
LATTICE DYNAMICS
AND PHASE TRANSITIONS

Polaron Band Collapse in Concentrated and Diluted Polaron Systems

A. N. Titov

Institute of Metal Physics, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi 18, Yekaterinburg, 620019 Russia
Ural State University, pr. Lenina 51, Yekaterinburg, 620083 Russia
e-mail: alexander.titov@usu.ru

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Abstract—The dependence of the character of the phase transition that accompanies the polaron band collapse in Ag_xTiTe_2 on the concentration of polaron centers determining the density of states of the polaron band was studied by differential thermal analysis and by measuring the magnetic susceptibility. In the low-concentration limit, the transition is found to be smooth. As the concentration of impurity centers increases, the transition changes to the first order. On the temperature–concentration diagram, the line along which the change in the phase transition order occurs is determined by percolation laws. It is shown that the thermal effect accompanying the transition can be related to the decrease in the electron free energy due to polaron localization.

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The polaron state of charge carriers in intercalation compounds of titanium dichalcogenides with transition metals and silver causes a number of unusual features in the phase diagrams of these compounds. The most dramatic of them is that the single-phase state becomes unstable upon polaron band collapse (PBC) if the degree of band filling is less than one-half [1]. This effect is associated with the Fermi level shift due to the change in the density of states upon PBC [1]. If less than half the polaron band is filled, its compression under heating must cause an increase in the Fermi energy, which is equivalent to a negative entropy of the process and contradicts the second law of thermodynamics. For this reason, a uniform material breaks into regions enriched and depleted in charge carriers to concentrations that provide the fulfillment of the second law and the absence of an E_F shift upon PBC. This transition is likely to be of first order and, hence, is accompanied by a stepwise change in the volume, the chemical potential, and other thermodynamic parameters characterizing a material with localized and delocalized (band) polarons. This means impossibility of intermediate degrees of polaron localization. However, according to theory (see, e.g., [2–4]), the temperature dependence of the degree of polaron localization is a continuous function. The reason for this discrepancy could be that the theoretical consideration was performed for an infinitely low polaron concentration. In this case, the density of states at the Fermi level remains unchanged upon PBC and, therefore, the E_F does not shift.

An alternative reason for the stepwise transition accompanying PBC can be an increase in the dielectric constant ϵ due to an increase in the density of states at

the Fermi level [5]. An increase in ϵ means an increased screening of interatomic interactions, which causes “softening” of the lattice. Since the degree of localization is determined by the competition between the gain in polaron free energy and the energy cost of lattice deformation, it is clear that lattice softening can provide an increase in the degree of localization even in the absence of changes in the external thermodynamic parameters. Thus, PBC leads to an increase in ϵ , which, in turn, favors subsequent polaron localization. This positive feedback can cause a stepwise change in the degree of polaron localization.

In both cases, the effect is related to a change in the density of states at the Fermi level. Therefore, it can occur only in materials wherein the polaron concentration is sufficiently high for a polaron band to form. At extremely low concentrations of polarons, their states form a level rather than a band and PBC is accompanied by a smooth transition. At high polaron concentrations, this transition is a stepwise first-order transition. Thus, the phase diagrams of such materials have a boundary between regions with high and low polaron concentrations. The position of this boundary can be determined theoretically in terms of percolation theory [6].

Intercalation materials based on titanium chalcogenides are convenient objects for testing these concepts. In these materials, polarons are localized at impurity centers, which are denoted, for brevity, as Ti– M –Ti, where M is the intercalated atom. Thus, by changing the concentration of an intercalated impurity, one can vary the polaron concentration. However, in the compounds with transition metals, the positions nearest to the impurity are blocked in the direction normal to

