DETERMINATION OF DEFECTFORMATION PARAMETERS IN Ag_2Te

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On the basis of electrical, thermoelectrical and thermodynamic parameters the concentration of defects N and energy of defectformation in Ag_2Te up to and at phase transitions are calculated. It is shown that the transitions $\alpha \rightarrow \alpha'$ and $\beta' \rightarrow \beta$ occur in the sublattice of Ag_2Te structure, and the transition $\alpha' \rightarrow \beta'$ is accompanied simultaneously by a change of vacancy concentration of Te atoms in a lattice site and interstitial atoms of Ag in the sublattice. It is established that the probability of spontaneous formation of nuclei in the transitions $\alpha \rightarrow \alpha'$ and $\beta' \rightarrow \beta$ is less than in the $\alpha' \rightarrow \beta'$ transition.

Tellurid of silver belongs to compounds such as $Ag_2^{I}B^{VI}$, having native defects owing to an arrangement of silver atoms in interstitials and presence of vacancy at sites of a crystal lattice. The concentration of defects (N) in them increases with temperature and at certain temperature due to defects there is a structural phase transition (PT) accompanied by a drastic change of electrical, thermal and other physical parameters.

In the work [1] it is shown that in Ag_2Te PT from monoclinic α-phase into face-centered cubic β-phase is accompanied by additional transitions $\alpha \rightarrow \alpha'$ and $\beta' \rightarrow \beta$ approximately according to the scheme $\alpha_{385} \rightarrow \alpha'_{405} \rightarrow \beta'_{420} \rightarrow \beta_{440K}$.

A number of works [2-3] is devoted to study of defects in Ag_2Te. However, there is no information on the domain of PT in them, which is actual and important for an explanation of PT process, therefore a present work is devoted to determination of defectformation parameters in Ag_2Te up to and in the domain of PT.

METHOD OF CALCULATION

At present with reference to compounds $A^{I}_{2-x}B^{VI}$ there are two models of possible defects formation: models of Rau [4] and Weiss [5], in each of which there is a dominant type of defects causing a deviation from stoichiometry. In the first model it is necessary, that the formation of defect goes in two stages: the jump forms neutral vacancy of metal V_A, then there is an ionization of vacancy, therefore a hole is formed. Hence, the complete concentration of defects is determined as $N=V_A+V'_A$ and the holes concentration is $p=V'_A$.

In the second model the introduction of metal atoms in interstitials is possible: $A_i=A_i^+ + n$, where A_i, A_i^+ and n concentrations of neutral, ionized donors and electrons, respectively

A complete concentration of defects is

$$N = V_A + V'_A - A_i - A_i^+$$

or

$$N = V_A + p - A_i - n \qquad (1)$$

where $p - n = V'_A - A_i^+$

The concentrations V_A and A_i are determined by the method described in [3], p and n are determined according to [6],

$$p = \frac{(2m_p k_0 T)^{3/2}}{4\pi^{3/2}h^3} F_{r+1}(\mu_p^*)$$

$$n = \frac{(2m_n k_0 T)^{3/2}}{3\pi^2 h^3} I^0_{3/2,0}(\mu_n^*, \beta) \qquad (2)$$

Here m_n and m_p are effective masses of electrons and holes, $\beta=\varepsilon_g/k_0T$ is a parameter of nonparabolocity of a band, ε_g is a width of the forbidden band (7), $\mu_p^* = \mu_p/k_0T$ and $\mu_n^* = \mu_n/k_0T$, μ_p and μ_n are chemical potentials, $I^0_{3/2,0}(\mu_n^*, \beta)$ is two-parametric integral of Fermi. The chemical potentials, determined from the following expressions [6], are

$$\alpha_p = -\frac{k_0}{e}\left[\frac{F_{r+2}(\mu_p^*)}{F_{r+1}(\mu_p^*)} - \mu_p^*\right] \qquad (3),$$

$$\alpha_\infty = -\frac{k_0}{e}\left[\frac{I'_{3/2,0}(\mu_n^*, \beta)}{I_{3/2,0}(\mu_n^*, \beta)} - \mu_n^*\right] \qquad (4)$$

where α_p is a thermo-emf of holes at absence of magnetic field, α_∞ is a thermo-emf of electrons in strong magnetic fields, $F_r(\mu_p^*)$ and $I^m_{n,k}(\mu_n^*, \beta)$ are one and two-parametric integrals of Fermi, respectively.

