
LATTICE DYNAMICS
AND PHASE TRANSITIONS

Stability of the Polaron Form of Charge Carrier Localization in Misfit Titanium Disulfide Compounds

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Abstract—The behavior of the thermodynamic functions of the silver-intercalated isostructural misfit compounds $\text{Ag}_x\text{PbTi}_2\text{S}_5$ and $\text{Ag}_x\text{GdTi}_2\text{S}_5$ is studied. The region of instability of the homogeneous state, which is typical of materials with less than half-filled polaron band, is revealed in the phase diagram of $\text{Ag}_x\text{PbTi}_2\text{S}_5$. It is shown that the substitution of GdS for PbS gives rise to charge transfer to the TiS_2 sublattice, which fills the polaron band above the critical level and suppresses this instability. The behavior of the entropy of silver in both materials fits well the proposed polaron band filling model. It is demonstrated that the peak of the entropy near the boundary of stability of the homogeneous state is universal in character for materials with polaron-type carriers and that it can be associated with a strong variation in the density of states at the Fermi level upon polaron band filling.

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1. INTRODUCTION

Intercalation of titanium dichalcogenides with transition metals and silver gives rise to formation of covalent centers denoted for brevity by Ti–Int–Ti (Int stands here for the intercalant) [1]. Because such centers act simultaneously as traps for free electrons and lattice strain centers, the electrons localized at these centers may be considered as polarons. The electron binding energy with the centers is strongly temperature dependent because of the localized states being of the hybrid nature, so that the temperature dependence of the degree of localization fits qualitatively the one predicted theoretically for the polarons. The closeness of the energy of polaron states to the Fermi level makes it subject to displacement when the degree of polaron localization changes. This brings about a nontrivial temperature dependence of the thermodynamic stability of phases in such materials. The reason for this dependence can be readily seen from Fig. 1. If the polaron band is filled to less than one half, its collapse gives rise to an increase in the Fermi level, which is equivalent to a negative entropy of the process (Fig. 1a). Therefore, a material with a less than half-filled polaron band breaks up as the latter collapses into a phase in which this band is filled to no less than one half, thus satisfying the stability condition for it, and a phase depleted in electrons in which no polarons are present (Fig. 1b). Experiment reveals separation into a phase enriched in the intercalant and another phase that does not contain it [2–4]. The region of the mixture of these

phases is limited by the intercalant concentration which would provide filling of the impurity band to no less than one half throughout the sample. Hence, by varying properly the Fermi level position in the intercalated material, one can cross over from homogeneous state to the regime where this state is unstable, and vice versa.

This potential is inherent in the so-called intergrowth materials whose lattice, in the particular case of interest to us here, consists of alternating layers of TiS_2 and monosulfide of a rare-earth or non-transition metal (*MS*) [5]. The lattice constants of TiS_2 and *MS* fragments being different, the combined lattice turns out incommensurate (whence the term “misfit”) in one or both directions of the basal plane, depending on the actual relation between the parameters. Of most interest are materials with the TiS_2 and *MS* layers stacked in the sequence $\text{TiS}_2\text{--TiS}_2\text{--MS--TiS}_2\text{--TiS}_2$, which are denoted by the formula MTi_2S_5 and whose structure is shown in Fig. 2. We readily see that half of the gaps between the TiS_2 layers in such a material remain unfilled and, thus, are fit for intercalation by various metals. It was shown [6] that only these gaps are suitable for intercalation, at any rate in the case of silver incorporation.

The insertion of silver into TiS_2 does not entail polaron formation. This was shown to be the result of low lattice polarizability, as well as of the comparatively narrow interlayer gap [7]. Adding TiS_2 structural fragments containing a heavy metal should obviously increase the polarizability of the lattice and, hence,