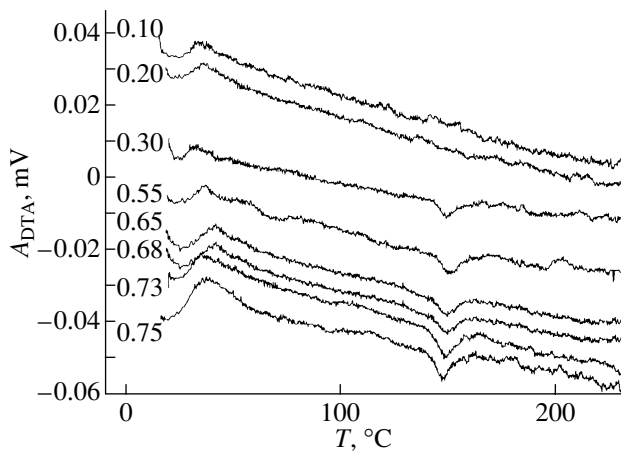


Fig. 1. DTA curves of Ag_xTiTe_2 samples near the phase transition associated with the collapse of the polaron band. The silver content x is indicated near the curves. The non-monotonic behavior near room temperature is related to the instability of measurements when the derivatograph is turned on.

the basal plane [7]. As a result, the range of low polaron concentrations is limited to an impurity concentration of only several mole percent. For example, in the Fe_xTiSe_2 system, the critical concentration x is close to 0.05 [8]. It is clear that the error in determining the intercalant content in this case is large and the accuracy in determining the boundary position and establishing its existence is unacceptably low. This difficulty can be overcome by using the Ag-TiTe_2 system, in which the blocking effect is absent and, hence, overlap of impurity centers is possible. This overlap can be described as the formation of Ag-Ti-Ag centers in addition to the Ti-Ag-Ti centers [9]. Although both the centers can capture an electron with the formation of a distorted cluster, a polaron band can be formed only by Ag-Ti-Ag centers [10]. The reason for this is the existence of topological features that do not permit the Ti-Ag-Ti centers to achieve a concentration large enough for overcoming the percolation threshold in their sublattice. Thus, the density of states in the polaron band in the Ag-TiTe_2 system increases with the intercalant content more slowly than in the compounds intercalated with transition metals. For topological reasons, the Ag-TiTe_2 system should exhibit two percolation thresholds corresponding to silver concentrations $x = 0.293$ and 0.707 [9]. At concentrations lower than $x = 0.293$, the percolation over all types of centers is absent and, hence, none of the types of polaron centers forms a band. The composition $x = 0.707$ corresponds to the onset of percolation over the Ag-Ti-Ag centers and, therefore, the formation of a band by the polarons localized on these centers [10]. It should be noted that all of the above topological results are obtained for the problem of site percolation under the assumption that there is only interaction between nearest neighbors.

This work is devoted to studying the effect of the polaron concentration on the character of the phase transition associated with PBC. The character of the transition was determined from the presence of a thermal effect in a differential thermal analysis (DTA) curve, and the density of states at the Fermi level was characterized by the Pauli magnetic susceptibility.

DTA curves were measured using an automatic complex based on a $Q-1500$ derivatograph. The samples under study (of the same mass, 1 g) were sealed into pyrex ampoules evacuated to 10^{-5} Torr; the ampoules have a special shape following the shape of the bottom of standard crucibles of a derivatograph. When sealed, the samples underwent an uncertain heat treatment due to heating of the ampoule. Since the PBC temperature for Ag_xTiTe_2 is as low as 130°C , this heating could fix a high-temperature state. For this reason, before measurements, all of the samples were subjected to slow cooling in the derivatograph at a rate of 2 deg/min. An inspection showed that, as a result of this procedure, the samples achieve an equilibrium state and subsequent cycles of slow cooling at this or lower rate do not influence the shape of DTA curves. The use of samples in ampoules permitted us to check the reproducibility of the results; the DTA measurements were repeated three times for each of the samples. The thermal effect was calibrated by the tin melting heat measured under precisely the same conditions. It should be noted that the shape of a DTA curve is dependent not only on the heat release in the sample but also on the sample heat conductivity. Clearly, the heat conductivities of tin and an Ag_xTiTe_2 powder are different, and this leads to a systematic error in measuring the thermal effect.

