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## Observing of Ti, Cr and Mn 2p-3d resonance in valence band of titanium dichalcogenides

M.V.Yablonskikh<sup>b</sup>, A.S.Shkvarin<sup>a,c</sup>, Yu.M.Yarmoshenko<sup>a</sup>, A.I.Merentsov<sup>a,c</sup>,  
M.V.Kuznetsov<sup>d,c</sup>, A.N.Titov<sup>a,c</sup>

<sup>a</sup>Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620990 Ekaterinburg, Russia

<sup>b</sup>Sincrotrone Trieste SCpA, Basovizza I-34012, Italy

<sup>c</sup>Ural Federal University, 620083, Ekaterinburg, Russia

<sup>d</sup>Institute of Solid State Chemistry, Russian Academy of Sciences – Ural Division, 620990, Ekaterinburg, Russia

shkvarin@ifmlrs.uran.ru

**Abstract.** Ti, Mn, Cr 2p-3d resonant photoemission for compounds with substitution of Ti atoms of host lattice by the Cr atoms  $\text{Cr}_x\text{Ti}_{1-x}\text{Se}_2$  and for compounds with intercalation of Mn and Cr atoms  $\text{Mn}_x\text{TiSe}_2$ ,  $\text{Cr}_x\text{TiTe}_2$  is studied. It is shown that the resonant behaviour depends on the geometry of survey, on 3d metal atoms lattice positions and on the magnitude and localization of atomic magnetic moment.

### 1. Introduction

Titanium dichalcogenides and their derivatives - intercalation compounds  $\text{TM}_x\text{TiX}_2$  (TM-transition metal, X-chalcogen) and substitution compounds  $\text{TM}_x\text{Ti}_{1-x}\text{X}_2$  are natural analogues of artificial layered structures with the possible spin polarization at the Fermi level. The degree of spin polarization is associated with the effective magnetic moment of the intercalated metal [1]. The effective magnetic moment depends on the method of doping - substitution or intercalation. The reason for this dependence is a covalent bond between the TM and the lattice, leading to the hybridization TM3d/Ti3d - states. In the case of substitution this hybridization is absent due to the geometrical reasons, therefore the degree of spin polarization is higher. On the other hand, the degree of spin polarization of the charge carriers, which has important practical value, is determined by the position of TM3d/Ti3d - states in relation to the Fermi level. RPES is able to give information about the position of TM3d/Ti3d - band relative to the Fermi level and the localization of the electrons in the Brillouin zone.

The angular dependence of photoemission, which is detected even at relatively high excitation energy and high crystal symmetry, is often observed in single-crystal samples. This dependence is highly pronounced in the resonant photoemission of two-dimensional titanium dichalcogenides single crystals [2, 3]. The angular dependence is easily observed in the vicinity of high-symmetry points of the Brillouin zone for the 2p edges of Ti, Cr and Mn where the excitation energy is relatively small (from

460 eV to 640 eV, respectively). In the setup used in these experiments a polar angle range is within  $3.5^\circ$ , therefore, the projection of the wave vector  $k_{\parallel}$  is smaller than the size of a typical Brillouin zone in the titanium dichalcogenides ( $1 \text{ \AA}^{-1}$ ). For the investigated samples the change of the polar angle in the highly-symmetric direction  $\Gamma$ -M, K is within the range from the maximal  $\vartheta_{\text{MAX}}=5.5^\circ$  to minimal  $\vartheta_{\text{MIN}}=4^\circ$  for Ti 2p and Mn 2p excitations, correspondingly.

The Ti 3d and chalcogen np electronic states create strong bands symmetrical relative to the  $\Gamma$  point. Additionally, 3d states of intercalated TM create bands symmetrical relative to the M point of the Brillouin zone [4]. The electronic states of the intercalated TM form bands just below the Fermi level which are delocalized and blurred over the Brillouin zone [3].

In this situation, the 2p-3d TM resonance in the valence band spectra is usually diffused over the intense chalcogen contribution, in contrast to the case of 2p-3d Ti for which 3d states are usually localized in the  $\Gamma$  point of the Brillouin zone.

