LATTICE DYNAMICS. PHASE TRANSITIONS

Nonequilibrium phase transition in quenched samples of $Fe_{0.1}TiTe_2$

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The influence of the heat treatment of $Fe_{0.1}TiTe_2$ samples on the appearance of thermally induced ''levitation'' is investigated. It is postulated that this phenomenon is most probably caused by undamped fluctuations of the electric charge on the surface of particles of the material. © *1999 American Institute of Physics.* [S1063-7834(99)02504-6]

New intercalates based on the titanium dichalcogenides M_xTiX_2 (M = Ag, Fe, Co; X = Se, Te) exhibit several unusual phase transitions, which are accompanied by a change in the conductivity type from metallic to thermally activated.[1–4] Special interest has been aroused by the discovery of thermally induced ''levitation'' in these materials,[5] which is observed as continuous motion (hopping, swinging, rotation about an axis, and hovering without support on the ampul walls) of particles of these materials within an evacuated ampul in the temperature range $100-500$ °C. The motion of crystals upon phase transitions is not unique and has previously been observed in many materials (see, for example, Ref. 6). Such behavior has traditionally been attributed to sharp changes in the dimensions of the crystals upon a martensitic phase transition or a phase transformations associated with the Jahn–Teller effect. However, this explanation is not convincing in the case of M_xTiX_2, since the motion of crystals of these materials is observed over a broad temperature range and is not restricted in time. Two possible causes of ''levitation'' were suggested in Ref. 5: fluctuations of the dimensions of the crystals due to the formation and dissociation of covalent Ti–M–Ti complexes or fluctuations of the electrostatic surface charge due to a pyroelectric effect. The hypothesis that there is a pyroelectric effect is unconvincing because of the high conductivity of the materials under consideration ($1-100$ S/cm). This paper is devoted to an investigation of the typical ''levitating'' material $Fe_{0.1}TiTe_2$ for the purpose of obtaining additional information regarding this unusual phenomenon.

The samples of $Fe_{0.1}TiTe_2$ were prepared by the thermal intercalation of powered iron, produced by reducing iron carbonyl in a hydrogen atmosphere, in $TiTe_2$ preliminarily obtained by ampul synthesis from the elements (Ti of 99.95% purity and Te with a purity no less than 99.5%). The $TiTe_2$ synthesis temperature was 950 °C, while the intercalation temperature was 800 °C. The lower value of the intercalation temperature in comparison to the $TiTe_2$ synthesis temperature was used to prevent the mixing of titanium and iron

atoms, which has been observed, for example, for the Fe_xTiSe_2 system.[7]

The phase composition of the samples was monitored by x-ray diffraction analysis at room temperature (DRON-UM-1 diffractometer, Cu $K\alpha$ radiation). The temperature dependence of the crystal-lattice parameters was determined on samples quenched from the respective temperatures. The accuracy of the determination of the unit-cell periods was $\Delta a/a = 3 \times 10^{-4}$ and $\Delta c/c = 5 \times 10^{-4}$, respectively. The conductivity σ was measured by a four-point probe on cold-pressed samples of rectangular shape. The experimental procedure was described in detail in Ref. 8.

The phase transitions were detected by differential thermal analysis (DTA) combined with thermogravimetric analysis (TG). The measurements were performed on a Q-1500 derivatograph in a dynamic regime with a heating rate of 5 K/min using powdered $Fe_{0.1}TiTe_2$ samples. Samples weighing ~ 1 g, which were single-phase according to x-ray diffraction analysis, were placed in special evacuated Pyrex ampuls of small dimensions fitting derivatograph arm. This enabled us to avoid, not only oxidation of the samples in air, but also variation of their composition during the experiments, as well as to perform all the derivatographic measurements for a given composition on the same samples and to avoid errors associated with the inaccuracy of determining the composition when the influence of various heat treatments on the phase composition was investigated. To standardize the original state before rapid cooling, the sample was heated to 550 °C, held at that temperature for about an hour, and slowly cooled together with the furnace over the course of roughly 6 h. For rapid cooling, the ampul with the sample was placed in a furnace heated to the respective temperature, held at that temperature for 10 min, and then withdrawn and forcibly cooled in a jet of air with sprayed drops of water at the rate of ~ 30 K/s.

