THE PHENOMENON OF A HYSTERESIS IN $AgFeTe_2$ IN PHASE TRANSITION REGION

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The electric properties are investigated and the differential thermal analysis is carried out in $AgFeTe_2$. The additional PT are observed on the temperature dependence of DTA before and after SPT. The phenomenon of hysteresis is observed on the temperature dependences of electric properties in PT region in the direction of heating and cooling. The results are interpreted in the limits of DPT theory. It is shown, that the phenomenon of hysteresis is explained by the temperature dependence of the inclusion function in the second approximation of $L_2(T)$ and dL_2/dT. The diffusion region of PT and the width of hysteresis loop are defined. It is shown, that phase coexistence region is proportional to the width of hysteresis loop.

Introduction

The investigation of physical properties of bodies near and in PT region is the one of the developing directions of physics of solid body. The most actual task of the given direction is the definition of the region and diffusion degree of PT, the regularity of transition of one phase to another one, and also the thermodynamical parameter changes at PT. The double and triple argentum halcogenids, having structural PT, are the most suitable objects for the studying of these questions. In the last years the works in the given direction are carried out very intensive [1-14]. In a particular, in the refs [3-9], interpreting the expert results with DPT theory [15-16], PT parameters are calculated, defining the region and degree of diffusion, and also allowing to calculate the change of some thermodynamical parameters. For this is enough to define the temperature dependence of inclusion function $L_0(T)$ and its derivation on the temperature in the zero approximation dL_0/dT.

At the same time the phenomenon of hysteresis is observed at the investigation of electric and thermal properties of Ag_2Te near and in PT region in the direction of heating and cooling [17]. The DPT theory is applied for the explanation of phenomenon of hysteresis nature. It is proved, that the temperature dependence of inclusion function and its temperature velocity in the second approximation $L_2(T)$, $dL_2(dT)$ well enough explain the phenomenon of hysteresis.

The triple argentum halcogenid $AgFeTe_2$ is analog of Ag_2Te, has the structural phase transition, in it the phase transition is strongly scoured, the additional PT takes place [7]. Moreover, in the given work, with the aim of the result comparison and obtaining of new informations about phenomenon of hysteresis in argentum halcogenids, the electric properties of $AgFeTe_2$ in PT region in the direction of heating and cooling are investigated and differential thermal analysis (DTA) is carried out.

Experimental results

The measurement of electric properties and carrying out of differential thermal analysis are carried out on the installation, allowing to create the adiabatic and isotherm conditions [18].

The temperature dependence of DTA $T_y(T)$ in $AgFeTe_2$ is represented on the fig.1(a). As it is seen, the transitions (413 and 429K) with the absorption of few quantity of heating, revealing only in the adiabatic conditions take place before and after the main structural PT (423K). The temperature units are presented on the fig.1(b) in the directions of the heating and cooling.

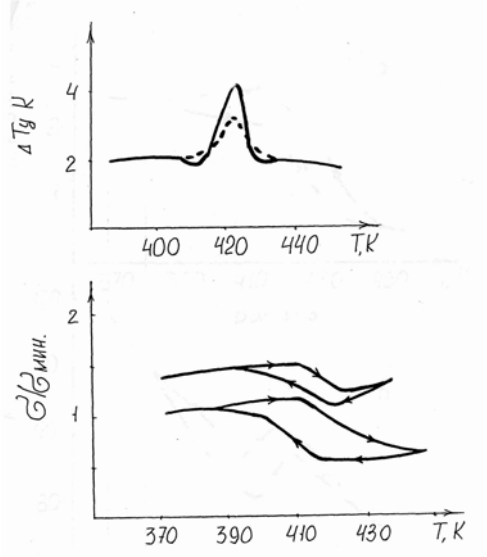

Fig.1. The temperature dependence of DTA $\Delta T_y(T)$ (α) and electroconductivity $\sigma/\sigma_{mun}^{(b)}$ in $AgFeTe_2$