## 2. Experiment.

Single crystals for the X-ray spectra measurements were grown by the gas transport reaction method in evacuated quartz ampoules with iodine as the gas carrier [5]. The single crystals had a shape of thin plates  $\approx 2 \times 3$  mm large and  $\approx 0.05$  mm thick. X-ray resonance photoelectron and absorption spectra were measured using the standard setup of BACH [6] and CIPO [7] beamlines of the ELETTRA synchrotron. All measurements were performed at room temperature. To obtain a fresh surface, the crystals were cleaved in a working chamber at a pressure lower than  $1 \times 10^{-9}$  mbar. The binding energy scale was calibrated through the Au  $4f_{7/2}$  binding energy and through the Fermi edge. The photoelectron analyzer resolution was set to 0.19 eV. The valence band spectra “at resonance” were obtained using excitation energy corresponding to the resonant excitation maximum ( $E_{\text{MAX}}$ ) [8]. At this energy the resonance behavior is observed as additional peaks in the valence band due to the existence of localized electrons under the Fermi level [8]. The spectra labeled as “Before resonance” and “After resonance” was obtained using excitation energies at approximately 10 eV lower and 10 eV higher from  $E_{\text{MAX}}$  respectively.

## 3. Results and discussion.

Resonant photoemission spectra for  $\text{Cr}_{0.2}\text{Ti}_{0.87}\text{Se}_2$  and  $\text{Cr}_{0.78}\text{Ti}_{0.36}\text{Se}_2$  substitution compounds and for  $\text{Mn}_x\text{TiSe}_2$ ,  $\text{Cr}_{0.5}\text{TiTe}_2$  intercalation compounds are investigated.

In intercalated compound  $\text{Mn}_x\text{TiSe}_2$  intense Ti 2p-3d resonance behavior is observed (fig.1.). In intercalated compound  $\text{Cr}_{0.5}\text{TiTe}_2$  a resonance peak is also detected. It is established that in host  $\text{TiTe}_2$  resonant Ti 3d band is caused by the increasing occupancy of Ti 3d band compared with  $\text{TiSe}_2$  and  $\text{TiS}_2$  [9]. In the  $\text{Cr}_{0.5}\text{TiTe}_2$  Ti 2p-3d resonance behavior is almost absent if we consider the contribution to the resonance due to the effect of increasing occupancy of Ti 3d band in titanium ditelluride [9]. When compared with  $\text{Mn}_x\text{TiSe}_2$ , the intensity of resonance peak in  $\text{Cr}_{0.5}\text{TiTe}_2$  is low though the  $\text{Cr}_{0.5}\text{TiTe}_2$  and  $\text{Mn}_x\text{TiSe}_2$  have an identical crystal structure. Likely, this effect indicates that the degree of charge transfer in  $\text{Cr}_{0.5}\text{TiTe}_2$  is lower than that for  $\text{Mn}_{0.2}\text{TiSe}_2$  since a covalent contribution to the chemical bond between Cr and Ti is higher than that between Mn and Ti in  $\text{Mn}_x\text{TiSe}_2$  in which the chemical bond is partially ionic [3]. In  $\text{TiSe}_2$  and substitution compound  $\text{Cr}_x\text{Ti}_{1-x}\text{Se}_2$  the Ti 2p-3d resonance behavior is not observed (fig.1.). It means that the Ti 3d states do not form a narrow localized band just below the Fermi energy [9].