The main experimental results are presented in Figs. 1–4. It is clearly seen that the DTA curve of the sample quenched from 350 °C exhibits an endothermic effect at
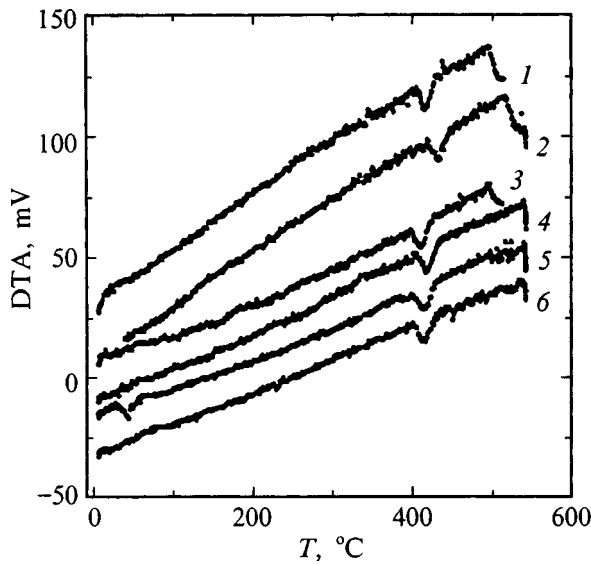
FIG. 1. Temperature dependences of the DTA signal for $Fe_{0.1}TiTe_2$ subjected to various heat treatments: *1* — slow cooling; *2* — quenching from 600 °C; *3* — quenching from 550 °C; *4* — quenching from 450 °C; *5* — quenching from 350°C; *6* — holding at 350°C for a week followed by rapid cooling by the standard method.

FIG. 3. Values of the crystallographic parameters of the hexagonal $Fe_{0.1}TiTe_2$ lattice for quenched samples as a function of the temperature before quenching.

67°C, which is not observed following the other heat treatments (Fig. 1). This effect can attest to a first-order phase transition with a heat of 4.8 kJ/mol. The TG curve of this sample exhibited a large spread of readings of the derivatograph balance from the temperature of the endothermic effect up to 450°C (Fig. 2). This instability of the TG signal was not observed in samples rapidly cooled from other temperatures and was detected just for the case of quencing from 350°C. We believe that such anomalous behavior of the TG signal can be produced only by the mobility of particles in the sample, since any movement of the lattice (even chaotic) leads to variation of the moment of the force exerted by the sample on the derivatograph arm. Thus, the thermogravimet-
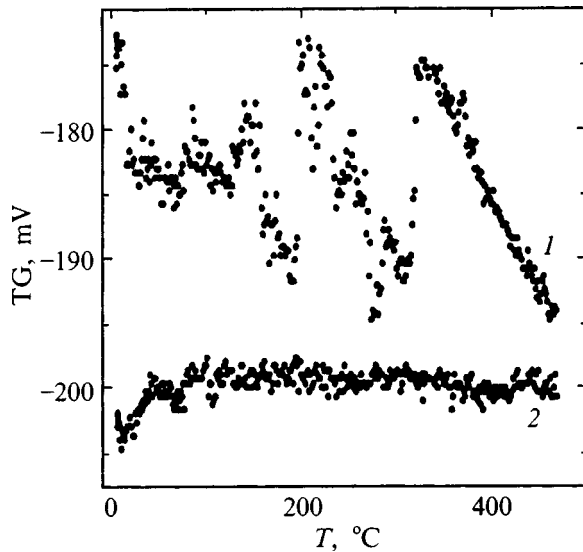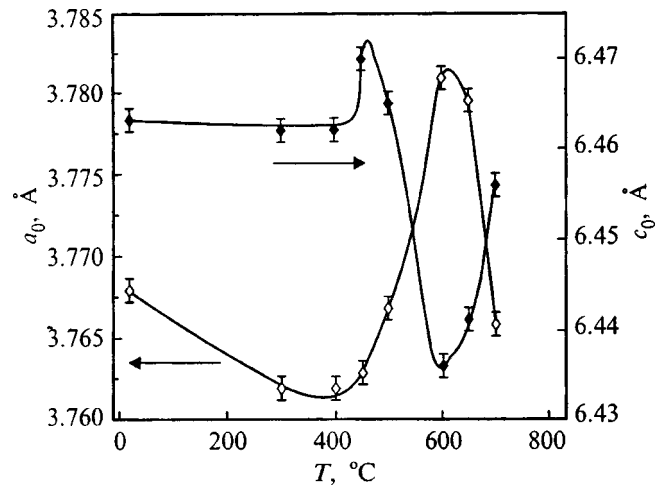
ric curve can be regarded as a record of the motion of particles in a temperature range.