It is seen, that PT begin in the heating direction, for example from the initial temperature of additional PT 410K and end at 430K for the sample with the higher electron concentration (p) PT. At the cooling the $\delta(T)$ curves goes below, than burned, than at the heating, the beginning and end of PT shift to the side of high T, the curves mix only at T=390K, i.e. the phenomenon of hysteresis with the big enough loop square is observed. The identical phenomenon is observed on the temperature dependencies of R (fig.2a) and therma (-----) (fig.2b). The hysteresis loop in the case of $\alpha(T)$ is more big, than in the cases of $\sigma(T)$ and $R(T)$. This is connected with the fact, that $\alpha(T)$ is measured at the presence of temperature drop in the sample deep, that leads to the additional diffusion of curves as at the heating, so at the cooling. It is need to note, that the additional transitions aren't significant on the temperature dependencies of electric properties of $AgFeTe_2$ in the difference from Ag_2Te [17]. Probably, this is connected with the fact, that the change of electric properties is insignificant and agrees by the direction with the change at the main PT, at the additional PT.

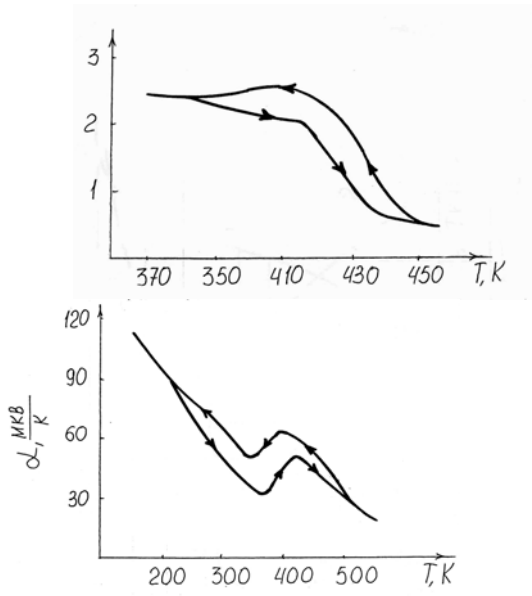

Fig.2. The temperature dependence of Hall coefficient *R(T)* *(α)* and thermoe.m.f. with *α(T)* in $AgFeTe_2$.

The result analysis

As it was mentioned, according to DPT theory, the temperature dependence of inclusion function in the zero approximation $L_0(T)$ allows us to understand and interpret the many PT peculiarities, in a particular, to reveal the law of mutual transition from the existing phases, to calculate PT parameters, defining the region and degree of diffusion, and also the change of some thermodynamical parameters in PT region. However, besides the general properties and regularities of PT, it is need to consider the another decomposition members of function *F(T)*, defining *L(T)*. The different values of $F_n(T)$ are correspond to the different approximations of $L_n(T)$

$$L_n^{(T)} = \frac{1}{1+exp\,F_n(T)} \tag{1}$$

As the zero approximation results are given in the refs. [3-9], so in this ref. we are limited by the consideration of first and second approximation (*n*=1 and 2), In DPT case [15,16]

$$F_1^{(T)} = a_0(T-T_0)+a_1(T-T_0)^2 \tag{2}$$

then

$$L_1^{(T)} = \frac{1}{1+exp\left[a_0(T-T_0)+a_1(T-T_0)^2\right]} \tag{3}$$

$$\frac{dL_1}{dT} = -\frac{a_0}{2\left[1+chF_1(T)\right]}\left[1+\frac{2a_1}{a_0}(T-T_0)\right] \tag{4}$$

In the second approximation of DPT

$$F_2^{(T)} = (T-T_0)\left[a_0+a_1(T-T_0)+a_2(T-T_2)^2\right] \tag{5}$$

$$L_2^{(T)} = \frac{1}{1+exp\,F_2(T)} \tag{6}$$

$$\frac{dL_2}{dT} = -\frac{a_0}{2\left[1+chF_2(T)\right]}\left[1+\frac{2a_1}{a_0}(T-T_0)+\frac{3a_2}{a_0}(T-T_0)^2\right] \tag{7}$$

