

FUNDAMENTAL MAGNETIC PROPERTIES

Titanium Diselenide Intercalated with 3d Metals: Interplay between the Lattice and Magnetic Properties*

N. V. Toporova¹, V. I. Maksimov¹, V. G. Pleschov¹,
A. N. Titov^{1,2}, and N. V. Baranov^{1,2}

¹ Ural State University, Ekaterinburg, 620083 Russia

² Institute of Metal Physics, Ekaterinburg, 620219 Russia

Abstract—The effective magnetic moment per intercalated M atom in $M_x\text{TiSe}_2$ layered compounds has been found to be lower than that expected for free M ions. Because of the presence of a pronounced correlation between the concentration dependences of the lattice parameter c and μ_{eff} , the value of μ_{eff} is suggested to be controlled by the degree of the M 3d–Ti 3d hybridization, which implies an itinerancy of the 3d electrons of inserted atoms. The presence of different magnetic states depending on the type and concentration of M ions in $M_x\text{TiSe}_2$ is attributed to the variations of intralayer and interlayer exchange interactions with intercalation.

1. INTRODUCTION

The titanium dichalcogenide TiX_2 ($X = \text{S}, \text{Se}, \text{Te}$) compounds are of special interest since their hexagonal crystal structure of the CdI_2 type allows one to intercalate various guest ions into the van der Waals gap between triple $X\text{–Ti–}X$ layers [1]. Depending on the nature of the guest M ions and their concentration, the intercalated $M_x\text{TiX}_2$ compounds reveal a rich variety of different physical properties. When M is a 3d-transition metal, the intercalated $M_x\text{TiX}_2$ compounds can be considered as analogues of artificial multilayered structures with magnetic layers consisting of M atoms, which are separated by nonmagnetic layers. The existence of different magnetic states ranging from spin-glasslike behavior up to states with three-dimensional magnetic order was established in $M_x\text{TiS}_2$ and $M_x\text{TiSe}_2$ intercalated by 3d transition metals [2, 3], while the parent TiX_2 ($X = \text{S}, \text{Se}$) compounds are Pauli paramagnets. According to the band structure calculations and photoelectron spectroscopy studies performed for some $M_x\text{TiX}_2$ ($X = \text{S}, \text{Se}$) compounds, the 3d-electron states of M ions are hybridized with TiX_2 bands [4, 5].

The aim of this work is to study how the intercalation of different 3d-metal ions ($M = \text{Cr}, \text{Mn}, \text{Ni}$) influences the crystal structure and magnetic properties of $M_x\text{TiSe}_2$ compounds.

2. EXPERIMENTAL

Polycrystalline $M_x\text{TiSe}_2$ samples ($M = \text{Cr}, \text{Mn}, \text{Ni}$; $0 < x \leq 0.5$) were prepared by the two-stage ampoule synthesis method as was described in [3]. The lattice parameters were measured by X-ray diffraction with an

error of 3×10^{-3} Å. The static magnetization and magnetic susceptibility were measured using a Quantum Design SQUID magnetometer in the temperature interval from 2 to 300 K in a magnetic fields of up to 50 kOe.

3. RESULTS AND DISCUSSION

As is seen from Fig. 1, the $M_x\text{TiSe}_2$ compounds with $M = \text{Cr}$ or Mn exhibit a paramagnetic behavior with a nonlinear monotonic temperature dependence of the inverse susceptibility at temperatures above ~ 40 K. Unlike this, the $\chi^{-1}(T)$ curves for Ni_xTiSe_2 demonstrate a pronounced nonmonotonic character. Nevertheless, it turned out that all these curves may be well described by the expression $\chi(T) = \chi_0(T) + C/(T - \theta_p)$, which includes two temperature-dependent contributions: the first can be ascribed to the temperature-dependent Pauli paramagnetic contribution from the itinerant electrons and the second one is of the Curie–Weiss (CW) type. For the Cr_xTiSe_2 and Mn_xTiSe_2 systems, we succeed in the description of $\chi(T)$ assuming that the Pauli paramagnetic contribution does not depend on the temperature, while for all Ni intercalated compounds an appreciable growth of χ_0 with increasing temperature was revealed after subtraction of the CW contribution. This is clearly seen from the inset in Fig. 1. It should be noted that the pronounced temperature dependence of the magnetic susceptibility was found to exist in many transition d metals which do not possess a magnetic order. Such a temperature dependence of χ_p is associated with the change in the density of electron states $N(E_F)$ at the Fermi level E_F and in its first N' and second N'' derivatives [6]. The $\chi_0(T)$ dependences for Ni_xTiSe_2 are found to follow quite well the expression $\chi_0(T) = \chi_{p0} - PT^2$. The growth of the Pauli paramagnetic contribution with increasing temperature allows us to sug-

* The text was submitted by the authors in English.

