
LATTICE DYNAMICS
AND PHASE TRANSITIONS

Anomalies in the Structure and Properties of Titanium Diselenide Intercalated by Iron

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Abstract—The transition between the heavy and localized polaron modes in the Fe_xTiSe_2 compounds used as an example is studied by methods of thermal analysis, neutron diffraction, and dc conductivity. It is found that the transition under investigation is accompanied by an anomaly in the behavior of the crystallographic parameters. The changes observed in the character and magnitude of the electrical conductivity at a higher temperature, as well as the thermal effect, are attributed to thermal broadening of the polaron band. The difference between the data for Fe_xTiSe_2 and the previously obtained results for Ag_xTiTe_2 correlates with the difference in the binding energies of the polaron bands in these materials.

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1. INTRODUCTION

Intercalation compounds based on titanium dichalcogenide exhibit polaron-type carrier localization [1]. The simplicity of the structure and the broad range of possibilities for varying the binding energy of the polaron states and the polaron concentration make this class of materials convenient for use as model compounds in studying the effect of the polaron form of carriers on the structure, physical properties and thermodynamics of a material.

The basic phenomenon revealed in such systems is the existence of a first-order phase transition accompanying a change in the degree of carrier localization upon the transition from the heavy-polaron mode (non-activated conduction) to the localized-polaron mode (hopping conduction) at the so-called polaron band collapse (PBC) point. This observation is at odds with the theoretical concepts developed for the case of an isolated polaron (see, e.g., [2]). In the case where the polaron band is less than half-filled, the first order of the “heavy polaron–localized polaron” phase transition is successfully explained as resulting from the decomposition of a homogeneous material into fractions with the polaron band filling responsible for the thermodynamic stability of the material [3]. In those cases, however, where the polaron band is filled to more than one-half, the abrupt change in the characteristics of the material cannot be explained in a similar way. For instance, in Fe_xTiSe_2 compounds satisfying the condition of thermodynamic stability (the polaron band is more than half-filled) [4], the transition between the localized and delocalized states of the polaron subsystem is also

abrupt [5]. Moreover, the delocalized state can be fixed by quenching, and the transition between the localized and delocalized states is accompanied by an endothermal effect [5]. There are thus grounds to assume that the transition between the heavy-polaron and localized-polaron modes is a first-order phase transformation.

In this work, the specific features in the structure and electrical conductivity of Fe_xTiSe_2 under variations in temperature in the vicinity of the polaron band collapse are investigated using high-temperature neutron diffraction and differential thermal analysis (DTA).

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The Fe_xTiSe_2 samples with $x = 0.10$ and 0.25 were synthesized from elements [1, 5]. These compositions were chosen because they fall in the concentration interval within which one still does not observe intercalant ordering [6]. The electrical conductivity of ceramic samples was measured by the standard four-point probe technique. The samples used in these measurements were quenched from 800, 600, 400, and 220°C or cooled slowly from 800°C (referred to subsequently as slowly cooled samples). The quenching temperature range covered the whole temperature interval, including the polaron band collapse point $T_{\text{CPB}} \approx 500^\circ\text{C}$ (estimated from the measurement of electrical properties, Fig. 1). Prior to quenching, the samples were annealed in an evacuated quartz ampoule for a day at 800°C, after which the temperature was lowered to the quenching temperature, at which the samples were maintained for one more day. Quenching was effected