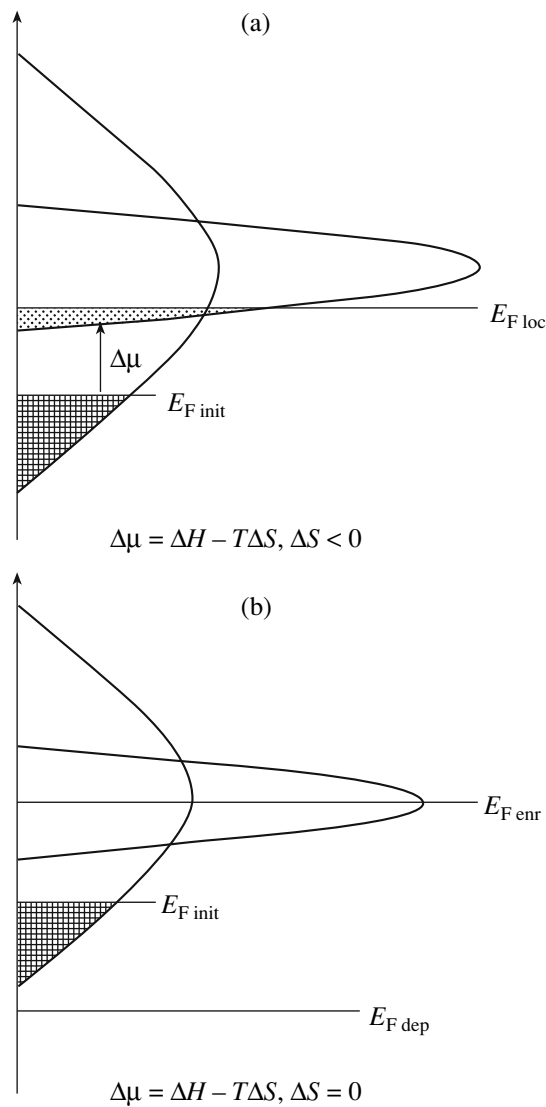


Fig. 1. (a) Schematic diagram of the Fermi level displacement initiated by collapse of the polaron band filled to less than one half and (b) separation of the material into phases with different electron concentrations. The graph shows the Fermi level position in the starting material ($E_{F\text{init}}$), the material with localized polarons ($E_{F\text{loc}}$), and the phase enriched ($E_{F\text{enr}}$) and depleted ($E_{F\text{dep}}$) in electrons.

reduce the energy required to deform it, thus opening the way to formation of covalent centers. In the case of PbTi_2S_5 , the high polarizability manifests itself in that its lattice is easier to deform. This is indicated, for instance, by its mechanical properties [8]. The higher softness of the lattice facilitates formation of a distortion and subsequent capture by it of a conduction electron. This conclusion is prompted, in particular, by the characteristic temperature dependence of the conductivity of silver-intercalated PbTi_2S_5 [6], which suggests polaron formation. The polarons may in this case be the electrons localized at covalent centers through involvement of silver atoms. This assertion correlates well also

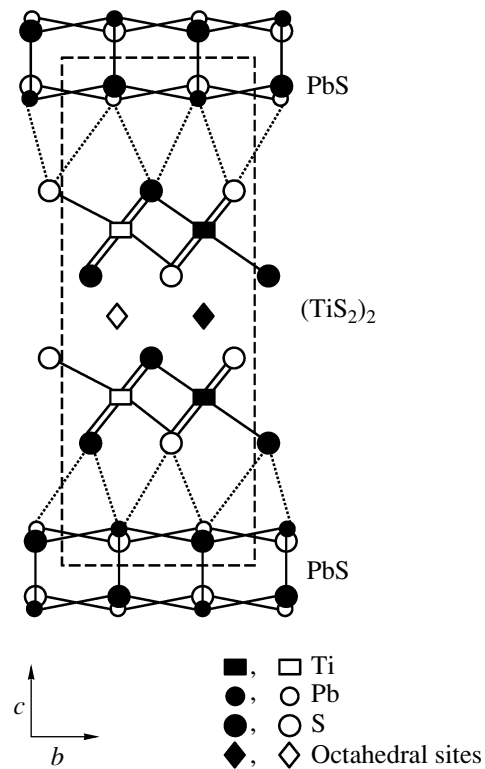


Fig. 2. Structure of the $(\text{PbS})_{0.59}\text{TiS}_2$ compound denoted in the text as PbTi_2S_5 in the projection onto the [100] direction [5]. The unit cell is bounded by the dashed line. Closed symbols correspond to the position of atoms in the plane of the figure, and open symbols correspond to those below the plane of the figure. The GdTi_2S_5 compound has a similar structure.

with the deformation pattern of the lattice layers of the TiS_2 fragment, whose size along the normal to the basal plane decreases after intercalation. This behavior is characteristic of the formation of covalent centers described above [9]. Because rare-earth metals are close in mass to such metals as Pb and Sn, adding a structural fragment with such a metal likewise should bring about lattice softening.