The PT temperature is defined from the equations $F_1(T)=0$ and $F_2(T)=0$. The roots of the equation $F_1(T)=0$, are correspond to:

$$T_{0_1} = T_0\ ;\quad T_{0_2} = T_0 - \frac{a_0}{a_1} \tag{8}$$

In this case two PT take place at T_{0_1} and T_{0_2}. The one temperature is agree with T_0, and second temperature in the dependence on the values *a* and a_1 is shifted to the left or to the right from T_0. The second root of T_0 strives for the infinity at $\alpha_1 \to 0$.The temperature difference between both points of PT is equal

$$\Delta T_0 = T_{02} - T_{01} = -\frac{a_0}{a_1} \tag{9}$$

The roots of equation $F_2(T)=0$, are correspond to

$$T_{0_1} = T_0\ ;\ T_{0_2} = T_0 - \frac{a_1}{2a_2} + \sqrt{\left(\frac{a_1}{2a_1}\right)^2 - \frac{a_0}{a_2}} \tag{10}$$

$$T_{0_3} = T_0 - \frac{a_1}{2a_2} - \sqrt{\left(\frac{a_1}{2a_2}\right)^2 - \frac{a_0}{a_2}} \tag{11}$$

As it is seen, $F_2(T)$ takes place at in the second approximation. In the formulae (10) and (11), the substance roots are present the interest, that gives the limit on the constant decomposition coefficients α_0 ; α_1 ; α_2 according to which the inequality $a_1^2 > 4a_0a_2$ should be carried out, taking place at, $\alpha_0>0$, $\alpha_1>0$, $\alpha_2<0$ from which it is followed $T_{0_3} < T_0 < T_{0_2}$ .The negative value of α_2 proves the main demand, which is function *L*. At $T<<T_0$ $L_2 \to 0$, and at $T>>T_0$ $L_2 \to 1$.

The concrete crystal is need to define the parameter values α_0 , α_1, α_2 and T_0. for use of equations (3) - (7). The

values α_0 and T_0 are easily defined by the temperature dependences $\Delta T_y(T)$, $\sigma(T)$, $R(T)$, $\alpha(T)$ on the method, approved in the refs [3-9]. The obtained data α_0=0.17; and T_0=423 are almost agree with the data of the refs [4,7,2]. The value α_1 can be calculated by the given experimental data with the use of ratio (8), and value α_2 is estimated from the condition of corporeality limit of the roots (10) and (11).

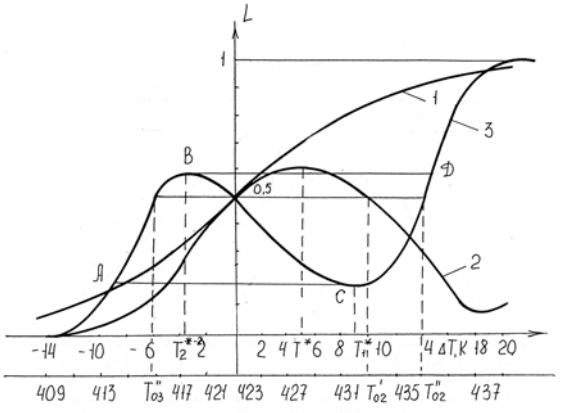

Fig.3. The temperature dependence of inclusion function in $AgFeTe_2$ 1 - $L_0(T)$; 2 - $L_0(T)$; 3- $L_0(T)$

