
SEMICONDUCTORS
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Determination of the Polaron Shift in Titanium Diselenide-Based Intercalation Compounds

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Abstract—A study is reported of the dependence of the TiSe_2 lattice constants on the concentration of an intercalated metal in various valence states and external pressure. The strain energy and the polaron shift created in the intercalation of TiSe_2 with metals in various valence states have been determined. The position of the polaron band is shown to decrease linearly with the increasing intercalant ionization potential. © 2000 MAIK “Nauka/Interperiodica”.

In many cases, the intercalation of layered titanium dichalcogenides results in carrier localization in the form of small-radius polarons [1]. The effect of this factor on the phase diagram reduces to limiting the region of single-phase stability to meeting the condition [2] ($E_d - \mu) < 0$, where E_d is the energy corresponding to the center of the polaron band and μ is the electron chemical potential (the Fermi level). In titanium dichalcogenides intercalated with silver, the single-phase state forms only when the concentration of the donor impurity reaches a certain critical level at which the polaron-band center drops below the Fermi level. By contrast, when the intercalants are metals with a higher valence, the single-phase state is stable at arbitrarily low intercalant concentrations. This implies that the polaron band in such materials lies below the Fermi level of the starting compound. This is corroborated by x-ray spectroscopy data available for some of the above compounds [3]. It can thus be suggested that the position of the polaron band is determined by the Coulomb interaction of conduction electrons with the ionized impurity. Therefore, it appears reasonable to choose as a parameter determining the polaron band position the ionization potential of the impurity in the experimentally established valence state for the same starting host matrix. In this case, the polaron shift can be estimated from the experimentally determined lattice distortions induced by the polaron formation [4], provided the elastic constants are known.

The TiSe_2 structure belongs to the CdI_2 type, the space group is $P3m1$, and the unit cell contains one formula unit. Titanium atoms make up plane hexagonal networks and occupy one half of the octahedral voids in the hcp array formed by selenium atoms. The intercalated atoms are located in free octahedral voids lying midway between the two titanium atoms along the nor-

mal to the titanium network plane. Intercalation of transition metals into titanium diselenide intercalant concentrations that [5, 6] are not too high corresponding to the region of a dilute solid solution, where impurity atoms can be considered as isolated, results in the unit cell parameters becoming linearly dependent on the impurity concentration, without any change in the space group. Such a dependence may be treated as a result of substitution of $\text{Ti}-M-\text{Ti}$ (where M stands for the intercalant) for $\text{Ti}-V-\text{Ti}$ (V is the vacancy) centers, which have different characteristic dimensions. The deviation from linearity observed for $x > 0.25$, where x is the intercalant concentration, is due to the strain fields in the host matrix around the impurity-containing centers reaching the percolation threshold [7]. Thus, the size of a center strained by intercalation can be derived from the concentration dependence of the lattice constants within the intercalant content range $0 < x < 0.25$.

This work deals with the determination of the polaron shift in titanium diselenide intercalated by different metals. Using the same starting material permits one to reckon the position of the polaron band from its Fermi level. To find the energy associated with the intercalation-induced strain, we invoked the pressure dependence of the lattice constants obtained by x-ray diffraction.

The samples for the x-ray studies were prepared by the standard technique of elemental synthesis in an ampoule. The details of preparation and characterization of the material can be found elsewhere [8]. After the synthesis and the characterization, the $M_x\text{TiSe}_2$ materials (here M stands for Cr, Fe, Co) were quenched from 850°C to prevent intercalant ordering and to eliminate a possible effect of this factor on the lattice constants. The x-ray diffraction measurements were car-

ried out on a DRON-3M setup with $\text{CuK}\alpha$ radiation. The lattice parameters were calculated with an error $\Delta a_0 = 0.001 \text{ \AA}$ and $\Delta c_0 = 0.002 \text{ \AA}$. The results are displayed in Fig. 1 together with the available literature data. The x-ray diffraction study of the compressibility of TiSe_2 was performed in a quasi-hydrostatic regime in a diamond-anvil high-pressure chamber (the diameter of the working surface 0.6 mm) capable of delivering pressures of up to 20 GPa [10]. The diffractometer used was

RIGACU R200 ($\text{MoK}\alpha$, graphite monochromator, rotating-anode tube). Ruby and NaCl crystals were employed for the calibration of the pressures applied to a sample. The pressure was determined to within $\pm 0.2 \text{ GPa}$, and the lattice constants, to within $\Delta a_0 = 0.005 \text{ \AA}$ and $\Delta c_0 = 0.01 \text{ \AA}$.

