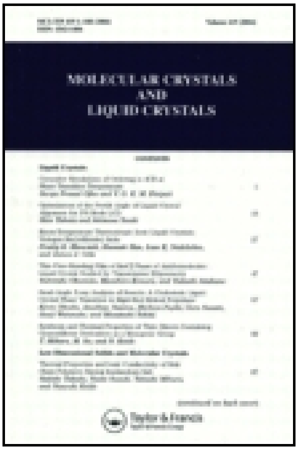

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Charge carriers localization in intercalation compounds based on dichalcogenides of titanium

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Charge carriers localization in intercalation compounds based on dichalcogenides of titanium

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X-ray photoemission study for Fe_xTiTe_2 and investigation of thermodynamic functions for Ag_xTiTe_2 were carried out. It was shown that intercalation of Ag and Fe into $TiTe_2$ leads to a rising of a narrow band at the Fermi level, probably due to appearance of the covalent "bridges" between the host lattice layers.

Keywords: band structure; localized states; thermodynamic function

INTRODUCTION

As it was shown recently, intercalation of Ti, Fe, Co, Ni and Ag into TiX_2 (X= Se, Te) leads to decrease of c_0 unit cell dimension[1-4] in contrary with alkali metals intercalates. For M_xTiX_2 (M=Ti,Fe,Co,Ni) a linear dependence of unit cell constants with $0 < x < 0.25$ was observed[2-4]. This fact allows us to consider an intercalation as a substitution of Ti-[]-Ti centres ([] is the vacancy) by Ti-M-Ti centres with another characteristic size. Silver intercalated materials demonstrate more complicated behaviour due to appearance of two-phase region at low value of x[1,5]. Nevertheless a decrease of c_0 for Ag_xTiTe_2[1] or its very low increase for Ag_xTiSe_2[5] point out on the similarity of all these compounds. This situation may appear if an electron of the intercalated metal transfers into the molecular orbital of the Ti-M-Ti centre rather than into conduction band of the host material.

DC-conductivity data for these materials are in a good accordance with this assumption: upon intercalation all the materials demonstrate a decrease of the conductivity up to $x = x_{th}$ (x_{th} is the percolation threshold) in comparison with host material, and sharp increase for the higher x value[1,4]. For $x < x_{th}$ the conductivity decreases with decreasing of c_0, see Fig.1.

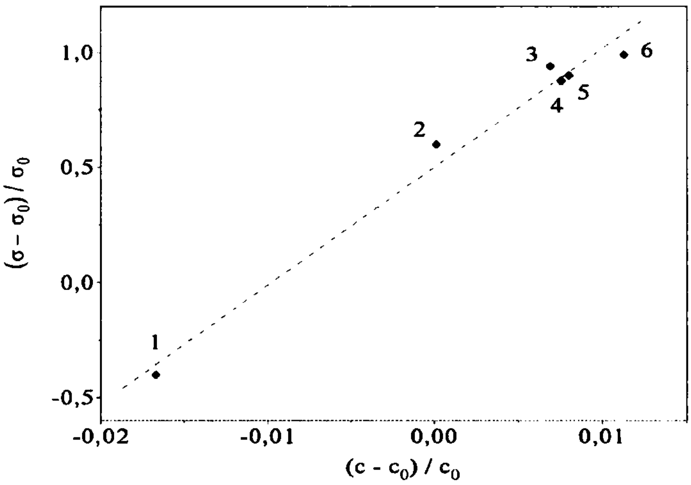

FIGURE 1 Relative change of DC-conductivity as a function of the relative change of the unit cell constant c_0 for 1-$Ag_{0.23}TiS_2$[6], 2 - $Ag_{0.25}TiSe_2$[7], 3 - $Ag_{0.55}TiTe_2$[1], 4 - $Co_{0.25}TiSe_2$[8], 5 - $Fe_{0.25}TiSe_2$[9], 6 - $Fe_{0.25}TiTe_2$[4].

In this work we investigate the changes induced in the band structure of $TiTe_2$ by intercalation of Ag and Fe. These materials are the typical compounds which demonstrate a localization of charge carriers upon intercalation (see Fig.1). Their structure, electric and magnetic properties were recently reported[1,4]. At the first step we performed XPS measurements on Fe_xTiTe_2 and studied the main features of the band structure by relatively direct way.

Then we refined the details of the band structure near Fermi level utilizing thermodynamic experimental data for $Ag_x TiTe_2$.

RESULTS

Single crystals of Fe_xTiTe_2 for X-ray photoemission spectroscopy were grown by the gas transport technique with I_2 as a carrier. XPS patterns were obtained utilizing Perkin-Elmer spectrometer with Al K_α - radiation, the total resolution was set to about 0.35 eV. Thermodynamic functions vs. silver content in Ag_xTiTe_2 were obtained electrochemically using the $Ag/AgI/Ag_xTiTe_2/Pt$ cell in temperature range 420-650 K.

XPS patterns for Fe_xTiTe_2 with x = 0, 0.12, 0.25 and 1.0 are shown in Fig.2. One can see that increasing of x leads to increase of spectral intensity at the Fermi level. The differential spectrum obtained by subtracting the $TiTe_2$ - spectrum from the $Fe_{1.0}TiTe_2$ one shows the appearance of a narrow band of additional states (BAS) near the Fermi level (see lower curve in Fig.2).

