

SEMICONDUCTORS  
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## Phase Diagrams of Intercalation Materials with Polaron-Type Carrier Localization

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**Abstract**—A study is reported on the effect of the position of the polaron band relative to the Fermi level on the phase diagram. The validity of the phase stability criterion obtained is tested in the specific example of silver-intercalated  $\text{TiSe}_2$  and  $\text{TiTe}_2$ . © 2000 MAIK “Nauka/Interperiodica”.

Phase diagrams of intercalation compounds based on layered titanium dichalcogenides with a common formula  $M_x\text{TiX}_2$  ( $M = \text{Ag, Ti, Cr, Fe, Co, Ni}$ ;  $X = \text{Se, Te}$ ) can be divided in two groups. The compounds with  $M = \text{Ti, Cr, Fe, Co, and Ni}$  belong to the first group. For low intercalant concentrations, these materials exhibit the presence of disordered solid-solution regions [1–3]. The second group comprises materials with  $M = \text{Ag}$ , where insertion of arbitrarily small amounts of an intercalant brings about decomposition into a phase enriched in silver and the starting material [4, 5]. It was shown [6, 7] that intercalation of titanium dichalcogenides with the above metals results in carrier localization in the form of small-radius polarons, which can provide a dominant contribution to thermodynamic functions. Viewed from this standpoint, the materials of the first and second groups differ in the position of the polaron band relative to the Fermi level of the starting material. In materials of the first group, the polaron states lie below the Fermi level and can be probed with X-ray photoelectron spectroscopy [6]. In materials belonging to the second group, the kinetic properties [8, 9] and the behavior of thermodynamic functions [10] can be interpreted only by assuming that the polaron band is located above the Fermi level of the starting material. The difference between the phase diagrams of these two groups of materials should be obviously associated with different concentration dependences of the thermodynamic functions, which is related to differing positions of the polaron band relative to the Fermi level of the material to be intercalated.

Because the main distinctive feature of the polaron-type carrier localization consists in the density-of-states being temperature dependent, it appears reasonable to study the effect of the Fermi level position on its change induced by the polaron band collapse (the polaron shift).

To do this, we performed simulation of the concentration dependences of the chemical potential, which were derived from the charge neutrality condition similar to the way this was done in [11]

$$\int_{-\infty}^{\infty} \rho(\epsilon) f(\epsilon) d\epsilon = p_v + N, \quad (1)$$

where  $p_v$  is the hole concentration and  $N$  is the intercalant concentration. The density of states in the conduction band was written as a sum of the original and impurity densities of states

$$\rho = \rho_1 + \rho_2, \quad (2)$$

$$\rho_1 = (1 - g(x))\rho_0(\epsilon), \quad (3)$$

$$\rho_2 = g(x)N\Delta/\{(\epsilon - E_p)^2 + \Delta^2\},$$

where  $\rho_0(\epsilon) \sim \epsilon^{1/2}$  is the conventional band density of states for a quadratic dispersion law (i.e., the density of states in the starting material),  $g(x)$  is a function relating the concentration of the localization centers to that of the intercalant, depending on the extent of ordering of the latter,  $\Delta$  is the width of the impurity band, and  $E_p$  is

Electronic structure parameters derived by fitting the edge of the homogeneity region for  $\text{Ag}_x\text{TiSe}_2$  and  $\text{Ag}_x\text{TiTe}_2$  together with literature data

Parameter	$\text{Ag}_x\text{TiSe}_2$		$\text{Ag}_x\text{TiTe}_2$		
Electron effective mass, $m_e$	$0.5m_0$	$1.7m_0$ [12]	$0.59m_0$	$0.1m_0$ [10]	$m_e + m_h = 3$ [9]
Hole effective mass, $m_h$	$1.0m_0$	$0.2m_0$ [12]	$2.4m_0$	$2.9m_0$ [10]	$m_e + m_h = 3$ [9]
Polaron band position $E_p$ , eV	0.28		0.73	0.75 [10]	

its position. Because structural studies of Ag–TiSe<sub>2</sub> and Ag–TiTe<sub>2</sub> do not reveal intercalant ordering along the *c* axis, the polaron center concentration can be written in the gas approximation (as in [9]), and the *g(x)* function can be presented in the form  $g(x) = 2x(1 - x)$ , where *x* is the intercalant concentration.

The concentration dependences of the chemical potential were calculated in this way for the cases of a wide impurity band (2 eV) and a narrow one (0.001 eV) for the temperatures below (100 K) and above (550 K) its collapse, respectively (Fig. 1). All the other parameters were fixed.

The numerical values of the effective electron and hole masses and the character of disorder on the intercalant sublattice were chosen close to the realistic ones for TiSe<sub>2</sub> [12] and TiTe<sub>2</sub> [9, 13].

