

## THE COMPENSATION EFFECT DURING DIFFUSION ALONG ISOLATED TIN-GERMANIUM PHASE INTERFACES\*

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(Received 19 January 1983)

The diffusion of indium along a number of isolated twist boundaries  $\langle 001 \rangle$  in the tin-germanium system is studied. A linear dependence between activation energy of boundary diffusion and the logarithm of the pre-exponential multiplier, the compensation effect, is revealed. The compensation temperature at which the values of the diffusion coefficient are the same for all the boundaries is different for the low- (313-433 K) and high-temperature (453-493 K) ranges. In the low-temperature range it is close to the allotropic transformation point in tin, in the high-temperature range to the melting temperature. The temperature dependence of the coefficient of volume diffusion is found to deviate from the Arrhenius law. The effect is analyzed phenomenologically and it is suggested that there is a possible connection between the diffusion kinetics and first-order phase transformations in the system.

The kinetic compensation effect, that is, the linear dependence between changes of activation energy and the logarithm of the pre-exponential multiplier, has been observed in the study of systems which differ greatly in chemical, biochemical, physical and other respects. The theory of the compensation effect has not yet been developed. Some investigators have even attributed it to peculiarities of the measurement procedure [1].

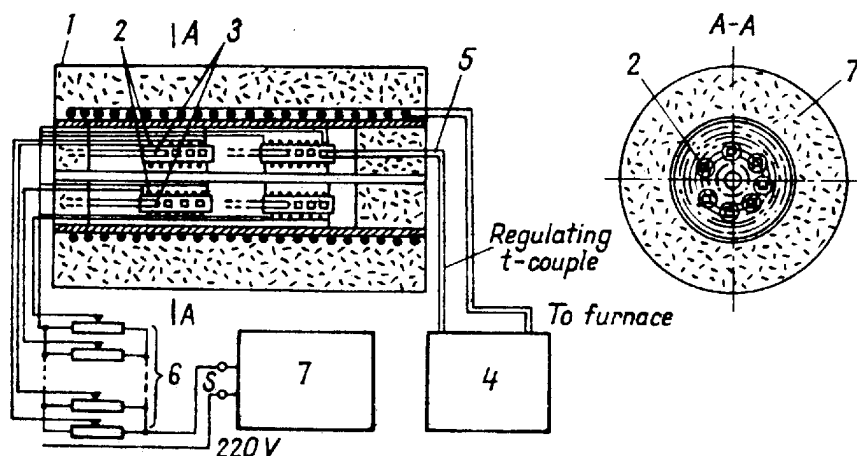


FIG. 1. Apparatus for simultaneous annealing at 12 temperatures.

The effect has already been observed during grain boundary migration in aluminium and zinc [2, 3], and during diffusion of zinc on grain boundaries in aluminium [4].<sup>†</sup> In all those cases the compensa-

\* *Phys. metal. metallog.*, 56, No. 5, 979-984, 1983.

<sup>†</sup> The compensation effect has also been observed during diffusion of different substitutional impurities in one matrix [5].

tion temperature at which the values of the kinetic coefficient are the same for all the boundaries was close to the melting point.

In a previous investigation [6] we have studied the diffusion of indium on Sn–Ge  $\langle 001 \rangle$  twist boundaries in the temperature range 313–433 K. A linear dependence is observed between the activation of boundary diffusion  $E'$  and the value  $\ln D'_0 \delta$  ( $D'_0$  – pre-exponential multiplier of boundary diffusion;  $\delta$  – diffusion width of boundary) for all 23 investigated boundaries over a wide range of variation of the parameters. The compensation temperature ( $T_c = 300$  K) lies below the investigated range and is close to the  $\alpha$ -Sn– $\beta$ -Sn phase transition point (290 K [7]). That led us to think that there might be a connection between the diffusion compensation effect and the presence of a first-order phase transformation in the system. If that were so, we should expect a second compensation point to exist in the high-temperature range, near the melting point. We therefore decided to take measurements on phase interfaces of the tin–germanium system in that range.