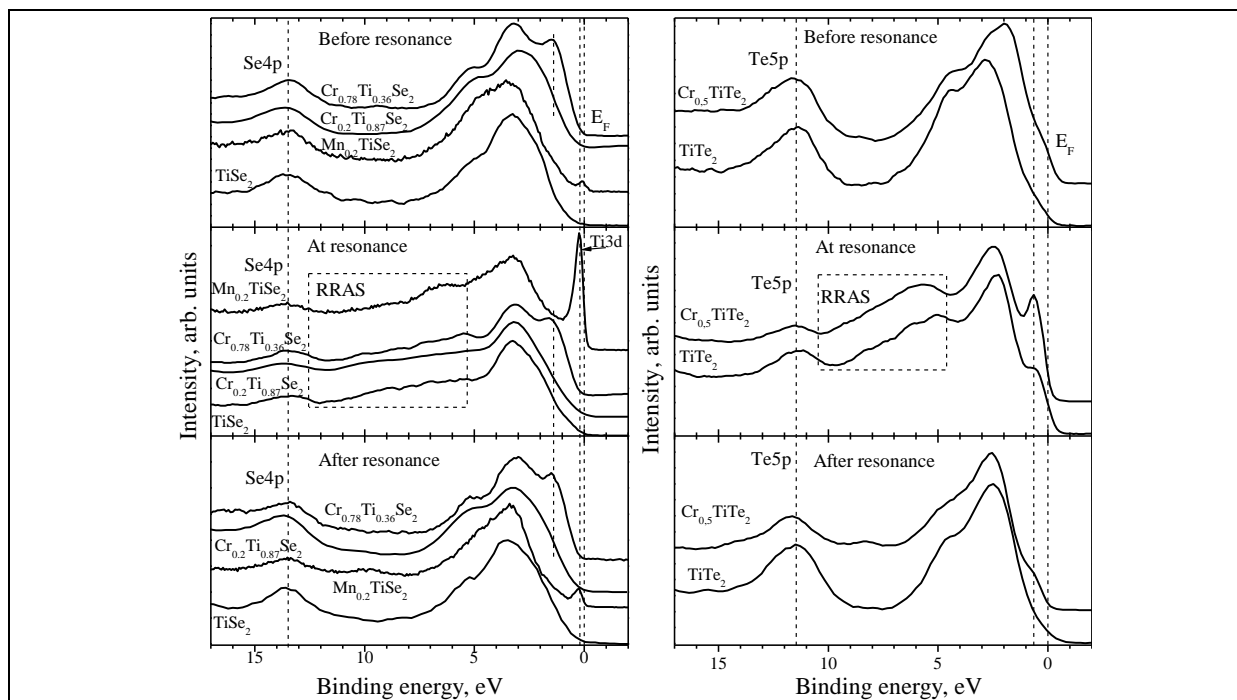


Fig 1. Valence band spectra. Left panel: before, at and after Ti 2p-3d resonance (top to bottom) for intercalated compound  $\text{Mn}_{0.2}\text{TiSe}_2$ , for substitution compounds  $\text{Cr}_{0.2}\text{Ti}_{0.87}\text{Se}_2$ ,  $\text{Cr}_{0.78}\text{Ti}_{0.36}\text{Se}_2$  and pristine  $\text{TiSe}_2$ . Right panel: before, on and after Ti 2p-3d resonance (top to bottom) for intercalated compound  $\text{Cr}_{0.5}\text{TiTe}_2$  and pristine  $\text{TiTe}_2$ .