The temperature dependences $L_1(T)$, $L_2(T)$ and dL_1/dT dL_2/dT at the obtained values for $AgFeTe_2$, α_0 =0.17; α_1 =0.017 and α_2 =-0.002 are given on the figures 3 and 4. The curves $L_0(T)$ and dL_0/dT at the zero approximation are given on these figures for the comparison. From the fig.3, it is seen, that $L_1(T)$ strongly differs from $L_0(T)$, especially in $T>T_0$ region. The curve $L_1(T)$ in the difference from $L_0(T)$ is asymmetrical in $T<T_0$ $L_1(T)$ region, $L_0(T)$ by the form looks like the curve $L_0(T)$, and in $T>T_0$ the extremum $\Delta T=T^*$=5K takes place, which connects with the diffusion region of PT. The conditions of $L_1(T)$ in this region are carried out at $T>>T_0$ (curve $L_1(T)$), going through the minimum at $\Delta T=18k$, strives for $kL>>1$). The value of the observable asymmetry is defined by the value α_1. The cross-section of horizontal line, taken from value $L_1=0.5$ (which is constant for every approximation), is equal to the temperature of second PT, T_{θ_2} =433K. It is seen, that T^* is between the both temperatures $L_1(T)T_0$=433K, the ratio $T^*=T_0+\alpha_\theta/2\alpha_1$ =428K is in the agreement.

According to the refs [15, 16], the one of the physical meaning of such stroke $L_1(T)$ can be in the case of one phase existence in the definite temperature interval $\left(T_{0_2}-T_0\right)$ in PT region. The experimental data and temperature dependence $L_0(T)$ (fig.3) for $AgFeTe_2$ show on the absence of such ΔT region, which are represented on the figures 1 and 2. In this purpose says the law of α phase transition in β phase, established in the ref [7]. But informations about the existence of such regions at PT meet in the signet crystals σ [16]. This is one of the possibilities, that's why in the common case it is need to consider another approximations of inclusion function under its derivation.

The temperature dependence $L_2(T)$ for $AgFeTe_2$, calculated on formulae (6) is given on the fig.3.

The look of this curve is strongly differs not only from curve $L_0(T)$, but the peaks situate on the left and right sides from T_0 axis, moreover they are asymmetrical according to the axis. According to DPT theory [15,16] the experimental value L_2 corresponds to the temperatures

$$T_1^* = T_0 - \frac{a_1}{3a_2} + D \text{ and } T_2^* = T_0 - \frac{a_1}{3a_2} - D \qquad (12)$$

where

$$D = \frac{1}{3a_1}\sqrt{a_1^{\,2} - 3a_0a_2}$$

The ratio $T_1^* > T_\theta > T_2^*$ takes place at $\alpha_0>0$, $\alpha_1>0$, the curve $L_2(T)$ is more asymmetrical and it tells on the values T_1=9K and T_2=4,4K correspondingly. The cross-section of horizontal line, taken from the point $L_2=0.5$ till the cross-section of the curve $L_2(T)$, corresponds to the temperatures of PT, T_{θ_2} =437K, T_{θ_3} =417K. The value for T_{0_2} , defined on $L_2(T)$ is bigger on the one degree, than on $L_1(T)$.

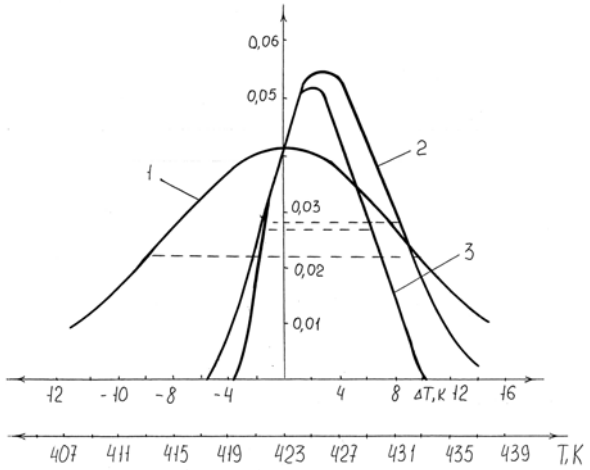

Fig. 4. Temperature dependence of PT velocity dL/dT in $AgFeTe_2$ 1 - dL_0/dT; 2- dL_1/dT; 3 - dL_2/dT