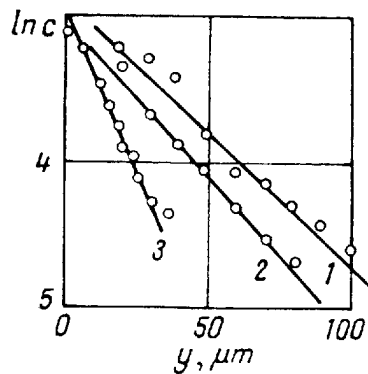


FIG. 2

FIG. 2. Dependence of indium concentration  $c$  near phase interface on distance from surface  $y$  for Sn–Ge  $\langle 001 \rangle$  twist boundary, misorientation  $14^\circ$ , temperatures: 1–489.9; 2–482.3; 3–466.2 K.

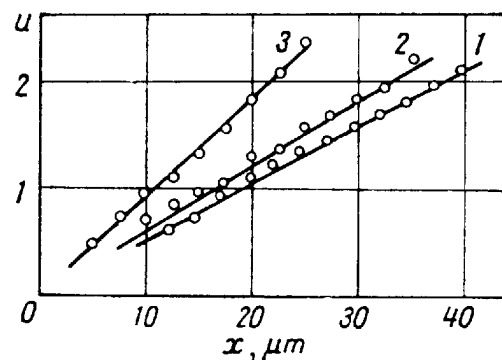


FIG. 3

FIG. 3. Coefficient of volume diffusion of indium in tin: 1–482.3; 2–480.7; 3–456.5 K.

There was another reason for taking high-temperature measurements. In [6], besides boundary diffusion, we studied the temperature dependence of the coefficient of volume diffusion of indium in tin. The results were very different from published data [8]: the activation energy was almost half, and the pre-exponential 7 orders of magnitude smaller than in [8]. However, the measurements in [8] were taken in the high-temperature range (453–493 K). For comparability we needed to repeat those measurements with our experimental procedure.

We studied the diffusion of indium on six  $\langle 001 \rangle$  twist boundaries of the Sn–Ge system with angles of turn  $\varphi$  of axes  $\langle 100 \rangle$  in the plane of the boundary 2, 3, 10, 14, 39 and  $40^\circ$  in the temperature range 453–493 K, close to the melting point of tin (505 K). The narrow temperature range and the required accuracy demanded a large number of diffusion anneals with small temperature step ( $\sim 3^\circ$ ). A special apparatus was designed for that purpose (Fig. 1), comprising thermostat 1, in which were placed 12 small ovens 2 with separate heating coils and verifying thermocouples 3. The temperature in the thermostat ( $\sim 450$  K) was maintained to within  $\pm 0.2$  K with the help of the VRT-3 automatic instrument 4. Regulating thermocouple 5 was placed in one of the small ovens. Voltage from stabilized supply 7 was fed to the coils via dividers 6, used to select the temperatures in the 12 ovens (456.5; 458.9; 649.5; 464.1; 466.2; 469.7; 473.8; 549.9; 480.7; 482.3; 485.1; 489.9 K for specimens with  $\varphi = 2, 3, 10$  and  $14^\circ$ ; specimens with  $\varphi = 39$  and  $40^\circ$  were annealed at 453.2; 456.1; 464.6; 481.1 and 483.1 K). There was a thermocouple in each oven; the temperatures were checked throughout diffusion annealing and did not

vary by more than  $\pm 0.5$  K. The important feature of the annealing apparatus is that equal temperature changes took place simultaneously in all the ovens. The accuracy with which the temperature difference between any pair of ovens was maintained was therefore much higher than  $\pm 0.5$  K. The annealing lasted 8 hr ( $28.8 \times 10^3$  sec). The coefficients  $D'\delta$  and  $D$  of boundary and volume diffusion were determined with the method previously developed (see [6]) using dependences of the form  $\ln c - y$  (Fig. 2) and  $U(k)$  (Fig. 3), where  $U$  is found from the equation  $1 - c/c_0 = \text{erf}(U/\sqrt{2})$ .  $c$  is the indium concentration,  $c_0$  - maximum solubility. The Fisher method was used to calculate  $D'\delta$ .