By using for MS fragments compounds with different donor activities, one can produce the desired initial conduction electron concentration without changing at the same time the structure of the intercalated gap. As pointed out in a review paper [5], compounds with PbS as MS fragments do not practically affect the carrier concentration in a TiS_2 fragment. This is suggested by the characteristic behavior with temperature of the electrical resistivity of PbTi_2S_5 and TiS_2 , which in both cases scales as T^2 [10, 11]. One measured also the pressure dependence of the PbTi_2S_5 conductivity within the basal plane of single crystals [12]. The dependence thus obtained revealed two characteristic features. One of them, at a pressure of ~ 2 GPa, consists in a stepwise decrease of the electrical resistivity. This pressure can be identified with the structural phase transition in the

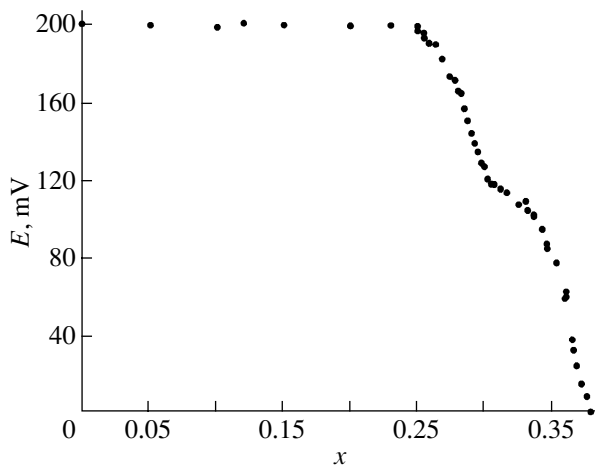


Fig. 3. Specific free energy of formation of $\text{Ag}_x(\text{PbS})_{0.59}\text{TiS}_2$ as a function of the silver content x .

PbS compound. The second anomaly is seen in a smooth falloff of the electrical resistivity within the pressure interval of 4–6 GPa. TiS_2 as a separate phase features the same behavior [13]. It was shown [14] that this transition, rather than being associated with structural changes, is mediated by the pressure dependence of the gap separating the valence from the conduction band. Thus, the pressure dependence of the resistivity of PbTi_2S_5 leads one to a conclusion that the state of structural fragments of a misfit compound does not differ, within the instrumental accuracy, from that of the constituent phases. The carrier concentration derived from Hall coefficient measurements [11] is also the same for PbTi_2S_5 and TiS_2 .

The situation observed when monosulfides of rare-earth metals are used as *MS* fragments is radically different. A number of studies reviewed in [5] report a noticeable charge transport from *MS* to TiS_2 in these materials, which is about 0.5 electron per formula unit. Hence, in MTi_2S_5 , where *M* stands for a rare-earth metal, the Fermi level should lie at a substantially higher energy than that in the starting TiS_2 . Indeed, estimation of the Fermi level shift in $(\text{CeS})_{1.19}(\text{TiS}_2)_n$, $n = 1, 2$, compared to TiS_2 , as derived from measurements of the plasma reflection edge and kinetics properties, yields 0.68 eV [15].

Thus, by comparing the results of insertion of materials with $M = \text{Pb}$ or Sn with those in which *M* is a rare-earth metal should establish how the Fermi level position affects the stability of the Ti-M-Ti covalent centers, because while these fragments bring about approximately the same softening of the lattice, they result in different positions of the Fermi level relative to the impurity band.

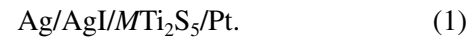
We chose PbS and GdS as *MS* fragments. This choice rests upon the fairly well known properties of PbTi_2S_5 and a stable trivalent state of Gd in GdS, which

accounts for the donor behavior of this fragment. We used silver as the intercalant. The availability of a good solid electrolyte AgI featuring unipolar conductivity in Ag^+ ions permitted us to apply the electrochemical EMF method to discriminate between the homogeneous/inhomogeneous states of the material.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The starting PbTi_2S_5 and GdTi_2S_5 compounds were synthesized by standard ampoule technique, the only difference being that synthesis of GdTi_2S_5 requires higher temperatures, $\sim 1200^\circ\text{C}$. The reader interested in details of the experiment and sample characterization can be referred to [6].