The magnetic susceptibility was measured on pressed samples with masses of 100–150 mg using a SQUID magnetometer (Quantum Design, USA) in the temperature range 4–400 K. Thus, the temperature range includes the temperature of the onset of the transition; however, the high-temperature phase wherein polaron localization is observed is beyond the temperature range accessible for this technique. In the temperature range $\sim 4\text{--}35$ K, the magnetic susceptibility was observed to have a Curie–Weiss contribution, which is likely related to the inevitable presence of magnetic impurities in the sample. This conclusion is based on the fact that Ag_xTiTe_2 itself does not contain any magnetic ion. Even titanium is in the Ti^{4+} state, which corresponds to the $3d^0$ configuration. It is apparent that this material must exhibit a Pauli magnetic susceptibility [11]. To separate the Pauli contribution, the low-temperature contribution of the impurities was approximated by the Curie–Weiss law and then it was subtracted from the temperature dependence of the susceptibility.

Figure 1 presents the DTA curves measured for the samples with various silver concentrations. It is seen that the thermal effect near a temperature $T = 150^\circ\text{C}$ is

observed only starting from a silver concentration $x = 0.3$. This starting point coincides (to within the experimental error) with a percolation threshold $x = 0.293$. At lower values of x , the thermal effect is absent, which can be associated with the absence of a polaron band. As can be seen from the concentration dependence of the thermal effect presented in Fig. 2, the magnitude of this effect drops abruptly to zero as the value $x = 0.3$ is reached. This unexpected behavior seems to be a result of measurements at insufficiently small concentration intervals. The actual dependence must be smooth and consistent with the proper behavior near the percolation threshold. In the x range between the percolation thresholds, the $Q(x)$ dependence is close to a straight line. It is likely that this corresponds to accumulation of similar localization centers leading to a monotonic increase in the polaron band width. Near a threshold composition $x = 0.707$, a deviation from the linear dependence takes place. In the range $x > 0.7$, an abrupt increase in the slope of the $Q(x)$ curve is observed. According to the above discussion, this corresponds to an increase in the polaron band width due to the onset of percolation over the Ag–Ti–Ag centers. The same conclusion follows from analyzing the concentration dependences of the conductivity and the Seebeck coefficient [10].

The temperature dependence of the magnetic susceptibility χ at high temperatures is shown in Fig. 3. As is seen, heating causes a certain increase in χ . An analogous effect was observed in Ni_xTiSe_2 [12], where the Curie–Weiss contribution is also small because of suppression of the magnetic moment of Ni caused by hybridization of its $3d$ orbitals with the states of the host lattice [13]. This unusual $\chi(T)$ dependence can be explained in terms of a polaron band with a high density of states near the Fermi level. The same argument is also applicable to the Ag_xTiTe_2 system in which the existence of such a band follows from many thermodynamic and kinetic data [14]. Since the $\chi(T)$ dependence is complicated, the magnitude of χ cannot be directly related to the density of states at the Fermi level. However, the concentration dependence of χ allows us to determine the change in the density of states at the Fermi level. The reason for this is that the correction to the temperature-independent χ is much smaller than the value of χ . For example, for the Ni_xTiSe_2 system, it was shown in [13] that the correction to χ is five orders of magnitude smaller than χ . Figure 4 shows the quantity χ measured at 350 K as a function of the silver content. It can be seen that, as the silver concentration and, hence, the density of electrons increase, the Fermi level “scans” the density of states sweeping through a narrow band, in which the maximum density of states corresponds to $x = 0.65$. This value of x does not coincide with any percolation threshold; so, the states in this band are likely metallic. This conclusion is confirmed by the metallic character of the conductivity at temperatures lower than the PBC temperature [9].