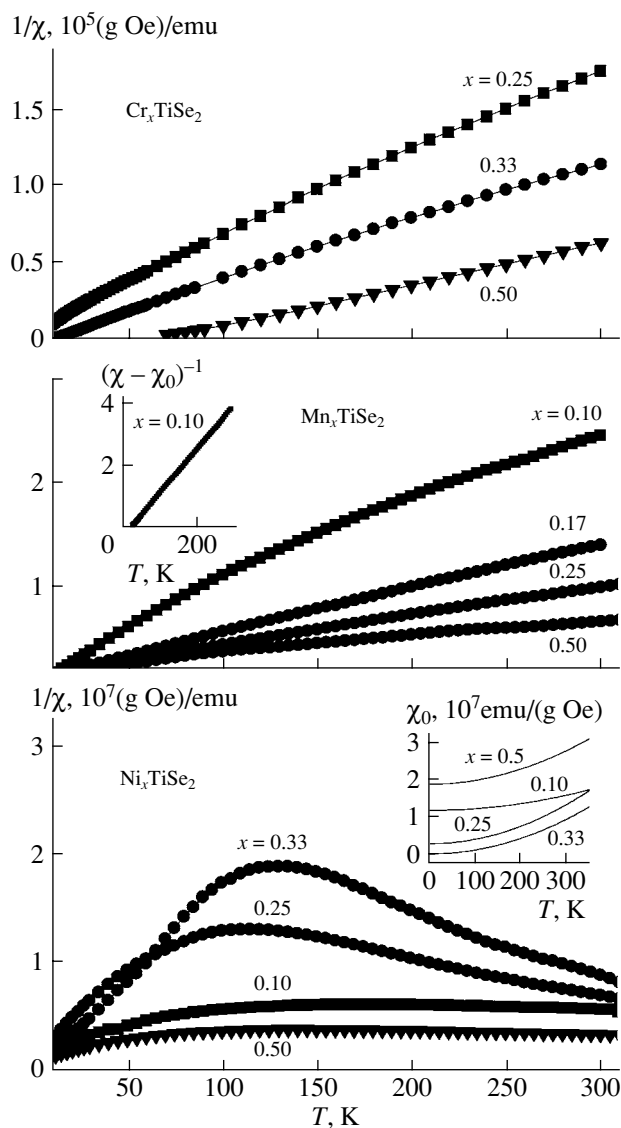


Fig. 1. Temperature dependences of the inverse magnetic susceptibility of $M_x\text{TiSe}_2$ ($M = \text{Cr}, \text{Mn}, \text{Ni}$). Insets: $(\chi - \chi_0)^{-1}$ versus T dependence for $\text{Mn}_{0.1}\text{TiSe}_2$ and $\chi_0(T)$ for Ni_xTiSe_2 .

gest that the Fermi level in Ni_xTiSe_2 is located in the part of the $N(E)$ dependence with a positive curvature ($N'' > 0$).

The CW contribution after being subtracted from the $\chi(T)$ curves allowed us to estimate the effective magnetic moment (μ_{eff}) per M atom for $M_x\text{TiSe}_2$, as well as the paramagnetic Curie temperature (θ_p). Figure 2 displays the $\mu_{\text{eff}}(x)$ dependence together with the concentration dependence of the lattice parameter c of the crystal structure for several $M_x\text{TiSe}_2$ systems. The data for Co_xTiSe_2 were taken from [7]. For all $M_x\text{TiSe}_2$ systems with $M = \text{Cr}, \text{Mn}, \text{Co}$, and Ni , the value of μ_{eff} is found to be significantly lower than that expected for free M ions. Moreover, a pronounced correlation between $\mu_{\text{eff}}(x)$ and $c(x)$ dependences is observed. The intercalation of Cr, Co , and Ni leads to a decrease in the