Silver was inserted electrochemically using the cell



Under isobaric and isothermal conditions, the EMF of this cell E is related with the chemical potential of silver atoms in the compound to be intercalated as follows:

$$eE = (\mu_{\text{Ag}}^{\text{Ag}} - \mu_{\text{Ag}}), \quad (2)$$

where $\mu_{\text{Ag}}^{\text{Ag}}$ and μ_{Ag} are the chemical potentials of silver atoms in metallic silver and in the compound, and e is the electronic charge. Thus, by the Gibbs phase rule the presence of more than one phase should give rise to E being independent of the intercalant content. The derivative of E with respect to temperature T yields the specific entropy of silver S_{Ag} in the compound:

$$S_{\text{Ag}} = -\left[\frac{\partial \mu_{\text{Ag}}}{\partial T}\right]_x. \quad (3)$$

The techniques of electrochemical experiments are described in considerable detail in [16].

3. RESULTS AND DISCUSSION

Figures 3 and 4 present graphically EMF's E of the cell (1) measured vs. silver content at $T = 200^\circ\text{C}$ for both systems under study. We immediately note two main features.

The first of them consists in that the maximum content of silver x at 200°C is approximately $x = 0.125$ for $\text{Ag}_x\text{GdTi}_2\text{S}_5$, to be contrasted with 0.38 for $\text{Ag}_x\text{PbTi}_2\text{S}_5$ and 0.44 for Ag_xTiS_2 [16]. The difference in solubility between the latter two materials can be ascribed to the fact that in $\text{Ag}_x\text{PbTi}_2\text{S}_5$ only half of interlayer gaps can be involved in intercalation (with the second half being filled by the PbS fragments). Therefore, the enhancement of ion-ion repulsion caused by increasing intralayer silver density should indeed bring about a faster increase of free energy with increasing silver concentration. We believe that it is this that may account for

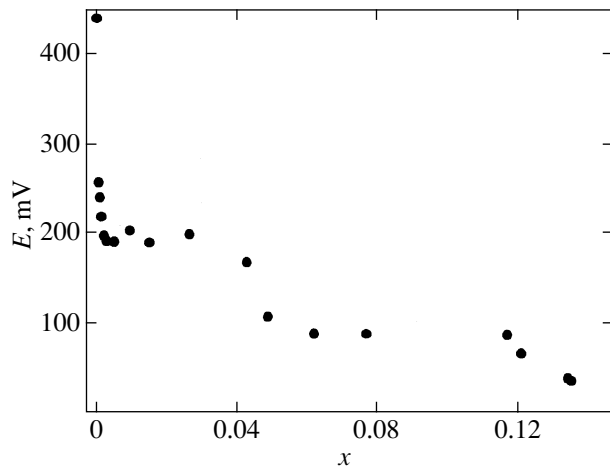


Fig. 4. Specific free energy of formation of $\text{Ag}_x(\text{GdS})(\text{TiS}_2)_2$ as a function of the silver content x .

equilibration with metallic silver at a lower intercalant concentration than in the case of Ag_xTiS_2 .

The solubility of silver in GdTi_2S_5 is substantially lower than that in PbTi_2S_5 . It is well known that the major contribution to \bar{E} comes from the difference between the chemical potentials of electrons in metallic Ag and $\text{Ag}_x\text{MTi}_2\text{S}_5$ ($M = \text{Pb}, \text{Gd}$) [17]. Because the conduction band in both materials derives from $\text{Ti}3d$ orbitals, the conduction-band density of states is the same in both materials. That silver ions reside in locally identical environments suggests that the ionic contribution in both systems should likewise be approximately the same. Hence, the difference in the solubilities can be assigned only to a difference in electron concentration in the starting GdTi_2S_5 and PbTi_2S_5 . Now because the GdS fragment can be the only source of additional electrons in GdTi_2S_5 , the difference between the limiting silver solubilities in $\text{Ag}_x\text{PbTi}_2\text{S}_5$ and $\text{Ag}_x\text{GdTi}_2\text{S}_5$ offers a possibility of determining the electron transport in the latter case, namely, $0.380 - 0.125 = 0.255$ electron per formula unit of TiS_2 . Allowing for stoichiometry, this is equivalent to approximately 0.5 electron per formula unit of GdS, in full agreement with the estimates given in [5]. This means that free electrons of the GdS sublattice are shared equally between the two structural fragments.