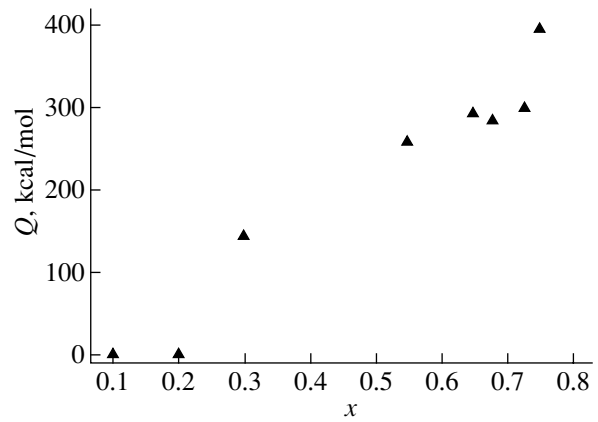


Fig. 2. Thermal effect Q as a function of the silver content x in Ag_xTiTe_2 .

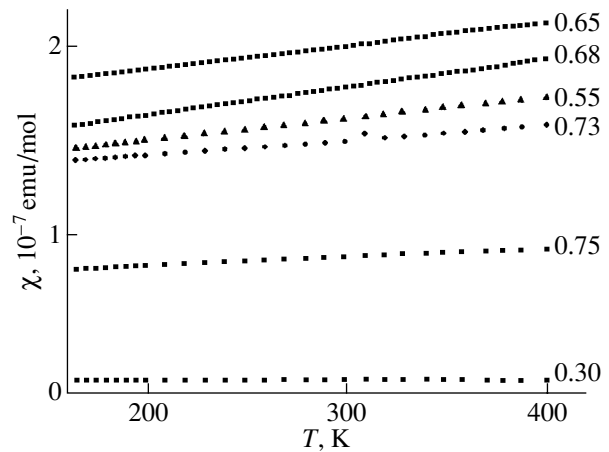


Fig. 3. Temperature dependences of the magnetic susceptibility χ of the Ag_xTiTe_2 system in the temperature range adjacent to the PBC temperature. The silver content x is indicated near the plots.

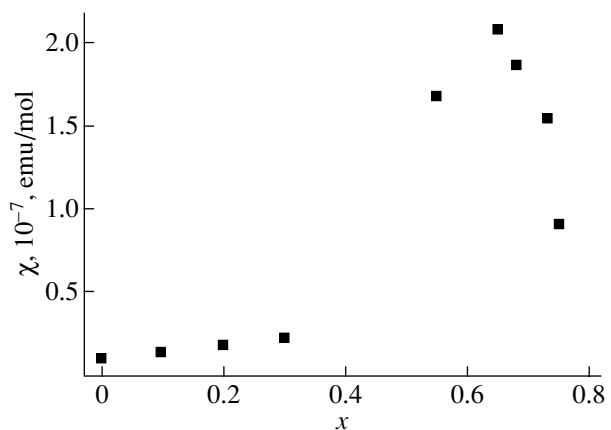


Fig. 4. Isothermal concentration dependence of the magnetic susceptibility χ of the Ag_xTiTe_2 system at a temperature $T = 350$ K.

It should be noted that when the silver content is higher than $x = 0.65$, χ decreases as x increases. Therefore, the density of states decreases over this concentration range. However, the thermal effect varies monotonically with x ; it increases over the entire concentration range $x > 0.3$. If a change in ϵ were the main reason for the stepwise transition, then the concentration dependence of the thermal effect $Q(x)$ would be a function with a maximum. However, at $x > 0.55$, the observed $Q(x)$ dependence follows the concentration dependence of the shift in the Fermi level upon PBC, which increases monotonically up to $x = 0.75$ [1].

Thus, the thermal effect should be associated with the Fermi level shift upon PBC (polaron shift), which is the change in the free energy of the electronic subsystem during the transition. The value of the thermal effect is related to the polaron shift, and it arises only when a polaron band forms.

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