The temperature dependencies of the PT velocity in $AgFeTe_2$ in the zero dL_0/dT, first L_1/dT and second L_2/dT approximations of inclusion function are given on the fig.4. From these data the velocity asymmetry of transition reveals, i.e. maximums dL_1/dT and dL_2/dT aren't situated on the T_0 axis, but are shifted in the side $T>T_0$, the maximum values are significantly bigger, than dL_0/dT, moreover, the value $dL_1/dT > dL_2/dT$ is shifted to the side of big T maximums $d<1$. As it is mentioned, the asymmetry is defined by the value of dL_2/dT, in the expression of which (7) the parameter α_2 includes with the negative sign, that decreases the maximum value and shifts in the side of the more small T. According to theory, the horizontal line, taken on the half dL_0/dT, defines the diffusion region of PT. If the given method will be applied for dL_1/dT, dL_2/dT then we obtain dL_0/dT $2T^*=20K$ at dL_1/dT $2T^*=10.4K$ and at dL_2/dT $2T^*=9.5K$. As it is seen the values of diffusion region of PT at the first and second approximations are almost in two times less, than at the zero approximations. However, if we take into consideration the negative sides of dL_1/dT and

dL_2/dT, which aren't presented on the figure, then the agreement between data can be achieved.

The analysis of temperature dependence $L_2(T)$ gives in the ref [5], according to which one of the possible variants is that new phase appears in AB region (fig.3), disappears in BC region, and then it appears in CD region. The authors consider that such case is almost unreal however it is possible at the existence of several transitions, situated closely enough from each other on the temperature axis. However, the more possible is the case, which connects with the fact that BC region corresponds to some metastable system state in the definite interval.

Then, picturing BD and AC curves, we obtain the hysteresis loop ABDC.

The experimental data of electric and heat properties of double [3,6,8,9] and triple [4,7,9,11] argentum halcogenids show on the presence in them the additional PT[17]. That's why the given both mechanisms, leading to the appearance of phenomenon of hysteresis, can be applied not only to these crystals, but they even add each other.

The some information about PT diffusion and phenomenon of hysteresis can obtain from the data of hysteresis loop width. According to theory [15,16] the hysteresis loop width in the second approximation of $F_2(T)$ function is defined by the ratio

$$h_2 = T_{0_3} - T_{0_2} = 2\sqrt{\left(\frac{a_1}{2a_2}\right)^2 - \frac{a_0}{a_2}}\,. \qquad (13)$$

From this formulae it is seen, that phenomenon of hysteresis takes place only at the inequality $\alpha_1>4\alpha_0\alpha_2$ carrying out and hysteresis loop width is defined by the ratio's α_1/α_2. and α_0/α_2.. In the limit case of the loops the condition $\alpha_1<<-4\alpha_0\alpha_2$, the width $h_{m.c.}$ is defined as

$$h_{m.c} = 2\sqrt{-\frac{a_0}{a_2}}\left(1 - \frac{a_1^2}{8a_0a_2}\right) \qquad (14)$$

In the case of symmetrical loops h is defined as

$$h_c = \lim_{a\to 0} \approx 2\sqrt{-\frac{a_0}{a_2}} \qquad (15)$$

For crystals $AgFeTe_2$, the h values, calculated on the formulas (13)-(15) are equal to $h_2=20k$, $h_{m.c}=19.4k$ and $h_c=18.4k$. In the experiment, the hysteresis width in the dependence on the investigated effect and temperature region (in PT region) changes, moreover in the several cases the hysteresis loops are strongly asymmetrical. But asymmetries $L_1^{(T)}$ and $L_2^{(T)}$ for $AgFeTe_2$ are bigger, than in the case of model consideration [15, 16]. In a particular, the hysteresis loop width, found from $\sigma(T)$ $h=25$-$30K$. It can be said, that agreement of calculated values of h and experimental ones is good, except from $\sigma(T)$. About the reason, leading to the additional PT diffusion we said above.