In work [3] it was reported that Ag_2Te is characterized by the defects of Frenkel, vacancies of Ag in interstitials, appearing for the account of statistically arranged atoms of Ag in sublattice. Then on distribution of Frenkel [8],

$$N/N_0 = Ae^{-\varepsilon_\phi/k_0T} \quad (5)$$

where N_0 is a general concentration of at oms, A is an integer (close to 1), describing the quantity of identical interstitials in account on one atom of a lattice and ε_ϕ is an energy of defectformation, measured in electronvolts. Using values of N/N_0 it is possible to find ε_ϕ (see a table).

At PT the general concentration of defects is equal to $\left(N + N_i \frac{\Delta N}{N_0}\right)$, where N_i is a concentration of silver atoms in interstitials, which is determined by the method [3], ΔN is a change of concentration of defects at PT. The relation $\Delta N/N_0$ is calculated as follows. Frenkel [8] has put forward an idea about a dynamic balance of nuclei, which essence consists of a fact that at given temperature the nuclei, which sizes are less critical, fluctuationally arising and disappearing, are in some statistic balance. It Is equivalent to the existence of some set of constant nuclei with the sizes less critical.

In Ag_2Te factor, promoting stabilization phase of fluctuations, is presence of defects in a crystal lattice, which is caused by deformation of structure. From [8] it is possible to conclude that at critical temperatures (T_0) fluctuation volumes (V_ϕ) are more than elementary subsystems (V_0). It is possible to expect that the following in this case is fulfilled

$$(V_\phi - V_0)/V_0 = \Delta N/N_0 \quad (6)$$

where $V_\phi = ak_0T_0^2/Q_0$, $V_0 = ak_0T_HT_0/Q_0'd$ here α is a temperature constant of the transition [9], Q_0 and Q_0' are a heat of PT for unit of volume and mass accordingly and d is a density of a crystal. Using the data of α, T_0 and Q_0 [9] and d [10] it is possible to calculate $\Delta N/N_0$ (see the table).

The calculated data for three samples are given in the table.

Table

Defectformation parameters in Ag_2Te

zamples \ paramdtas	Tran-sition	$N\cdot10^{18}$ cm^{-3}	T_0, K	$V_\phi\cdot10^{20}$ cm^{-3}	$V_0\cdot10^{20}$ cm^{-3}	$\frac{\Delta N}{N_0}$ %	ε_ϕ, eV	$E_{\alpha t}$, Ccal/mol	B, eV	ε'_ϕ, eV	$\frac{dL}{dT}$	ΔH^* cal/mol	ΔS^* cal/mol K	Q_0^* cal/g
Ag_2Te		1,2	300				0,13							
	$\alpha\to\alpha'$	2,1	400	2,28	2,09	8,3	0,10	24,02	1,00	0,12	0,13	309	0,77	0,9
	$\alpha'\to\beta'$	6,0	416	0,82	0,42	48,0	0,07	20,01	0,08	0,05	0,17	1304	3,13	3,9
	$\beta'\to\beta$	2,8	432	2,90	2,66	8,3	0,12	23,51	1,30	0,11	0,14	285	0,69	0,83
Ag_2Te+ 0,75at% Te		22,0	300				0,13							
	$\alpha\to\alpha'$	41,0	394	1,70	1,57	7,6	0,12	23,80	0,99	0,20	0,14	412	0,52	1,2
	$\alpha'\to\beta'$	78,0	416	0,89	0,51	43,0	0,08	1961	0,06	0,05	0,18	1340	3,32	3,9
	$\beta'\to\beta$	39,0	430	2,38	2,21	11,7	0,11	23,1	1,04	0,13	0,15	343	0,80	1,0
Ag_2Te+ 0,25at% Ag		0,4	300				0,13							
	$\alpha\to\alpha'$	0,6	393	1,30	1,20	7,7	0,10	25,10	0,97	0,12	0,14	549	1,40	1,6
	$\alpha'\to\beta'$	1,2	414	0,73	0,42	42,0	0,06	2100	0,06	0,06	0,18	1407	3,41	4,1
	$\beta'\to\beta$	0,7	430	2,38	2,10	11,8	0,13	24,80	1,23	0,14	0,15	378	0,88	1,1