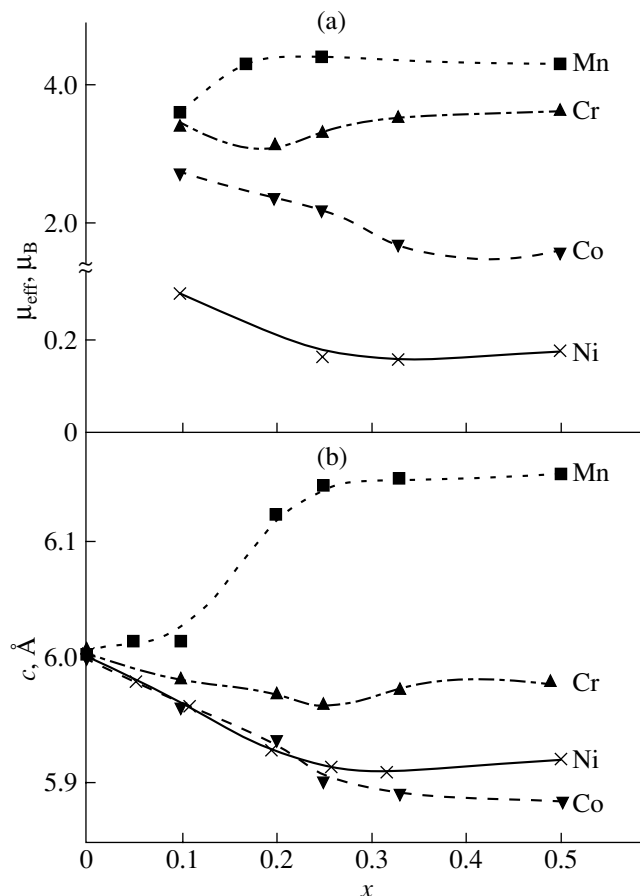


Fig. 2. (a) Concentration dependences of the effective magnetic moment μ_{eff} per M ion and (b) the lattice parameter c for $M_x\text{TiSe}_2$ systems with $M = \text{Cr}, \text{Mn}, \text{Co}, \text{Ni}$.

lattice parameter c with increasing intercalant content up to $x = 0.25$ (see Fig. 2b). The contraction of the lattice observed in the c direction may be associated with the bonding effect arising from the formation of the covalent-like links between $X\text{-Ti-X}$ layers via intercalated M ions. Since for $M = \text{Ni}$ or Co the reduction of the c parameter is more significant than in the case of the Cr intercalation, one can suggest a greater degree of hybridization of Ni and Co $3d$ states with Ti $3d$ and Se $4p$ states in comparison with Cr . As to the Mn_xTiSe_2 system, the increase of the c parameter owing to the Mn intercalation may be indicative of a lower hybridization effect in the case of the half-filled $3d$ -electron band of the intercalated $3d$ metal. The correlation between $\mu_{\text{eff}}(x)$ and $c(x)$ dependences indicates that the value of μ_{eff} in the $M_x\text{TiSe}_2$ compounds is controlled by the degree of hybridization of the M $3d$ and Ti $3d$ states. This finding, together with the low values of μ_{eff} , may be associated with the itinerant character of $3d$ electrons of intercalated M ions.

The magnetic state of the intercalated $M_x\text{TiSe}_2$ compounds at low temperatures depends on the concentration and the type of inserted atoms. Thus, all Ni_xTiSe_2 compounds in the concentration range of $0 \leq x \leq 0.5$