The good agreement of our with literature data (Fig. 1) on the Co_xTiSe_2 and Fe_xTiSe_2 systems apparently implies that the impurity ordering affects the lattice constant only insignificantly. The characteristic dimensions of the centers calculated from the data in Fig. 1 for the intercalant concentrations $x < 0.25$ are listed in the table.

The pressure dependences of the TiSe_2 lattice parameters are displayed in Fig. 2. The compressibilities in the a_0 and c_0 directions derived from these data are 2.51×10^{-12} and $1.53 \times 10^{-11} \text{ Pa}^{-1}$, respectively. These values are close to those calculated for the isostructural TiS_2 , for which the corresponding quantities calculated from the data of [12] are, respectively, 4.07×10^{-12} and $1.46 \times 10^{-11} \text{ Pa}^{-1}$ in the semiconducting pressure region, and 3.32×10^{-12} and $0.632 \times 10^{-11} \text{ Pa}^{-1}$ in the semimetallic region. A certain growth of the compressibility in the direction normal to the basal plane in TiSe_2 compared to TiS_2 can apparently be attributed to the increased width of the van der Waals gap of the first material.

The lattice strain energy induced by polaron formation is $\gamma_c(\Delta c_0)^2$, where Δc_0 is the strain created in the formation of the Ti-M-Ti center, and γ_c is the inverse compressibility in the c_0 direction. The strain energy (polaron shift) calculated in this way for the case of various metals intercalated into TiSe_2 is displayed in Fig. 3 as a function of the impurity ionization potential in the experimentally established (for Ag, Cr, Fe, Co, Ti) or the most probable (for Ni) valence state.

Intercalation with alkali metals, which do not form covalent bonds with the host lattice, results in an

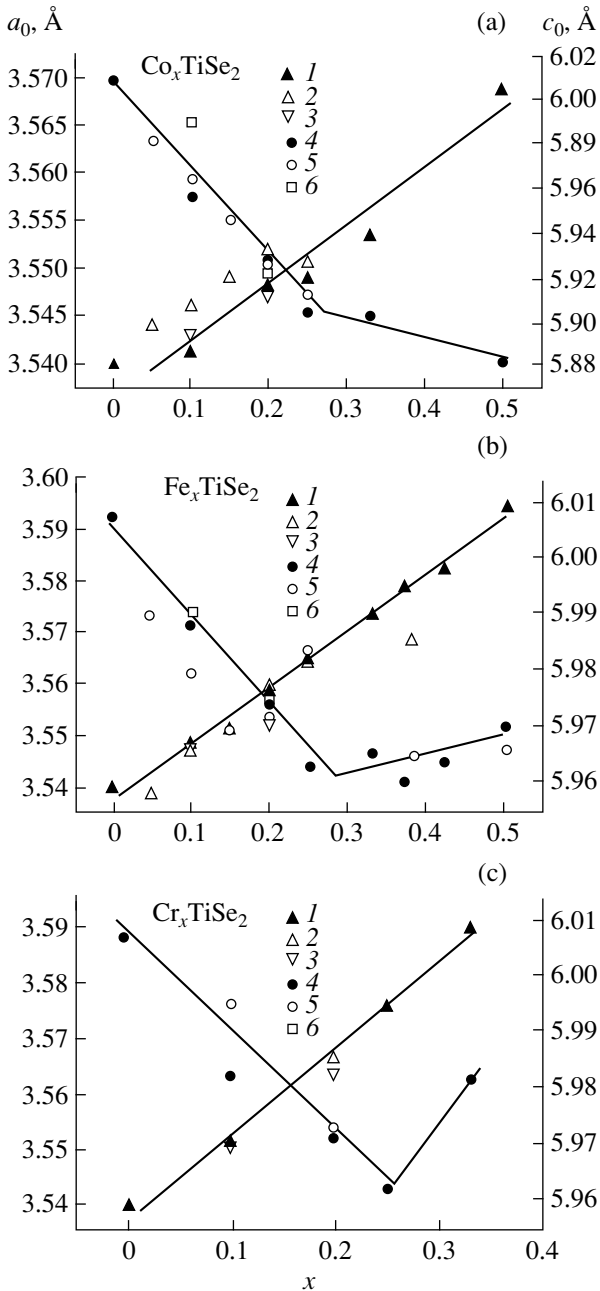


Fig. 1. Concentration dependences of the crystallographic parameters a_0 (1–3) and c_0 (4–6) for (a) Co_xTiSe_2 , (b) Fe_xTiSe_2 , and (c) Cr_xTiSe_2 . 1 and 4 are the data of this work, 2 and 5 are the data from [6] and 3 and 6 are the data from [9].