THE ANALYSIS OF THE RESULTS

As it is seen from the table, the value ε_ϕ for $\alpha\to\alpha'$ and $\beta'\to\beta$ transitions is more than for $\alpha'\to\beta'$. Apparently, it is connected to the following facts.

The temperature speed of transition dL/dT on the data [9] looks as follows:

$$(dL/dT)_{\alpha\to\alpha} < (dL/dT)_{\alpha\to\beta} > (dL/dT)_{\beta\to\beta}.$$

At the same time dL/dT depends on energy of activation E_α ($E_\alpha = RT_H^2/V\tau$ [11], R is a gas constant, τ is time of transition and V is a speed of heating), necessary for the transition to become allowed. With increase of temperature the internal energy of a crystal changes due to PT. If thus the crystal should pass through an intermediate state with energy exceeding energy of a final state, this intermediate state creates an energy barrier of height B, and the speed of transition is proportional to number of atoms having energy, sufficient for overcoming of this barrier, namely $\sim exp(-B/kT)$. If the portion of such atoms is less than unit, the speed of a transition is small. If the intermediate state of high energy does not prevent a transition, such transition occurs rapidly [12]. B can be determined, as the energy of activation of one defect (or energy of ionization of vacancy), i.e. $B = E_0/N'$, where $N' = N_i\frac{\Delta N}{N_0}$ Accordingly [12] it is possible to mention that the large value of B, ε_ϕ and small $\Delta N/N$ and dL/dT for $\alpha\to\alpha'$ and $\beta'\to\beta$ transitions testify that these transitions are limited by a speed of duffusion or carry of Ag from α- phase into α'- phase and from β'- phase into β - phase. It means that the atoms of Ag are hardly displaced from initial positions, that does not cause changes of symmetry of Ag_2Te structure and the transitions $\alpha\to\alpha'$and $\beta'\to\beta$ are of displacement type [9].

The high values of dL/dT and small B and ε_ϕ at the $\alpha'\to\beta'$ transition testify that the atoms Ag and Te easily overcome possible energy barriers (B) and the transition occurs rapidly.

For understanding of the received results about the $\alpha\to\alpha'$ and $\beta'\to\beta$ transitions it is necessary to note the following. As it is known [13], in Ag2Te structure in sites of monoclinic (α) and face-centered (β) cubic lattice the atoms of Te

(anions) and cations of Ag in interstitials in several positions forming sublattice are located. For displacement of Te atoms high ΔH (change of enthalpy at PT) is required, what is not energetically favourable. Therefore low ΔH at $\alpha \rightarrow \alpha'$ and $\beta' \rightarrow \beta$ transitions are provided only with displacement of Ag atoms. Due to their displacement relatively to Te atoms in a direction of one of a lattice edges to a new position there is a rearrengement in sublattice. Thus the changes of interatoms distances because of displacement of Ag atoms do not exceed the sizes of elementary cells, and for displacement of Ag high heat Q_0 is not required [9].

The authors [14] consider that the transition in a state of superionic conductivity (SIC) in $Cu_{2-x}Se$ is complex transformation of evtectic type. The occurrence of SIC in β-phase of Cu_2Se is caused by disorder of cation sublattice. In [15] it is also noted that PT in superionic state, when cation lattice is completely disordered, can preceed PT with partial ordering. The authors [16] on curve temperature dependence of ionic conductivity at room temperature have found PT, which has been attributed to the second order PT .