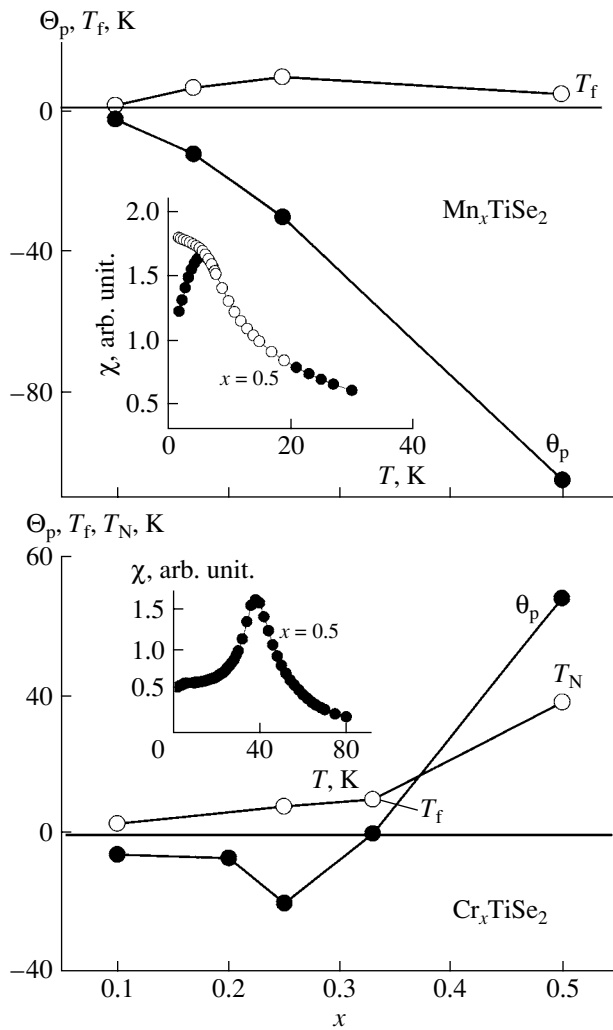


Fig. 3. Concentration dependences of the paramagnetic Curie temperature (θ_p) and magnetic ordering temperatures (T_f , T_N) for the Mn_xTiSe_2 and Cr_xTiSe_2 systems. Insets: temperature dependences of ZFC (full symbols) and FC (open symbols) susceptibility for the compounds with $x = 0.5$.

reveal a paramagnetic behavior above 2 K, while the Mn_xTiSe_2 compounds exhibit a spin-glass or cluster-glass state. Unlike this, within the Cr_xTiSe_2 series, the compounds with high Cr contents ($x \sim 0.5$) have assumingly an antiferromagnetic order. The difference in the magnetic states of the Mn_xTiSe_2 and Cr_xTiSe_2 systems is clearly seen from Figs. 3 and 4. The different magnetic behavior of the M_xTiSe_2 compounds at $x > 0.25$ may results from the competition between exchange interactions within M layers and between M layers. Because of the metallic type of conductivity, one can suppose that the exchange interaction between $3d$ electrons of M atoms located in one plane may be mediated by conduction electrons, i.e., via an s - d interaction [6]. The exchange interaction between M atoms located in neighboring planes may be considered to be of a super-

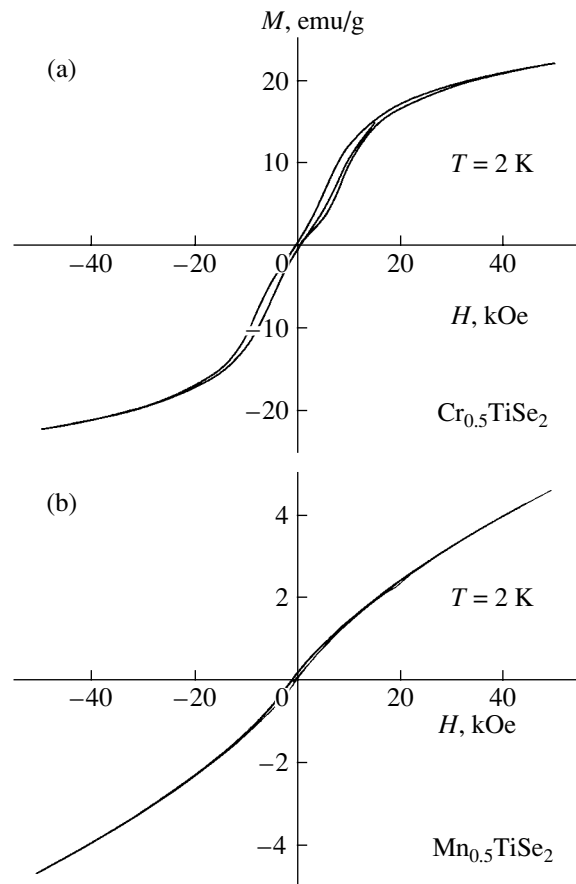


Fig. 4. M versus H dependences for (a) $Cr_{0.5}TiSe_2$ and (b) $Mn_{0.5}TiSe_2$ measured at $T = 2$ K.

exchange type, which occurs presumably through the intervening Se atoms because of the large M - M distances and significantly lower conductivity along the c axis. The interlayer exchange is suggested to be strongly influenced by the deformation of the lattice along the c direction and by the degree of hybridization of M $3d$ electrons with $TiSe_2$ bands.

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