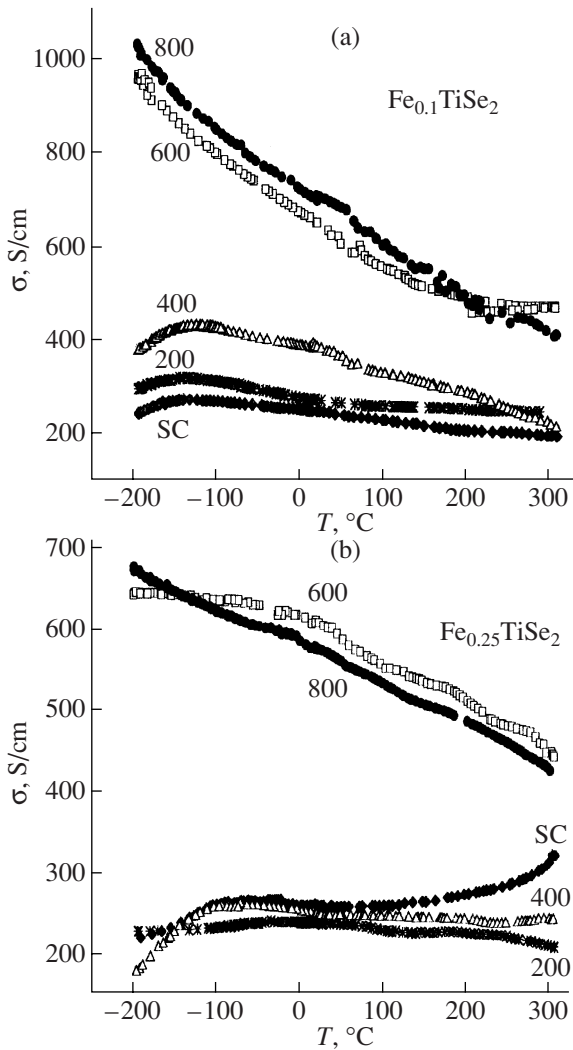


Fig. 1. Temperature dependences of the electrical conductivity of the quenched and slowly cooled samples of the (a) $\text{Fe}_{0.1}\text{TiSe}_2$ and (b) $\text{Fe}_{0.25}\text{TiSe}_2$ compounds. The quenching temperature (in $^{\circ}\text{C}$) is indicated near each curve. Designation: SC stands for slowly cooled samples.

in water with ice. The temperature of the slowly cooled samples was lowered from 800°C at a rate of 10 K/h.

The samples intended for DTA measurements were prepared as those used in conductivity studies, but only with quenching from 800°C (with the heavy-polaron mode fixed) and slow cooling (SC) (the localized-polaron mode). The DTA studies were performed on a Q-1500 computerized derivatograph. The samples were placed in a quartz ampoule evacuated to 10^{-5} Torr, which was provided with a special groove for a thermocouple. This made it possible to carry out preliminary thermal treatments and the measurements themselves without taking a sample out into the open air, thus preventing them from degradation caused by oxidation, uncontrolled chalcogen evaporation etc. The sample weight was ~ 1 g, the heating rate was ~ 5 K/min, and the

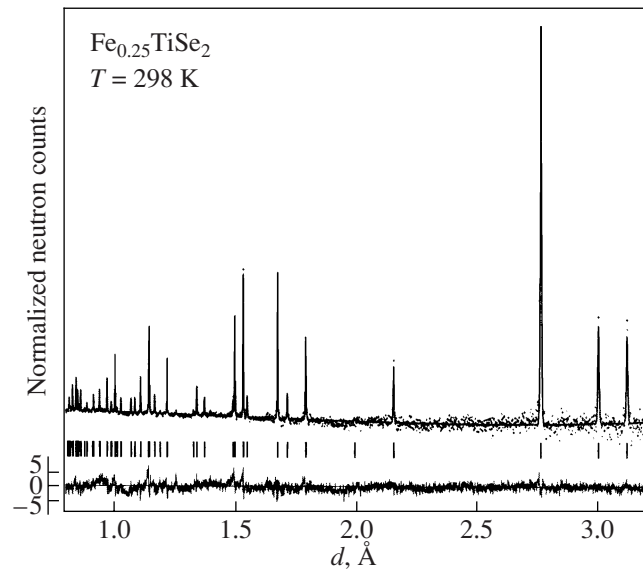


Fig. 2. Rietveld-refined neutron diffraction pattern of the slowly cooled $\text{Fe}_{0.25}\text{TiSe}_2$ sample at room temperature. Experimental points, the calculated diffraction pattern, and the difference curve are shown. Vertical ticks indicate the calculated positions of the diffraction peaks.

accuracy in the DTA signal measurement was ~ 1 μV . Each measurement was repeated three times to improve reliability, and the results were found to be in good agreement.