It is known that all compounds such as $A_2^{I}B^{VI}$ belong to SIC group, in particular in Ag_2Te interstitial ions of Ag^+ have high mobility and can be ordered before and after the $\alpha' \rightarrow \beta$ transition in sublattice, as a result the $\alpha \rightarrow \alpha'$ and $\beta' \rightarrow \beta$ transitions occur.

ABOUT THE MECHANIZM OF TEMPERATURE SMEARING OF TRANSITIONS

Using as a base the assumption [17], it is possible to accept that unit of volume of a crystal is divided into N areas, where $N^{-1}=V_0$ is the volume of one area accordingly. At temperatures close to T_0, i.e. "macroscopic" PT, state in microareas more and more intensively fluctuates, thus the ratio of number of areas not "transformed" (n') to number of spontaneously formed nuclei ($N-n'$), determined in each moment of time, varies depending on a temperature change. The probability of phase fluctuation in volume $exp(-V_\phi \Delta\Phi/kT)$, where change of thermodynamic potential ($\Delta\Phi$) under state of $\Delta T=T_0-T<<T_0$ is determined by expression $\Delta\Phi=Q_0\Delta T/T$ [18]. It is possible to assume that there is a connection between the ratio $\Delta N/N$ and $exp(-V_\phi \Delta\Phi/kT)$, i.e. for definition of $\Delta N/N$ there is

$$\Delta N/N=exp(-V_\phi \Delta\Phi/kT) \qquad (7)$$

Further more the question is reduced to a low value of $\Delta N/N$ and a large value of "smearing" $T_0/\Delta S$ (ΔS is a change of enthropy at PT) at the $\alpha \rightarrow \alpha'$ and $\beta' \rightarrow \beta$ transitions. It can occur by two reasons: 1) the probability of spontaneous formation of nuclei is small; 2) the structure of Ag_2Te does not allow an occurrence of distinct PT in the sublattice.

In case of Ag_2Te in the $\alpha \rightarrow \alpha'$ and $\beta' \rightarrow \beta$ transitions the probability of phase fluctuation (~7-10 %) is small, i.e. because of a high value of B the spontaneous formation of nuclei is weak. Thus transition of Ag atoms from one sublattice to another, on account of large ionic radius of Te, needs the large energy of activation E_α (see the table). Here the multiplicity of ratio of the periods of sublattice of different phases and closeness of parameters "c"and "a" low- and high- temperature phases correspondingly are possible, that does not cause a delay of the transition in time and on temperature, not observable experimentally [9]. The heat of transition Q_0 can result in weak change of interatom interaction at a variation of lengths and number of bonds. Therefore insignificant change of Ag_2Te structure can entail to evolutionary passage of PT in time and on temperature.

So, the offered versions are in complete agreement with experimental and calculated data.

A small value of $T_0/\Delta S$ and large values of Q_0 and $\Delta N/N$ at the $\alpha' \rightarrow \beta'$ transition cause preservation of distinct PT at T_0~415K. The high probability of fluctuation phase (~45 %) allows to assert that the essential spontaneous formation of nuclei takes place at the $\alpha' \rightarrow \beta'$ transition.

In Ag_2Te the $\alpha' \rightarrow \beta'$ transition is related to "order - disorder" category, for which the drastic change of the ratio of a number of disordered atoms of Ag to a number of interstitials is characteristic. It results in a growth of a number of defects: numbers of vacancies of Te atoms in sites and Ag atoms in interstitials, causing rearrangement in both lattices.

Thus, in Ag_2Te the $\alpha' \rightarrow \beta'$ transition is accompanied simultaneously by a change of a number of vacancies of Te atoms in the lattice and Ag atoms in interstitials of the sublattice.

[1] *J. Bartkowicz, S. Mrowec.* J.Phys. Stat. Sol., 1972, 42, 1, 101. *Andre and C. Simon.* J.Phys. Chem. Sol., 1983, 42, 295.

[2] *H. Rau.* J. Phys. Chem. Sol., 1974, v.35, №11, pp. 1553-1559.