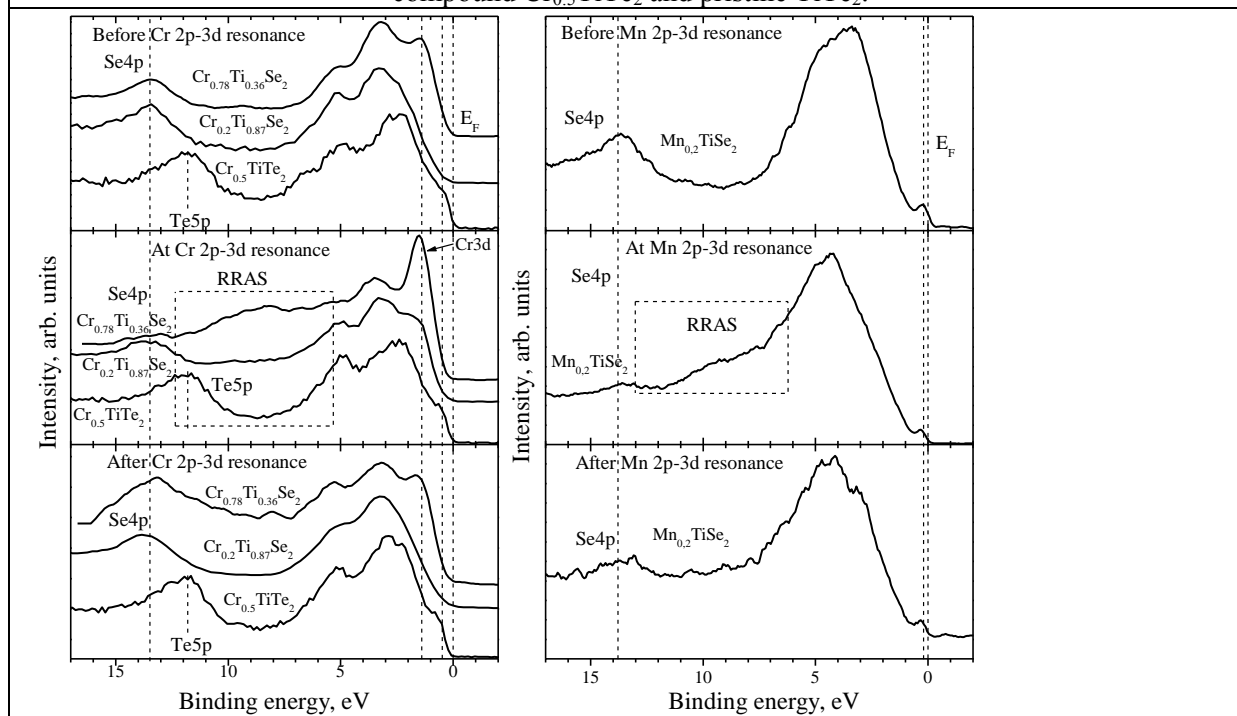


Fig 2. Valence band spectra. Left panel: before, at and after Cr 2p-3d resonance (top to bottom) for substitution compounds  $\text{Cr}_{0.2}\text{Ti}_{0.87}\text{Se}_2$ ,  $\text{Cr}_{0.78}\text{Ti}_{0.36}\text{Se}_2$  and intercalated compound  $\text{Cr}_{0.5}\text{TiTe}_2$ . Right panel: before, at and after Mn 2p-3d resonance (top to bottom) for intercalated compound  $\text{Mn}_{0.2}\text{TiSe}_2$ .

From the spectra in fig.2 follows that for the transition metal 2p-3d resonance behavior is observed for substitution compounds, while for intercalation compounds the resonance behavior is weak and almost invisible. For  $Mn_xTiSe_2$  the presence of a strong Ti resonance and of a weak Mn resonance indicates that the Pauli contribution to the magnetic susceptibility is caused by the Ti 3d electrons, but not by the Mn 3d electrons. For  $Cr_{0.5}TiTe_2$  both chromium and titanium resonances are weak due to the suppression of magnetic moments. This suppression is a result of formed covalent bonds between the Ti and Cr atoms. In  $Cr_xTi_{1-x}Se_2$  resonant behavior is caused by the Cr 3d electrons, which possess a magnetic moment, localized under the Fermi level [2]. The weak resonance in chromium and manganese intercalation compounds has two reasons. The first is the survey geometry, and the second is the delocalization of electron states in the Brillouin zone, which leads to the suppression of the atomic magnetic moment.

The experimental conditions used, where the c axis of the single crystal is coincident with that of the focal axis of the analyzer, are favorable for the observation of photoelectrons corresponding to the states localized in the vicinity of the Brillouin zone  $\Gamma$  point. For the substitution compounds the main contribution is made in the vicinity of the  $\Gamma$  point by both Ti 3d and the Cr 3d states. For the intercalation compounds the main contribution in the vicinity of the  $\Gamma$  point is also made by Ti 3d states in contrast to the 3d states of the intercalated ion of 3d-metals [4]. It allows detecting the resonance Ti 2p-3d behavior in  $Cr_{0.5}TiTe_2$  and  $Mn_{0.2}TiSe_2$ , but the Cr 2p-3d and Mn 2p-3d resonance behavior in these compounds is not observed.

#### 4. Conclusion.

The resonance behavior of 3d states of Cr, Mn and Ti has been studied in the two-dimensional titanium dichalcogenides  $Cr_xTi_{1-x}Se_2$ ,  $Mn_xTiSe_2$  and  $Cr_xTiTe_2$ .

The presence of the resonance behavior depends on the 3d metal atoms crystallographic positions.

When titanium and chromium atoms occupy the regular lattice positions a significant resonant behavior of the Ti 3d and Cr 3d states is detected. A resonant behavior was weak for the 3d states of the intercalated Mn and Cr.

The magnitude of the resonance peak depends on the degree of localization of the magnetic moment on the atom. Resonant photoemission allows one to determine which electrons of which atom contribute to the magnetic properties of the investigated compound. This value is well correlated with the magnitude of effective magnetic moments obtained from the measurement of magnetic susceptibility. The confirmation of the same degree of spin polarization could be obtained from the magnetoresistance experiment.

#### 5. Acknowledgments.

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