu_{eff}$) of the Cr-ions and the paramagnetic Curie temperature $\Theta_p$ were determined. All these values are collected in Table 1. As can be seen the values of $\mu_{eff}$ for all compounds are lower than the value $\mu_{eff} = 2\mu_B\sqrt{S(S+1)} = 3.87$ $\mu_B$ for the free $Cr^{3+}$ ion. It should be noted that the concentration dependence of the effective magnetic moment of Cr for intercalated $TiSe_2$ correlates quite well with the change of the lattice parameter $c$ which reflects the distance between the Se–Ti–Se layers (see Fig. 3). A decrease of $c$ with intercalation of $TiX_2$ by small

Table 1
The effective magnetic moment of the Cr-ions ($\mu_{eff}$), paramagnetic Curie temperature ($\Theta_p$), temperature-independent ($\chi_o$) contribution (see expression (1)) and Pauli paramagnetic ($\chi_p$) contributions to the magnetic susceptibility of $Cr_xTiSe_2$ compounds

| X | $\mu_{eff}$ ($\mu_B$) | $\Theta_p$ (K) | $\chi_o$ ($10^{-6}$ emu/g Oe) | $\chi_p$ ($10^{-6}$ emu/g Oe) |
|------|------|------|------|------|
| 0.1  | 3.4  | −6   | 0.12 | 0.64 |
| 0.2  | 3.1  | −7   | 0.26 | 0.78 |
| 0.25 | 3.3  | −20  | 0.40 | 0.92 |
| 0.33 | 3.5  | 0    | 0.60 | 1.12 |
| 0.5  | 3.6  | 68   | –    | –    |

amounts of the 3d-element was connected in Refs. [11,12] with the formation of covalency links between the intercalated 3d-ions and the X–Ti–X layers. The 3d-electrons of the intercalated Cr-ions can be involved in these links due to their partial delocalization. When the Cr-content reaches the value $x = 0.25$ a further increase of $x$ leads to an increase of $c$. Such a behavior of $c(x)$ may be attributed to the saturation of the covalency links at a Cr-content of $x = 0.25$ which corresponds to one-fourth of the possible Cr-positions in the layer between the $TiSe_2$ blocks. An increase of the Cr-concentration above $x = 0.25$ increases the $c$ value as well as in an usual solution. It is accompanied by localization of the 3d-electrons and consequently by increasing the effective magnetic moment of Cr. The assumption about the change of the degree of the localization of the 3d-electrons of Cr in the $Cr_xTiSe_2$ compounds upon substitution is confirmed by band structure calculations on intercalated compounds based on titanium disulfide. As it is shown in Ref. [13] the 3d-electrons of the atoms inserted between the X–Ti–X layers may be hybridized with the molecular orbitals of Ti and can form narrow bands near the Fermi level. As it follows from Table 1 the value of the Pauli paramagnetic contribution to the total magnetic susceptibility increases with increasing chromium content at least up to $x = 0.33$. Such an increase of $\chi_p$ we attribute to increasing density of electronic states
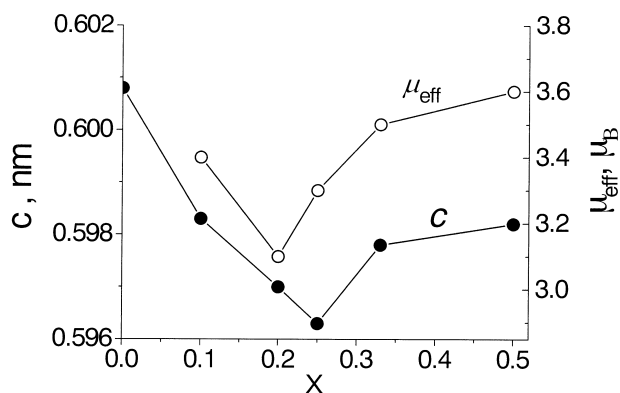
at the Fermi level. Unfortunately, the $\chi_p$ value cannot be estimated for the $Cr_{0.5}TiSe_2$ compound owing to the very high Curie–Weiss contribution to the total magnetic susceptibility in (1) in comparison with $\chi_0$.