The neutron diffraction data were obtained on an FDVR spectrometer [7] (IBR-2 pulsed reactor, Dubna) with a high resolution in interplanar spacing ($\Delta d/d \approx 0.001$), which ensured a high-precision structural analysis. The diffraction patterns were measured for the sample heating from 25 to 650°C , with a 4-h exposure at each temperature. Figure 2 demonstrates the diffraction pattern of the slowly cooled $\text{Fe}_{0.25}\text{TiSe}_2$ sample, which was measured at $T = 25^{\circ}\text{C}$ and Rietveld-refined with the MRJA program. The x-ray diffraction patterns were treated assuming space group $P\bar{3}m$ (no. 164), $Z = 1$, the Ti atoms occupying the $(1a)(0,0,0)$ positions, the Fe atoms, the $(1b)(0,0,0.5)$ positions, and the Se atoms, the $(2c)(1/3,2/3,z)$ positions. For 25°C , the unit cell parameters are as follows: $a = 3.5927(1)$ \AA , $b = 5.9904(1)$, and $z(\text{Se}) = 0.2553(2)$.

3. RESULTS AND DISCUSSION

Figure 1 plots the temperature dependences of the electrical conductivity of the samples subjected to the above thermal treatments for both compositions. We readily see that these dependences split into two groups following approximately the same pattern; namely, the samples quenched from 600 and 800°C exhibit metallic conductivity, whereas those quenched from lower temperatures and the slowly cooled samples reveal a lower

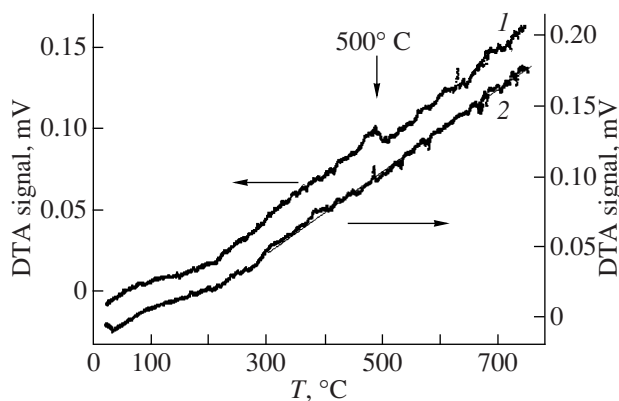


Fig. 3. DTA curves for the (1) slowly cooled and (2) quenched $\text{Fe}_{0.25}\text{TiSe}_2$ samples.

electrical conductivity which only weakly depends on temperature.

The experimental DTA data obtained for $\text{Fe}_{0.25}\text{TiSe}_2$ samples are presented in Fig. 3. The slowly cooled samples exhibit a clearly pronounced exothermal peak close to 500°C , whereas the $350\text{--}800^\circ\text{C}$ -interval for the quenched samples can be fitted well with a linear function, which indicates no thermal effects in this temperature interval. For both groups of samples, one observes a kink near $250\text{--}300^\circ\text{C}$, and the exothermal effect at 500°C for the slowly cooled samples can be assigned to the heavy-polaron-localized-polaron transition. The quenched samples with the quenched-in localized-polaron mode do not undergo this transition because of the absence of the annealing effect. The effect observed at 500°C lies close to the point of the transition between different conduction modes, whereas the kink at 300°C is not associated with anywhere near noticeable changes in the conductivity.