The second feature is the existence of a plateau in the $E(x)$ dependence for PbTi_2S_5 within the $x = 0-0.25$ interval and the absence of such a plateau for GdTi_2S_5 . By the Gibbs phase rule, this means the existence of a region of mixed phases in $\text{Ag}_x\text{PbTi}_2\text{S}_5$ in this concentration interval. Such a behavior was frequently observed in other materials characterized by the polaron form of carrier localization and treated as evidence for an instability of the homogeneous state in the case of the polaron band filled to less than one half. Obviously

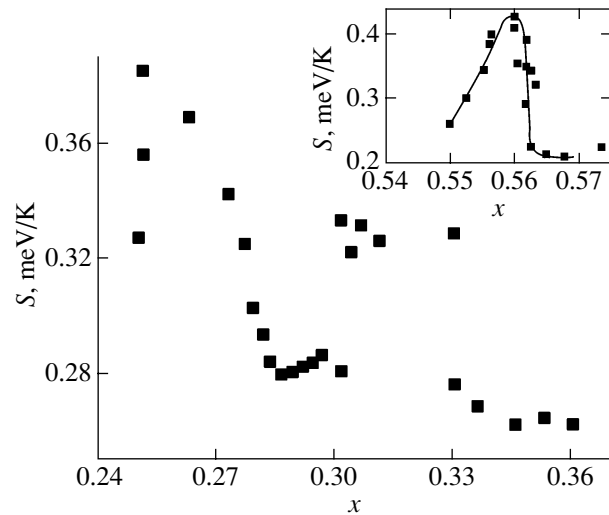


Fig. 5. Specific entropy of silver atoms in $\text{Ag}_x(\text{PbS})_{0.59}\text{TiS}_2$ as derived from the temperature dependence of the emf cell (1) and plotted as a function of the silver content. The inset shows a similar dependence for Ag_xTiTe_2 near the boundary of stability of the homogeneous state.

enough, an increase in electron concentration can increase the filling of this band and, thus, render the homogeneous state stable. The limiting electron concentration corresponding to the boundary of the homogeneous state stability (BHSS) is 0.25 electron per Ti atom (Fig. 3). As seen from a comparison of silver solubilities in GdTi_2S_5 and PbTi_2S_5 , it is this number of electrons that is donated by the GdS fragment.

Thus, straightforward increase of the electron concentration and, hence, an increase of the Fermi energy bring about stabilization of the homogeneous state at low concentrations of the inserted impurity. And it is this that is required by the above model.

One more argument for the validity of the proposed model can be obtained from an analysis of the concentration dependence of silver entropy S_{Ag} in the two systems under consideration. As follows from Eq. (3), the value of S_{Ag} can be derived from the temperature dependence of the EMF of cell (1). By virtue of Eq. (2), Eq. (3) now reads

$$S_{\text{Ag}} - S_{\text{Ag}}^{\text{Ag}} = e \left[\frac{\partial E}{\partial T} \right]_x, \quad (4)$$

where $S_{\text{Ag}}^{\text{Ag}}$ is the entropy of a silver atom in metallic silver.

The $S_{\text{Ag}}(x)$ relation is plotted in graphical form for $\text{Ag}_x\text{PbTi}_2\text{S}_5$ in Fig. 5. It turned out that, within the measurement accuracy, the entropy for the $\text{Ag}_x\text{GdTi}_2\text{S}_5$ system does not depend on x and is 0.27 meV/K. This behavior is typical of materials with a strongly disordered sublattice of mobile ions and a negligibly small contribution of electrons to the total entropy of a material [18]. A characteristic feature of the $S_{\text{Ag}}(x)$ relation

for $\text{Ag}_x\text{PbTi}_2\text{S}_5$ is the presence of a peak near BHSS. Similar features were observed also in other materials where the homogeneous state is stable only at carrier concentrations above the critical level [3, 19]. For the Ag_xTiTe_2 system, this relation is plotted in the inset to Fig. 5. This behavior of $S_{\text{Ag}}(x)$ defies interpretation in terms of the traditional approximation assuming a dominant contribution of ions to the entropy of silver; hence, one should attribute it to the electronic contribution.