The temperature dependencies of the susceptibility (Fig. 2) for the compounds $Cr_xTiSe_2$ with $x = 0.25$ and 0.33 show an essential hysteresis when the measurements were made on a sample cooled in zero field (ZFC) or on a sample cooled in an applied field (FC). This behavior can be associated with a cluster-glass-like behavior of these compounds below the freezing temperatures of 8 and 12 K, respectively. The shape of the hysteresis loops measured on the compounds with $x = 0.25$ and 0.33 (see Fig. 4) is typical for such materials. For the compound $Cr_{0.5}TiSe_2$ no difference between the $\chi(T)$ curves measured on a ZFC sample and on a sample cooled in the field 0.01 T is observed. Moreover, as can be seen in the Fig. 4, the field dependence of the magnetization measured on $Cr_{0.5}TiSe_2$ at $T = 2$ K shows a critical field which indicates the presence of a field-induced magnetic phase transition from one magnetic structure to another one. The value of the critical field is estimated to be about 0.9 T by using the maximum of $dM/dH$. All these data allow us to suggest that this compound has an antiferromagnetic order below the Néel temperature $T_N = 38$ K and exhibits a spin-flip transition in an applied magnetic field. The low value of the critical field in this compound may be attributed to the relatively low energy of the antiferromagnetic exchange interaction. Although the magnetic structure of $Cr_{0.5}TiSe_2$ is still unknown in order to analyze the magnetization data we can use as the first approximation a simple model of a two-sublattice antiferromagnet with ferromagnetic alignment of the magnetic moments in the Cr layer and with antiferromagnetic interaction between the layers. According to the molecular field theory for the two sublattice collinear antiferromagnet its ordering temperature $T_N$,
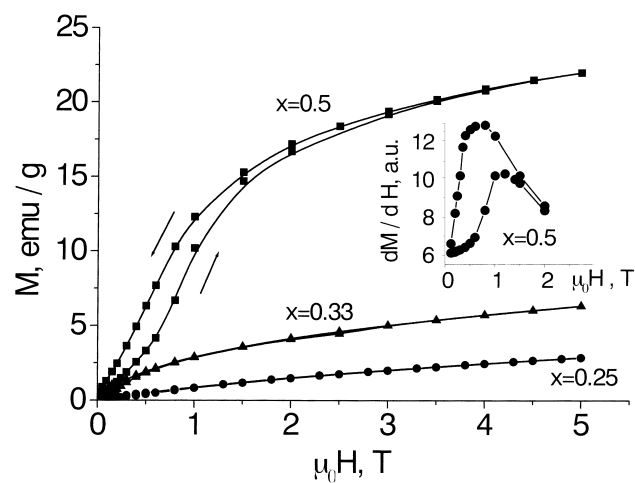


Fig. 3. Concentration dependencies of the lattice parameter $c$ and effective magnetic moment per Cr ion for $Cr_xTiSe_2$.



Fig. 4. Field dependencies of the magnetization of $Cr_xTiSe_2$ compounds measured at $T = 2$ K in steady fields. Inset: field dependencies of $dM/dH$ for $Cr_{0.5}TiSe_2$.

paramagnetic Curie temperature $\Theta_p$ and the maximal value of the magnetic susceptibility at $T = T_N$ can be expressed as [14]

$$T_N = \frac{1}{2}C(w_1 - w_2) \qquad (3)$$

$$\Theta_p = \frac{1}{2}C(w_1 + w_2) \qquad (4)$$

$$\chi_{max} = -1/w_2 \qquad (5)$$

where $w_1 > 0$ and $w_2 < 0$ are the molecular field coefficients associated with the intrasublattice and intersublattice exchange interaction. Moreover, the value of $w_2$ can be estimated using the critical transition field (Fig. 3b) from the expression

$$H_c \approx H_{ex} = |w_2| I_s / 2 \qquad (6)$$

Here $I_s$ is the saturation magnetization. Using the experimental data and expressions (3)–(6) a ratio between the molecular field coefficients $|w_1/w_2|$ is estimated to be about 185. That means that the value of the antiferromagnetic interlayer exchange interaction in $Cr_{0.5}TiSe_2$ is significantly lower than ferromagnetic one within the layer.

As it follows from Table 1 the paramagnetic Curie temperature $\Theta_p$ of the $Cr_xTiSe_2$ compounds changes its sign with increasing Cr-content from negative at $x < 0.33$ to positive at $x = 0.5$. One can suggest that the intercalation of small amounts of Cr-ions causes at first the appearance of the indirect antiferromagnetic exchange interaction between the Cr-ions. Further increase of the Cr-content leads to a large increase of the ferromagnetic exchange between the 3d-electrons of the Cr-ions situated in the same plane. Thus, the observed concentration dependence of $T_p$ in $Cr_xTiSe_2$ can be associated with the different rate of change in exchange interactions within the Cr-layer and between neighbor Cr-layers upon intercalation.