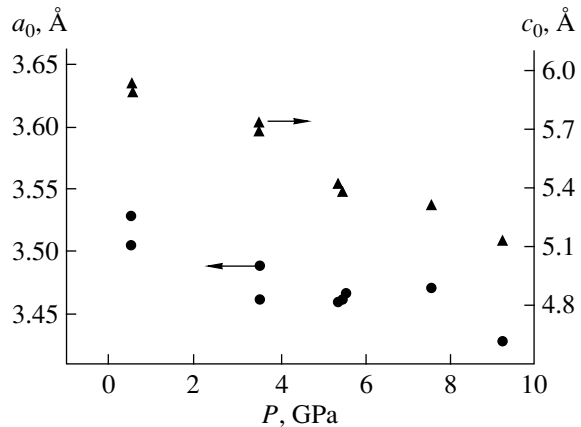


Fig. 2. Pressure dependences of the TiSe_2 lattice constants.

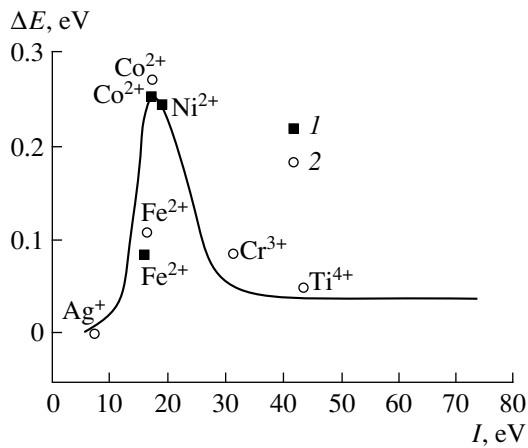


Fig. 3. Dependence of the polaron shift on the intercalant ionization potential. 1 is the data calculated from [6], 2 is this work, and solid line is the result of optimization by model [2].

increase in the lattice constant c_0 through the increase in the interlayer separation. It was shown [13] that an increase in c_0 is directly proportional to the ionic radius of the intercalant ion for the given host lattice. This suggests the conclusion that this effect is associated with the interaction of the filled shells of the intercalant atom and the host lattice. Obviously, in the case of intercalation with transition metals and silver, this effect will be masked by the observed decrease in c_0 . While considering this factor presently appears impossible due to the lack of data on the effect of covalent bonding on the intercalant coordination by chalcogen atoms, it is clear that suppressing an increase in c_0 should bring about an increase in the real work expended in straining the lattice. Thus, the numerical values of the polaron shift in $M_x\text{TiSe}_2$ obtained in this work should be considered as a lower estimate.

One can readily see that the dependence of the polaron shift on the impurity ionization potential

Characteristic dimensions of the Ti–M–Ti cluster calculated from the linear portion ($x < 0.25$, where x is the intercalant content) of the concentration dependence of the lattice parameters

Clusters	c_0	a_0
Ti–V–Ti (TiS_2)	6.008	3.540
Ti–Ag–Ti (Ag_xTiSe_2) [11]	6.008	3.540
Ti–Ti–Ti (Ti_xTiSe_2) [5]	5.953	3.552
Ti–Cr–Ti (Cr_xTiSe_2)	5.875	3.598
Ti–Fe–Ti (Fe_xTiSe_2) [6]	5.876	3.663
Ti–Fe–Ti (Fe_xTiSe_2)	5.837	3.638
Ti–Ni–Ti (Ni_xTiSe_2) [6]	5.611	3.584
Ti–Co–Ti (Co_xTiSe_2) [6]	5.583	3.594
Ti–Co–Ti (Co_xTiSe_2)	5.608	3.579

(Fig. 3) coincides in shape with the one calculated in [2]. This provides support for the starting assumption that it is the Coulomb interaction of conduction electrons with the intercalant that determines the position of the polaron band relative to the Fermi level of the starting material and, hence, the magnitude of the polaron shift. Optimization of the obtained dependence of the polaron shift on the ionization potential I with respect to the theoretical relation [2] shows that a fit can be reached if one replaces I with I/α , where $\alpha = 33$ is the proportionality coefficient which has the meaning of the ionization-potential screening constant (the static dielectric permittivity).

This model can be tested using information on the Mn_xTiSe_2 compound that has not been studied to date. These data will be obtained by our group and published in the near future.

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