[3] Sol. Stat. Comm., 1975, v.16, №8, pp.1041-1042.

[4] *K. Weiss.* Phys. Chem., 1969, v.75, pp.338-344.

[5] *B.M. Askerov.* Kinetik effects in semiconductors. L., "Nauka", 1970, s. 303 (in Russian)

[6] *Ya.I. Frenkel.* Statisticheskaya fizika M-L. Izd-vo AS USSR, 1958, s. 264. 8 (in Russian)

[7] *S.A. Aliev, F.F. Aliev, I.S. Qasanov.* FTP, 1998, t.40, №9, s.1693-1697 (in Russian).

[8] *V.M. Qlazov, N.M. Maxmudova.* Neorgan. materiali, 1970, t1, №8, s. 1409-1415 (in Russian).

[9] *Q.O. Piloyan.* Vvedenie v teoriyu termicheskoqo analiza. Nauka, 1962, s. 264 (in Russian)

[10] *M.D. Berger.* Kristallog. 1971, t.16, №3, s.1084-1092 (in Russian).

[11] Kristallokhimicheskie, fiziko-khimicheskie i fizicheskie svoystva poluprovodnikovikh veshestv. M. Izd-vo standartov. 1973, s. 101(in Russian).

[12] *N.X. Abrikosova, V.F. Baukina, M.A. Korjiev i dr.* FTP, 1983, t. 25, №10, s. 2911 (in Russian).

[13] *Y.Ya. Gurevich, Q.V. Reznik, Y.I. Kharkach.* FTP, 1978, t. 20, №6, s. 1661 in Russian).

[14] *E.S. Krupnikov, F.Y. Aliev, A.Q. Abdullaev.* FTP, 1983, t.25, №10, s. 2911(in Russian).

[15] *V.A. Ginzburq.* FTP, 1960, t.2, №9, s. 2031-2035(in Russian).

[16] *V.Ya. Frichberq, B.I. Rolov.* Izv. AN SSSR, S. Fizika. 1964, XXVIII, №4, s. 649-652 (in Russian)

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Ag_2Te KRİSTALINDA DEFEKTƏMƏLƏGƏLMƏ PARAMETRLƏRİNİN TƏYİNİ

Ag_2Te kristalında elektrikkeçirmə, termoeds və termodinamik parametrlərin əsasında defektəmələgəlmə parametrləri, konsentrasiya, defektərin əmələgəlmə enerjisi və faza fluktuasiya ehtimalı faza keçidlərində təyin olunmuşdur. Alınan hesablama nəticələri göstərmişdir ki, $\alpha \rightarrow \alpha'$ və $\beta' \rightarrow \beta$ keçidi alt qəfəsdə, $\alpha' \rightarrow \beta'$ keçidi isə əsas qəfəsdə baş verir. Müəyyən olunmuşdur ki, özəklərin spontan əmələ gəlməsi $\alpha \rightarrow \alpha'$ və $\beta' \rightarrow \beta$ keçidində azdır, nəinki $\alpha' \rightarrow \beta'$ kecidində.

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ОПРЕДЕЛЕНИЕ ПАРАМЕТРОВ ДЕФЕКТООБРАЗОВАНИЯ В Ag_2Te

На основании электрических, термоэлектрических и термодинамических параметров рассчитаны концентрации дефектов и энергия дефектообразования, а также вероятность фазовой флуктуации в Ag_2Te при фазовых переходах. Анализ расчетных результатов показал, что переходы $\alpha \rightarrow \alpha'$ и $\beta' \rightarrow \beta$ происходят в подрешетке структуры, а переход $\alpha' \rightarrow \beta'$ сопровождается одновременно изменением числа вакансии атомов Te в решетке и Ag в междоузлиях подрешетки. Установлено, что вероятность спонтанного образования зародышей в переходах $\alpha \rightarrow \alpha'$ и $\beta' \rightarrow \beta$ меньше, чем в $\alpha' \rightarrow \beta'$ переходе.

Received:30.04.01