## RESULTS AND DISCUSSION

The temperature dependence of the coefficient of volume diffusion of indium in tin in the range 313–490 K is shown in Fig. 4. (The low-temperature results are taken from [6]). The curve has the same shape as the anomalous diffusion curves, for  $\beta$ -titanium or  $\beta$ -zirconium, for instance, but with much

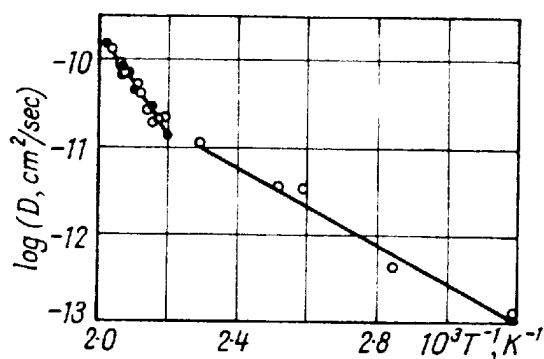


FIG. 4. Temperature dependence of coefficient of volume diffusion of indium in tin:  $\circ$  - present investigation;  $\bullet$  - [8].

greater curvature. Two intercepts with different slopes are observed, near the melting point and near the  $\alpha$ -Sn- $\beta$ -Sn transition. In the high-temperature range  $E$  was  $22.5 \pm 0.5$  kcal/mole, the pre-exponential multiplier  $D_0$  was equal to  $18 \pm 3$  cm<sup>2</sup>/sec, while in the low-temperature range they were found to be

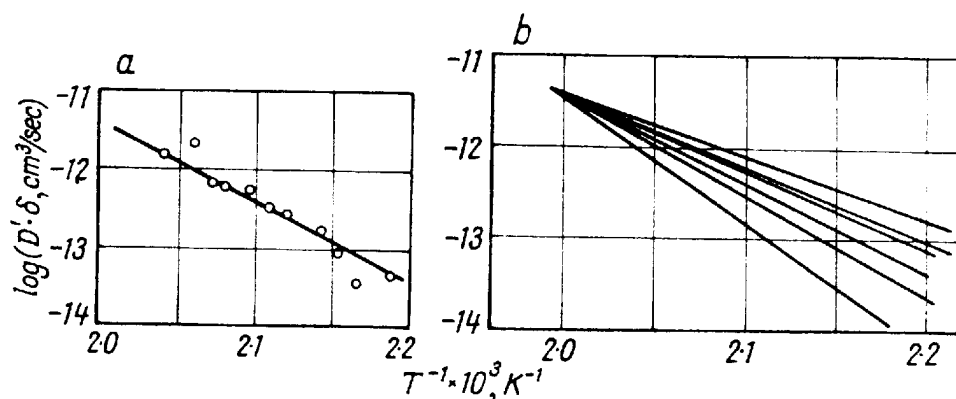


FIG. 5. Temperature dependences of  $D/\delta$ : a -  $\varphi = 14^\circ$ ; b - experimental straight lines for  $\varphi = 2, 3, 10, 14, 39$  and  $40^\circ$ .

$12.2 \pm 0.1$  kcal/mole and  $(2.2 \pm 0.1) \times 10^{-6}$  cm<sup>2</sup>/sec. There is a transitional region between 410 and 460 K. The results on diffusion of indium in tin from [8] are also shown.

Figure 5 shows a) the temperature dependences of the product  $D'\delta$  for one boundary ( $\varphi = 14^\circ$ ),

together with b) those for six boundaries on one graph, and Fig. 6 shows  $E'$  vs.  $\ln(D_0\delta)$ . A second compensation point is observed at 505 K, close to the melting point of tin.

The high values of the activation energy of boundary diffusion compared with volume diffusion of indium in tin are interesting. Indeed, the  $E'/E$  ratio is 1.5–2.5, whereas it is not more than one for grain boundaries and normally lies in the range 0.4–0.7 [4, 9, 10].

Although the theory of the compensation effect has not been developed, it is known that the effect is only observed in certain related systems. It has been suggested that the presence of the compensation effect is evidence for a single "mechanism" for the basic process [10]. Let us elaborate this idea.

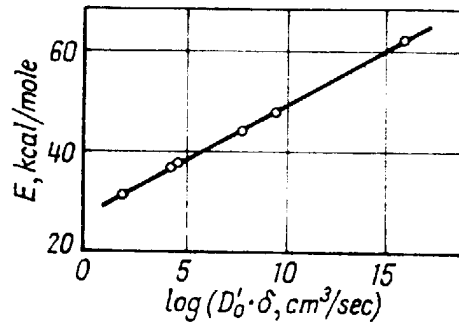


FIG. 6. Dependence of activation energy of indium diffusion on six Sn-Fe  $\langle 100 \rangle$  twist boundaries on logarithm of pre-exponential multiplier in range 457–490 K.