Fig. 5 presents the results of the magnetization measurements on $Cr_xTiSe_2$ in pulsed fields up to 40 T. As it follows from the $dM/dH$ curves the critical transition field is close to the value observed in steady fields. Only the hysteresis loop obtained in pulsed fields seems to be wider than in the steady field measurements. The pulsed field measurements allowed us to determine the spontaneous magnetic moment per Cr-ion ($\mu_S$). Using the extrapolation of the $M(H)$ curve from high fields to $H = 0$ the value $\mu_S$ was obtained to be about 2.3 $\mu_B$. This is essentially less than the effective magnetic moment obtained from the paramagnetic susceptibility measurements (see Table 1). The Rhodes-Wohlfarth ratio [15] $\mu_{eff}/\mu_S$ for this compound is estimated to be about 1.56. This value indicates a significant delocalization of the 3d-electrons of the Cr-ions intercalated between the Se–Ti–Se blocks and shows that $Cr_xTiSe_2$ cannot be well described in a local-moment model. A possible change of the amplitude of the local



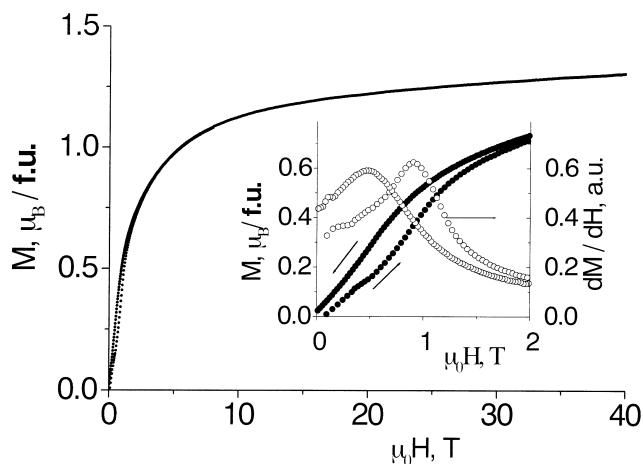Fig. 5. Field dependence of the magnetization measured on $Cr_{0.5}TiSe_2$ at $T = 4.2$ K in pulse field. Inset: initial part of the magnetization curve and field dependence of $dM/dH$.

spin density and a spatial extension of the spin correlation should be taken into account in this case [16].

For the compound with $x = 0.5$ the measurements of the magnetization have also been performed under applied hydrostatic pressure up to 12 kbar. As it was expected the change of the interatomic distance results in a appreciable change of the main magnetic characteristics of the compound. Fig. 6 shows the temperature dependencies of the magnetization measured in a field of 0.1 T under various pressures. As can be seen, increase in pressure decreases the Néel temperature with a rate $dT_N/dp = -0.19$ K/kbar and increases the maximal value of the magnetic susceptibility $\chi_{max}$ at $T = T_N$. Taking into account expressions (3) and (5) the observed pressure dependencies of $T_N$ and $\chi_{max}$ can be ascribed mainly to a weakening of the intersublattice (interlayer) exchange interaction under pressure. It was found, that an applied pressure of $p = 12$ kbar decreases both the $w_1$ and $w_2$ values but with a different rate, $w_1(0)/w_1(12) = 1.06$ and $w_2(0)/w_2(12) = 1.13$. These
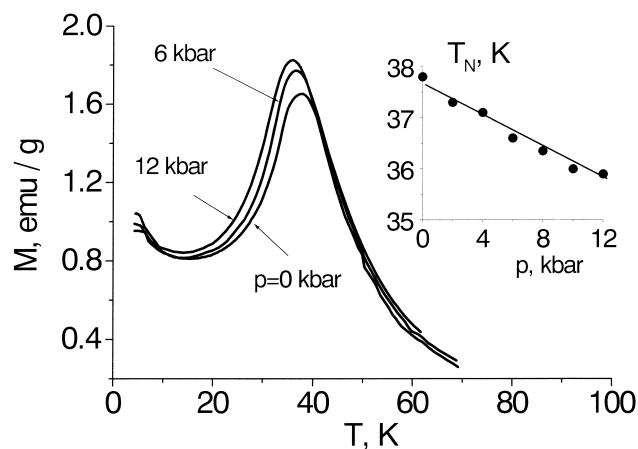


Fig. 6. Temperature dependencies of magnetization of $Cr_{0.5}TiSe_2$ measured in the field 0.1 T at various pressures. Inset: pressure dependence of the Néel temperature.