The dependence of the crystallographic parameters of the $Fe_{0.1}TiTe_2$ samples quenched from various temperatures (Fig. 3) demonstrates the absence of appreciable changes in the respective temperature range. Therefore, it seems more justified to postulate that ''levitation'' is due to an electrostatic process rather than an abrupt change in volume. To test this hypothesis, $Fe_{0.1}TiTe_2$ single crystals prepared in accordance with the method described in Ref. 5 were placed in an ampul, whose bottom was partially covered by a highly conductive tantalum foil. Upon heating, motion of the crystals was observed only above the insulating surface of the ampul, while there was no motion above the conducting surface. This allowed us to attribute the ''levitation'' to the interaction of fluctuations of the surface charge of the particles of the material with the induced charge of the dielectric sub-
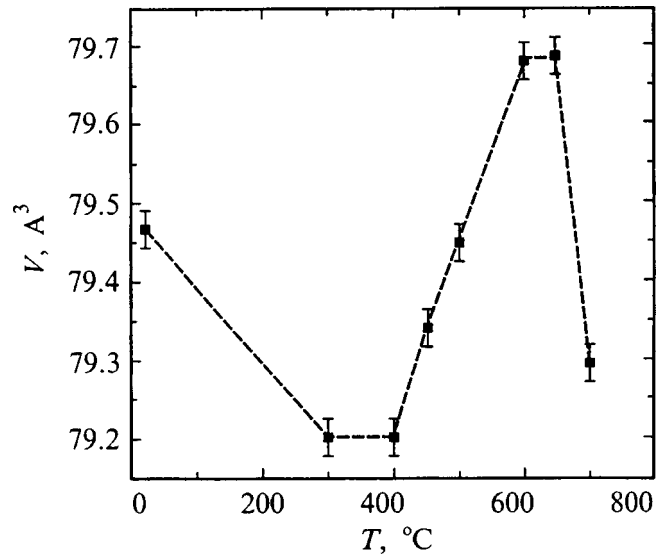

FIG. 2. Typical dependences of the readings of the derivatograph balance (the TG signal) for ''levitating'' (*1*) and ordinary (*2*) samples.

FIG. 4. Unit-cell volume of $Fe_{0.1}TiTe_2$ calculated from values of the crystallographic parameters as a function of the temperature prior to quenching.

strate. To test this hypothesis, we measured the electric charge on the (001) faces of an $Fe_{0.1}TiTe_2$ single crystal during heating. For this purpose, the short-circuit current of conductors connected to the various faces of the crystals was measured, and the potential of the faces was determined directly. The accuracies of the measurements were 1 μA and 1 μV, respectively. Neither method detected the appearance of a permanent surface charge.

The formation of macroscopic surface charges probably requires the presence of ferroelectric domains, whose restructuring with variation of the temperature can lead to fluctuations of the incompletely compensated charge. Such an explanation, however, can be reconciled with the fairly high conductivity of $Fe_{0.1}TiTe_2$ (Fig. 4) only under the additional assumption of high anisotropy of the electrical properties.

The possibility of the appearance of a state with domain fluctuations (switchings) was examined theoretically in a recent paper.[9] It was shown therein that a similar situation can be observed near the phase-transition point from the high-susceptibility phase to the distorted phase, which has a double-well potential. A microscopic mixture of nuclei of these phases has a triple-well potential.