The one of the important questions of investigations is the definition of the region of two phase ΔT coexistence. In the case of zero approximation, the definition of region ΔT, $L_0(T)$ and dL_0/dT is more simple, than in the cases $L_1(T)$, $L_2(T)$ and dL_1/dT dL_2/dT.

For the symmetrical loops ΔT can be defined as ref. [15]:

$$\Delta T \approx 2\left(T_2^* - T_{0_3}\right) \approx 2\left(T_{0_2} - T_1^*\right) \qquad (16)$$

For the loops with the small asymmetry with the exactness till the first order on α_1

$$T_{0_2} - T_1^* = \frac{1}{2}\left(1 - \frac{1}{\sqrt{3}}\right)h - \frac{a_1}{6a_2} \qquad (17)$$

$$T_2^* - T_{0_3} = \frac{1}{2}\left(1 - \frac{1}{\sqrt{3}}\right)h + \frac{a_1}{6a_2} \qquad (18)$$

For the total symmetrical loop α_1 =1 with the taking into consideration (13) as

$$\Delta T = \left(1 - \frac{1}{\sqrt{3}}\right)h = 0.42h\,. \qquad (19)$$

The calculations, done on (17) and (18) with the taking into consideration of corresponding h for $AgFeTe_2$, correspond to the values:

$$T_{0_2} - T^* = 5.5K, \quad T_2^* - T_{0_3} = 2.7K.$$

These data are in the agreement with the data on the fig.3. Thus, for the region of two phase coexistence we obtain: on $\Delta T = 2\left(T_{0_2} - T_1^*\right) = 11K$, on $\Delta T = 2\left(T^* - T_{0_3}\right) = 5.4K$ and in the case of total symmetry on $\Delta T = 0.42h_2 = 7.73K$.

These data show on the strong asymmetry of hysteresis loop in $AgFeTe_2$, and also show that temperature interval ΔT of two phase coexistence is less, than hysteresis loop width. From these data, it is followed, that coexistence interval.

Thus, from the given results and discussions, it is concluded, that taking into consideration the members of temperature difference $(T-T_0)$ in the function $F(x)$, defining the inclusion function $L_2(T)$, leads to the appearance of hysteresis.

The process carries out on the ACD curve at the heating and the process carries out on DBA curve at the cooling. The stroke along parts AB (at the heating) and DC (at the cooling) isn't benefit energetically, i.e. leads to the creation of BC metastable state region. From the above mentioned, it is followed, that thermodynamic formalism of DPT gives the principal possibility to explain the hysteresis presence. At the same time as in the limits of the general thermodynamic approach for point PT, the hysteresis interpretation is impossible without input of additional supposition.