To understand the electronic contribution to entropy, one can invoke the well-known concepts of the behavior of electronic heat capacity. This quantity can be written in a general form as follows [20]:

$$\begin{aligned} C_{\text{el}} &= \mu_e \rho(\mu_e) \frac{d\mu_e}{dT} \\ &+ \frac{\pi^2}{3} k^2 T \left[\rho(E) + \mu_e \frac{d\rho}{dE} \right]_{E=\mu_e} + O(T^2) \\ &= \frac{\pi^2}{3} k^2 T \rho(E_F) + \mu_e \rho(\mu_e) \left[\frac{d\mu_e}{dT} + \frac{\pi^2}{3} \frac{k^2 T}{\rho(E)} \frac{d\rho}{dE} \right]_{E=\mu_e}, \end{aligned} \quad (5)$$

where μ_e is the chemical potential of electrons, k is the Boltzmann constant, and ρ is the density of electronic states.

Recalling the well-known relations $\delta Q = TdS$ and $C \equiv \frac{\delta Q}{dT}$ we immediately come to

$$S = \int \frac{dS}{dT} dT = \int \frac{C}{T} dT. \quad (6)$$

Strictly speaking, Eq. (6) should contain the definite integral. In view, however, of the experimentally observed independence of entropy on temperature, it appears reasonable to drop concrete limits of integration while at the same time relating the quantity thus obtained to the single-phase region.

Because all terms in Eq. (5) are linear in temperature, it is clear that the integration and division by T cancel one another. If, however, we retain the contributions depending on temperature, the resultant entropy will be temperature dependent. In this case, the temperature dependences $E(T)$, rather than being straight lines, would contain an additional quadratic contribution. Experiment does not support this assumption. This makes us restrict ourselves to the temperature-independent contribution in Eq. (5). Now the electronic contribution to the total entropy will read

$$S_{\text{el}} = \mu_e \rho(\mu_e) \frac{d\mu_e}{dT}. \quad (7)$$

We readily see that this form of electronic entropy differs from Eq. (4) by the factor $\mu_e \rho(\mu_e)$, which is directly proportional to the density of states at the Fermi level. If this quantity is constant, the earlier approach based on Eq. (4) turns out fully valid, because

the entropy, like all the other thermodynamic functions, is referenced to an arbitrary origin. If, however, the density of states varies noticeably with impurity concentration, the electronic contribution should reflect the density of states scanned by the Fermi level as the electron concentration varies. As for the possible contribution of μ_e , its variation should be a monotonic function of the impurity concentration; hence, this quantity cannot account for the peak in the $S_{\text{Ag}}(x)$ dependence. Thus, the only way to explain the observed $S_{\text{Ag}}(x)$ relation in the vicinity of BHSS appears to assume the existence of a density of states peak at the Fermi level. Such a peak is observed in $\text{Ag}_x\text{PbTi}_2\text{S}_5$, which suggests partial filling of the polaron band. In the case of $\text{Ag}_x\text{GdTi}_2\text{S}_5$, no peak is observed, just as a non-single-phase region at impurity concentrations below the critical level, which should apparently be assigned to the polaron band being filled by electrons transported from the GdS fragment.

By the model shown in Fig. 1, BHSS should correspond to half-filling of the polaron band, whereas the experimental $S_{\text{Ag}}(x)$ plots suggests rather that BHSS should be identified with smaller polaron band filling. The boundary of stability of the homogeneous state is defined by the condition $\Delta S = 0$ (ΔS is the entropy of polaron band collapse) and

$$\Delta S = \Delta S_{\text{el}} + \Delta S_{\text{conf}} + \Delta S_{\text{vibr}}, \quad (8)$$

where ΔS_{conf} , ΔS_{vibr} , and ΔS_{el} are the configurational, vibrational and electronic contributions to the total entropy, respectively. Obviously enough, ΔS_{conf} and ΔS_{vibr} are positive. Hence, the condition $\Delta S = 0$ is satisfied at a lower polaron band filling than the $\Delta S_{\text{el}} = 0$ condition used in the model depicted in Fig. 1.

4. CONCLUSIONS

A comparison of the concentration dependences of thermodynamic functions for the $\text{Ag}_x\text{GdTi}_2\text{S}_5$ and $\text{Ag}_x\text{PbTi}_2\text{S}_5$ isostructural materials differing only in the electron concentration and, hence, in the degree of polaron band filling, lends support to the earlier model relating the stability of the homogeneous state in materials whose carriers are localized in the form of polarons with the degree of filling of the polaron band. An analysis of the concentration dependence of entropy near the boundary of stability of the homogeneous state offers a possibility of refining the numerical value of the concentration threshold of stability.

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