The concentration dependence of the polaron shift obtained by subtraction of these two dependences (see Fig. 2) reveals the presence of a maximum and acquires negative values for low carrier concentrations. By definition,  $\Delta\mu/\Delta T$  is the entropy of the electron subsystem, which, taking into account the constancy of the vibrational contribution [14] and assuming a constant configurational contribution (i.e., the absence of an order-disorder transition), can be equated to the total entropy of the material within the temperature interval including the polaron band collapse. Obviously enough, only the concentration region for which  $\Delta\mu/\Delta T > 0$  has a physical significance. Therefore, the condition  $\Delta\mu/\Delta T = 0$  (i.e.,  $\Delta\mu = 0$ ) at the boundary of the single-phase region ( $x = 0.22$  in Ag–TiSe<sub>2</sub> [4] and  $x = 0.55$  in Ag–TiTe<sub>2</sub> [5]) permits one to determine the parameters of the carrier energy spectrum in these systems. The values of the parameters obtained by this method are listed in the table together with literature data.

As is seen from the table, for Ag<sub>*x*</sub>TiTe<sub>2</sub>, one observes a satisfactory agreement between the obtained value of *E<sub>p</sub>* and the data quoted in [10]. The discrepancies between the carrier effective masses for Ag<sub>*x*</sub>TiTe<sub>2</sub> obtained in this work and in [10] are probably associated with the fact that the authors of [10] neglected the concentration dependence of the vibrational contribution, which is apparently wrong, because a change in the impurity concentration entails a change in the number of phonon modes. By contrast, the comparison with experiment in this work was made at one point (at the boundary of the single-phase region), where the vibrational contribution at a fixed concentration is constant [14]. The discrepancy between the parameters obtained and the literature data for TiSe<sub>2</sub> can be caused by the fact that the effective carrier masses in [12] were determined for the low-temperature charge-density-wave state (*T* ~ 200 K), whereas the present study was carried out above the decomposition temperature of this state (*T* ~ 500 K).

Thus, the dependence of the polaron shift on the mutual position of  $\mu$  and *E<sub>p</sub>*, presented graphically in

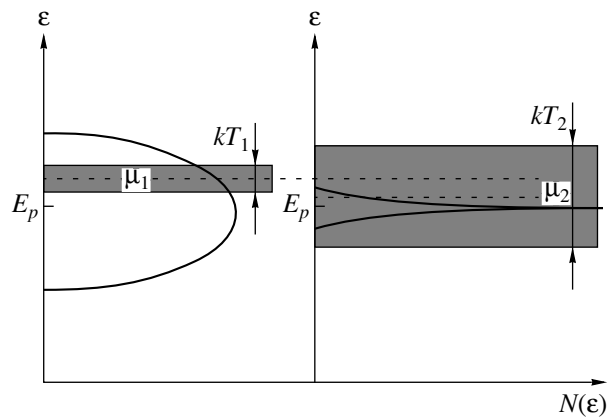


Fig. 1. Schematic illustration of the polaron band collapse with increasing temperature (*T*<sub>2</sub> > *T*<sub>1</sub>).

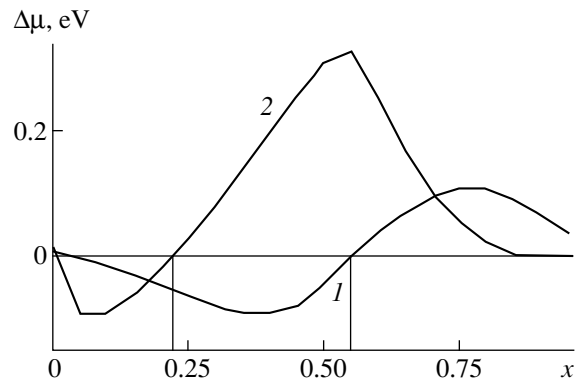


Fig. 2. Variation of the chemical potential (polaron shift) for Ag<sub>*x*</sub>TiSe<sub>2</sub> (curve 1) and Ag<sub>*x*</sub>TiTe<sub>2</sub> (curve 2) with concentration. Vertical lines identify the boundaries of single-phase regions.

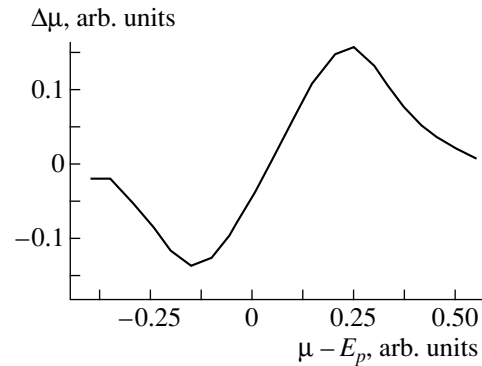


Fig. 3. Schematic illustration of the dependence of the polaron shift on the position of the polaron band (*E<sub>p</sub>*) relative to the chemical potential ( $\mu$ ).

Fig. 3, determines the stability criterion of phases with the polaron type of carrier localization. For compounds intercalated by transition metals  $\mu > E_p$ , i.e., the compound is stable for any intercalant concentration. If,

however,  $\mu < E_p$  (as is the case with  $\text{Ag}_x\text{TiSe}_2$ ), the compound is stable starting from the concentrations corresponding to  $\mu - E_p = 0$ .

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