[1] *S.A.Aliev, F.F.Aliev*. Neorg. Mater., 1989, 25, 2, 241. (in Russian).
[2] *S.A.Aliev, F.F.Aliev, G.P.Pashaev*. Neorg. Mater., 1993, 29, 8, 1073. (in Russian).
[3] *S.A.Aliev, F.F.Aliev, Z.S.Gasanov*. FP, 1998, 4, 9, 1693. (in Russian).
[4] *S.A.Aliyev, Z.S.Gasanov, S.M.Abdullayev*. Fizika Ins. Phys. NANA VIII 3,24, 2002
[5] *Z.S.Gasanov, S.M.Abdullaev, S.A.Aliev*. Az. Resp.Az. Univ. Nauch. Trudi fund. nauk., 3, 93, 2002. (in Russian).
[6] *S.A.Aliev, Z.S.Gasanov, Z.F.Agaev, R.K.Gusejnov*. AMEA, Izv. XXII 5, 76, 2002. (in Russian).
[7] *F.F.Aliev, E.M.Kerimova, S.A.Aliev*. FTP, 2002, 36, 8, 932. (in Russian).
[8] *Prof. Dr. Habil. Sabir Aliyev, Dr. Ziraddin Gasanov*. Abhandlunden dez WGB, Band 3, 98, Berlin 2003.
[9] *Prof. Dr. Habil. Sabir Aliyev, Dr. Ziraddin Gasanov, Dr. Zakir Agayev*. Dipl-Phys. Rasim Guseynov Abhandlunden dez WGB, Band 3, 103, Berlin 2003
[10] *С.А.Aliev, З.С.Гасанов,С.А.Abdullaev,R.K. Гусейнов*. Azer. Tekn. Univ. Nauch. Trudi, Fun., 4, 103, 2002. (in Russian).
[11] *S.V.Melnikova, A.V.Kartashev, V.A.Grankin, I.N.Flerov*. FP, 2003, 45, 8. (in Russian).
[12] *Z.S.Gasanov*. Nauch. trudi. MPGI.sb.stat.izd.Nauka, 200, 2003. (in Russian).
[13] *Z.S.Gasanov*. Nauch. trudi. MPGI.sb.stat.izd.Nauka, 205, 2003. (in Russian).
[14] *F.F.Aliev*. FTT, 2003, 37, 9. (in Russian).
[15] *B.N.Rolov*. Razmishiiye fazoviye perekhodi, 311s, Riga 1972. (in Russian).
[16] *B.N.Rolov, V.E.Jurkevich*. Fizika razmitikh fazovikh perekhodov. Izd. Rostovskogo Universiteta. 319s. 1983.
[17] *S.A.Aliev*. FTP,2004, t. 38, vip. 7, s. 830. (in Russian).
[18] *S.A.Aliev, Д. G.Arasly, etc*. Izv. AN Azerb. SSR, ser.. Fiz.-mat I tekh. nauk 6, 87, 1982. (in Russian).

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$AgFeTe_2$ KRİSTALINDA FAZA KEÇİDİ OBLASTINDA HİSTEREZİS HADİSƏSİ

$AgFeTe_2$ kristalında diferensial termiki analiz aparılmış və elektrik xassələri tədqiq olunmuşdur. SFK-dən əvvəl və sonra DTA asılılığında əlavə FK müşahidə olunmuşdur. FK oblastında elektrik xassələrin temperatur asılılığında qızma və soyuma zamanı histerezis müşahidə olunmuşdur. Nəticələr yayılmış faza keçidi nəzəriyyəsi əsasında təhlil olunmuşdur. Histerezis hadisəsi qoşulma funksiyasının və onun ikinci yaxınlaşmada yayılma sürətinin temperatur asılılığı ($L_2(T)$ və dL_2/dT) ilə izah olunur. FK-nın yayılma oblastı və histerezis ilgəyinin eni təyin olunmuşdur. Fazaların mövcud olduğu oblastın histerezis ilgəyinin eni ilə mütənasib olduğu göstərilmişdir.

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ЯВЛЕНИЕ ГИСТЕРЕЗИСА В $AgFeTe_2$ В ОБЛАСТИ ФАЗОВОГО ПЕРЕХОДА

Исследованы электрические свойства и проведен дифференциальный термический анализ в $AgFeTe_2$. На температурной зависимости ДТА до и после СФП обнаружены дополнительные ФП. На температурных зависимостях электрических свойств в области ФП в направлении нагрева и охлаждения обнаружено явление гистерезиса. Результаты интерпретированы в рамках теории РФП. Показано, что явление гистерезиса объясняется температурной зависимостью функции включения во втором приближении $L_2(T)$ и dL_2/dT. Определены области размытия ФП и ширина петли гистерезиса. Показано, что область сосуществования фаз пропорциональна ширине петли гистерезиса.

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