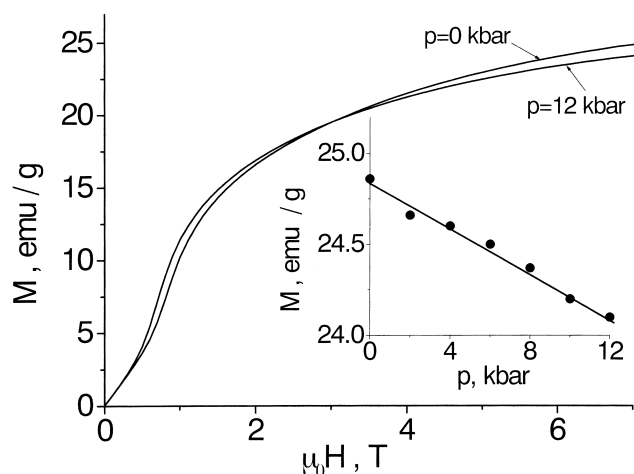Fig. 7. Magnetization curves measured on $Cr_{0.5}TiSe_2$ at $p = 0$ and 12 kbar at 4.2 K. Inset: pressure dependencies of the magnetization of $Cr_{0.5}TiSe_2$ at $\mu_0H = 7$ T.

ratios show that the interlayer interactions are more sensitive to an applied pressure than the intralayer one. In our opinion, such a behavior results from the layer crystal structure of the titanium dichalcogenides. The magnetization curves measured at 4.2 K demonstrate a gradual decrease of the high-field magnetization ($\mu_0H = 7$ T) with increasing pressure (see Fig. 7). The observed decrease of the magnetization (3.2% at 12 kbar) we can attribute to two reasons: (i) reduction of the magnetic moment per Cr-ion caused by the delocalization of the 3d-electrons due to shortening in Cr–Cr distance (see above); and (ii) change of the magnetization process owing to the variation of the magnetocrystalline anisotropy and exchange interactions under applied pressure. Further investigations are needed in order to determine the main origin of the observed pressure dependence of the magnetization.

## 4. Conclusion

The lattice parameters and main magnetic characteristics in steady and pulsed magnetic fields as well as pressure effects on the magnetic properties have been investigated on $TiSe_2$ compounds intercalated by chromium.

Owing to the intercalation the magnetic state of the $Cr_xTiSe_2$ compounds changes dramatically from Pauli paramagnetism at $x = 0$ to cluster-glass behaviour in the concentration range $0.25 \leq x \leq 0.33$ and then to antiferromagnetic order at $x = 0.5$. The paramagnetic Curie temperature changes its sign with increasing Cr content from negative at $x < 0.33$ to positive in $Cr_{0.5}TiSe_2$ due to a change of the ratio between the positive intralayer ($w_1$) and negative interlayer ($w_2$) exchange interaction. A small value of $w_2$ in comparison with $w_1$ results in the presence of a first-order transition from the antiferromagnetic to ferromagnetic state in $Cr_{0.5}TiSe_2$ upon application of a magnetic field. The effective magnetic moment of Cr changes nonmonotonously with increasing $x$. The concentration dependence of $\mu_{eff}$ correlates with the change of the lattice parameter $c$ which reflects the distance between Se–Ti–Se blocks. Such a behavior of $\mu_{eff}$ may be attributed to a change in degree of localization of the Cr 3d-electrons upon intercalation. The spontaneous magnetic moment per Cr-ion in the field-induced ferromagnetic state is found to be significantly lower than the effective magnetic moment. In our opinion, this discrepancy shows that the magnetic properties of $Cr_xTiSe_2$ cannot be well described in a local-moment model and a possible change of the amplitude of the local spin density and a spatial extension of the spin correlation should be taken into account in this case, according to the Moriya theory [16]. Because of the layer structure the interlayer Cr–Cr exchange interaction in $Cr_{0.5}TiSe_2$ is found to be more sensitive to the applied pressure than the intralayer one.

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