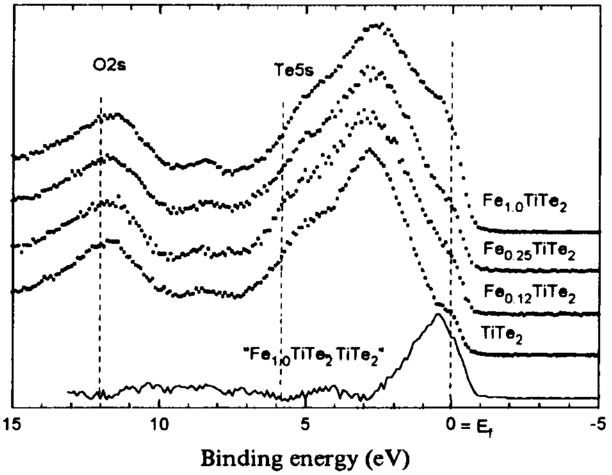

FIGURE 2 XPS data for Fe_xTiTe_2; the lower curve is the difference between $Fe_{1.0}TiTe_2$ and $TiTe_2$ spectra.

Similar behavior was observed for M_xTiS_2 ,M=Fe,Co,Ni[10] , and was related to a mixing of 3d-states of Ti and M. The BAS appearance was earlier proposed for interpretation of the electronic properties of Ag_xTiX_2[1,7,8]. The width of this band is estimated to be 0.01-0.001 eV[6], accuracy provided by spectroscopy is thus unsufficient for its study. For this reason, we studied the band structure near the Fermi level of Ag_xTiTe_2 utilizing the concentration dependence of thermodynamic functions obtained from electrochemical experiment.

The EMF of electrochemical cell[11] may be expressed as $eE = \mu_0 - \mu_{Ag} = \mu_0 - \mu_e - \mu_i$, where μ_0 and μ_{Ag} are the chemical potentials of silver atoms in the metal and in Ag_xTiTe_2, respectively; μ_e and μ_i are the same for electrons and silver ions in Ag_xTiTe_2, e is the electron charge.The calculated values of μ_e as a function of temperature and silver content were determined from the electrical neutrality condition[6]. The density of states (DOS) ρ was considered as the sum of the contributions of the band electrons, with a quadratic dispersion law ρ_1 , and of additional ρ_2 , related to BAS and represented by a Lorentzian curve. We took into account two possible origins of BAS rising:

$$\rho_1 = \rho_0 , \quad \rho_2 = x*N_{Ti}*\Delta/\pi\{(\varepsilon-\varepsilon_d)^2 - \Delta^2\} \qquad (1)$$

$$\rho_1 = [(1-x)^2 + x^2]\,\rho_0 , \quad \rho_2 = 2x*(1-x)*N_{Ti}*\Delta/\pi\{(\varepsilon-\varepsilon_d)^2 - \Delta^2\} \qquad (2)$$

(1) - virtual localized states[12], (2) - mixed states band due to Ti-Ag-Ti centres appearance[1], ρ_0 is the DOS of $TiTe_2$, N_{Ti} is the concentration of Ti atoms, ε_d is the BAS energy level, Δ is the BAS width. Model (1) leads to discrepancy with experimental thermodynamical data for any set of parameters. The results of fitting for model (2) are shown in Fig.3 together with experimental data.

The values of fitting parameters were confirmed independently. The mean mass of a charge carrier for $TiTe_2$[1] and band structure calculations[13] allow to estimate the electron and hole masses and ρ_1 as well. From the activation energy of conductivity for Ag_xTiTe_2[1] and temperature of charge carriers freezing T_f we estimated ε_d and $\Delta \sim kT_f$, k is the Boltzmann constant. These parameters are listed in Table 1 together with values obtained from optimization of concentration dependences of thermodynamic functions.

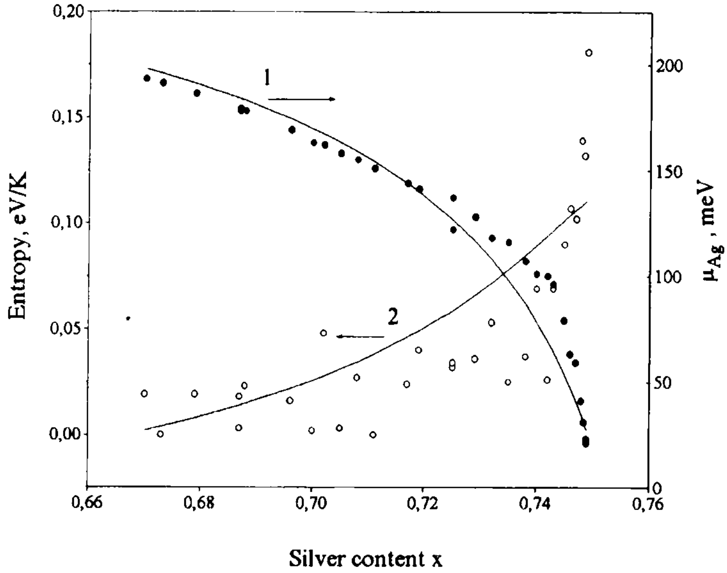

FIGURE 3 Chemical potential (1) and entropy (2) of Ag atom in Ag_xTiTe_2 vs silver content.

TABLE I Parameters of the electronic structure of Ag_xTiTe_2

Parameter	Calculation	Independent estimation
Electron mass Hole mass	$0.1m_0$ $2.9m_0$	$m_e+m_h=3m_0$
ε_d	0.75eV	0.75eV[1]
Δ	0.006eV	0.006-0.012eV[2]
Mean square deviation	0.013 eV	

SUMMARY

From the good accordance between the results of X-ray photoemission spectroscopy and thermodynamic functions behavior for M_xTiTe_2 (M= Ag, Fe) we conclude that M ions intercalation leads to appearance of a narrow additional states band (BAS) at the Fermi level. From the thermodynamic data analysis we conclude that the covalent "bridges" Ti-M-Ti compress the interlayer distances and lead to BAS appearance.

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