The temperature dependences of the unit cell parameters for both compositions studied, with $x = 0.10$ and 0.25 , exhibit an anomalous behavior of the structural parameters; indeed, for the slowly cooled $\text{Fe}_{0.25}\text{TiSe}_2$ sample, the temperature dependence of the unit cell parameters is seen to deviate in the $200\text{--}400^\circ\text{C}$ interval from a linear course (Fig. 4). For the low-iron composition ($x = 0.10$), the linear dependence of the unit cell parameters holds throughout the range covered; however, in the same $200\text{--}400^\circ\text{C}$ interval, the thermal expansion coefficient, i.e., actually the first derivative of the $a(T)$ and $c(T)$ functions, is seen to behave anomalously.

This suggests that the structural anomaly persists while becoming considerably weaker for low-iron contents, thus arguing for this anomaly being connected intimately with intercalated iron. Similar anomalies were observed earlier in the temperature dependences of the parameters in the form of local minima in $a(T)$ and $c(T)$ near the polaron band collapse point in

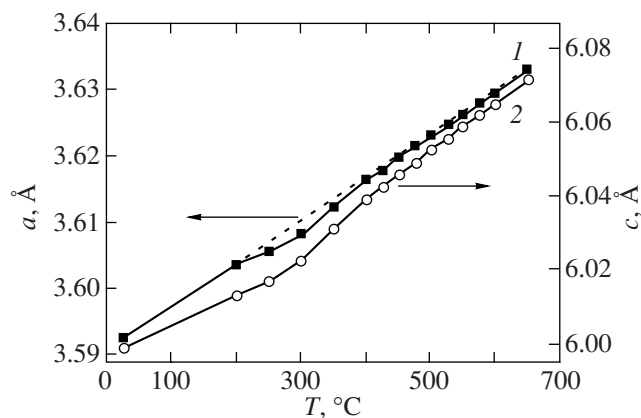


Fig. 4. Temperature dependences of the unit cell parameters (1) a and (2) c for the slowly cooled $\text{Fe}_{0.25}\text{TiSe}_2$ sample. Temperature dependence of the unit cell parameters at temperatures close to 300°C deviates from a linear behavior.

Ag_xTiTe_2 [8]. In the silver compounds, the structural anomaly at the polaron band collapse was accompanied by an endothermal effect at the same temperature [9]. The iron compounds under study exhibit a thermal effect at a higher temperature of 500°C ; at the same time, in the region where the electrical conductivity undergoes an abrupt change (Fig. 1), no change in the crystal structure was observed to occur at 500°C .

It can be assumed that the difference both between the temperatures of the structural anomaly near 300°C and between the physical properties at 500°C for different compositions is a consequence of the fact that the polaron band lies below the Fermi level by 0.3 eV in Fe_xTiSe_2 [4] and falls directly at the Fermi level in the Ag_xTiTe_2 system [3]. In this case, the enhanced localization of polarons in Fe_xTiSe_2 should not affect their kinetic characteristics, thus leaving the states at the Fermi level without any change. Such changes should appear only when, as a result of thermal broadening of the polaron band, its top reaches the Fermi level. Thus, the polaron localization accompanied by lattice deformation takes place at 300°C , while the transition to metallic conductivity associated with the polaron band reaching the Fermi level is observed only at 500°C . Obviously enough, the latter should entail an increase in the density of states at the Fermi level and, hence, an increase in the permittivity. It is probably this state with an enhanced permittivity that is quenched in.

The difference between the Ag_xTiTe_2 and Fe_xTiSe_2 systems (one and two anomalies, respectively) is associated with the position of the polaron band with respect to the Fermi level, i.e., with the difference between the polaron band binding energies. More specifically, in Ag_xTiTe_2 , the band lies directly at the Fermi level, whereas direct spectral measurements showed that, in Fe_xTiSe_2 , the polaron band lies 0.3 eV below the Fermi level. Thus, in the case of Ag_xTiTe_2 , both temperatures, i.e., the temperature of polaron localization and

the temperature of the maximum in the temperature dependence of the permittivity, coincide.

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