The maintenance of the form of the x-ray diffraction pattern after the samples are quenched points to the absence of phases which appear or decay during quenching. It can be theorized that such phases are present as fragments with a short correlation length and are consequently inaccessible to x-ray analysis. The decrease in c_0 upon the intercalation of iron in $TiTe_2$ (Ref. 10) and the simultaneous decrease in conductivity[5] indicate that intercalation leads to the formation of covalent Ti–Fe–Ti centers, which tie the layers of the matrix lattice together. This situation has been observed in many compounds of the type M_xTiX_2 (M=Ag, Ti, Fe, Co, Ni; X=Se, Te).[10–12] The thermally activated temperature dependence of the conductivity of a slowly cooled sample (Fig. 5) indicates that all the electrons introduced with iron are localized at Ti–Fe–Ti centers. Taking into account that iron exists in the divalent state in Fe_xTiTe_2 (Ref. 10), such a center can be described as $Ti^{3+}-Fe^{2+}-Ti^{3+}$ in the approximation of ionic bonding. It can be theorized that these centers dissociate upon heating, releasing free electrons to the conduction band. The increase in conductivity with increasing temperature agrees well with this hypothesis. However, the lack of an increase in c_0 and even some decrease in the unit-cell volume upon heating provide evidence that dissociation takes place not according to the scheme $Ti^{3+}-Fe-Ti^{3+}\rightarrow Ti^{4+}-Fe-Ti^{4+}+2e$ (e is a free electron), but according to the scheme $Ti^{3+}-Fe-Ti^{3+}$ $\rightarrow Ti^{3+}-Fe-Ti^{4+}+1e$, which leads to maintenance of the covalent bonds tying the layers of the matrix lattice together. A $Ti^{3+}-Fe-Ti^{3+}$ (''2'') center, like a $Ti^{4+}-Fe-Ti^{4+}$ (''0'') center, has a single-well potential, while a $Ti^{3+}-Fe-Ti^{4+}$ (''1'') center has a double-well potential. Thus, a mixture of regions of the crystal lattice where centers of types ''1'' and ''2'' dominate can satisfy the conditions for the existence of domain fluctuations.[9] Therefore, a center of type ''1'' has a dipole moment oriented along a normal to the basal plane of the lattice. The cause of the association of centers in domains may be minimization of the energy of the elastic lattice dis-
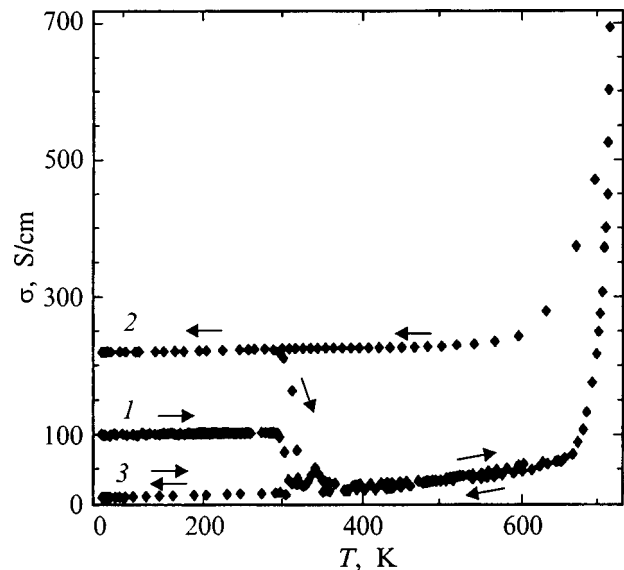

FIG. 5. Temperature dependence of the conductivity of $Fe_{0.1}TiTe_2$ for a sample after various heat treatments: *1* — quenching from 300 °C; *2* — quenching (dynamic regime) from 450 °C; *3* —slow cooling. The direction of the temperature variation is indicated by the arrows next to each curve.

tortions associated with each type of center. The fact that the rapidly cooled samples have a higher conductivity compared with the slowly cooled (equilibrium) sample can be evidence that rapid cooling fixes a state of the sample with a mixture of centers, leaving some of the electrons free. Dissociation of the centers is probably associated with kinetic hindrances, and the achievement of an equilibrium state requires a long time. In fact, samples held for a week at 350 °C exhibited an absence of ''levitation'' (see Fig. 1). It was shown in Ref. 9 that fluctuations can appear only in a very narrow range of values of the interaction parameters. Such conditions are probably created in part of a rapidly cooled sample as a result of the nonequilibrium process. The similarity of the results of rapid cooling from all temperatures below 600 °C is indicated by the identical slope of the temperature dependences of the DTA signal, which attests to a similar value for the specific heat of these samples. Thus, a temperature of 350 °C, from which quenching leads to ''levitation,'' is not characteristic; we were able to realize conditions for domain fluctuations under this rapid-cooling regime.

Under all the types of heat treatment the characteristic feature of the DTA curves is the presence of an endothermic effect at 440 °C, whose magnitude differs somewhat for different temperatures at the onset of rapid cooling and amounts to less than 1 J/g. The temperature of this effect is close to the melting point of tellurium, which can segregate as an impurity during heat treatment. Such a thermal effect can be caused by the presence of ~5 wt. % tellurium. This impurity was detected in the x-ray diffraction experiments, but in such cases they revealed an increase in the unit-cell volume of the $Fe_{0.1}TiTe_2$ samples quenched from temperatures above 440 °C, which attests to a possible connection between this endothermic effect and the phase transformation in $Fe_{0.1}TiTe_2$ itself.

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