Suppose that for certain systems which are similar in some sense there exists a parameter  $\lambda$  which varies by a small amount on transition from one system to another (it could be pressure, composition, boundary surface tension in the case of boundary diffusion, and so on). Suppose also that the Arrhenius law is satisfied for each system:

$$D = D_0 \exp\left(-\frac{E^*}{kT}\right). \quad (1)$$

We write it in the form

$$\ln D = \frac{S^*}{k} - \frac{E^*}{kT}, \quad (2)$$

where  $S^* = k \ln D_0$ . We choose the origin for  $\lambda$  so that the equation  $\lambda = 0$  applies to one of the systems. Confining ourselves to linear terms in  $\lambda$ , since  $\lambda$  is small, we have

$$\ln D_0 = \frac{S^*(0) + (dS^*/d\lambda)|_{\lambda=0} \lambda}{k}, \quad (3)$$

$$E^* = E^*(0) + (dE^*/d\lambda)|_{\lambda=0} \lambda, \quad (4)$$

so that there is a linear relation of the following form between  $\ln D_0$  and  $E^*$

$$\ln D_0 = \frac{S^*(0) - E^*(0)/T_c}{k} + \frac{E^*}{kT_c}, \quad (5)$$

where

$$T_c = \frac{(dE^*/d\lambda)|_{\lambda=0}}{(dS^*/d\lambda)|_{\lambda=0}} = \left(\frac{dE^*}{dS^*}\right)_{\lambda=0} \quad (6)$$

(the derivatives are taken with constant parameters, apart from  $\lambda$ ).  $T_c$  is the compensation temperature:  $D$  has the same value for all the systems at that temperature, since the changes of the pre-exponential for different  $\lambda$  are compensated by the change in activation energy.

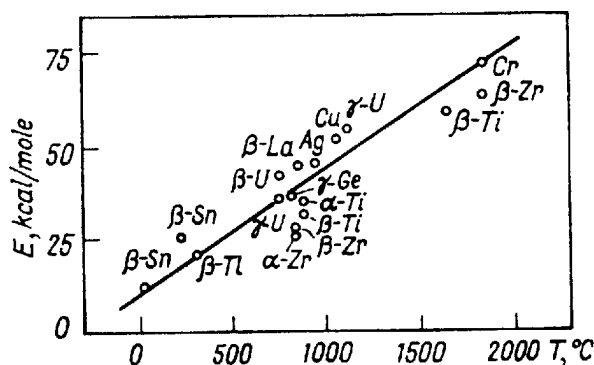


FIG. 7. Correlation between activation energy of volume self-diffusion and melting or allotropic transformation points.

The Arrhenius dependence is normally explained in terms of atomic transitions across a “potential barrier” [10]. Energy  $E' = E + E^*$  and entropy  $S' = S + S^*$  can be ascribed to an atom at the barrier ( $E$  and  $S$  the energy and entropy of an atom in the volume). Formally, this means that we can regard the state “at the barrier” as a special “barrier” phase with its own “thermodynamic functions” and “equation of state”. The compensation temperature

$$T_c = \frac{dE' - dE}{dS' - dS} = \frac{d\Delta E}{d\Delta S} \tag{7}$$

then signifies the hypothetical temperature of equilibrium between volume and barrier phases. In no way do we wish to interpret these words in their normal sense, but the fact that the compensation temperature normally lies near the first-order phase transition point suggests that the thermodynamic properties of the barrier phase are close to those of the (temperature-wise) close volume phase.

In addition to the closeness of  $T_c$  and the transition temperature, the known correlation between the activation energy of volume self-diffusion and the melting temperature also suggests that there:

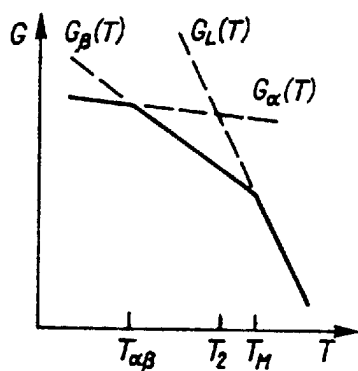


FIG. 8

FIG. 8. Diagrammatic temperature dependence of free energy  $G$  for system with first-order phase transition at  $T_{\alpha\beta}$ .

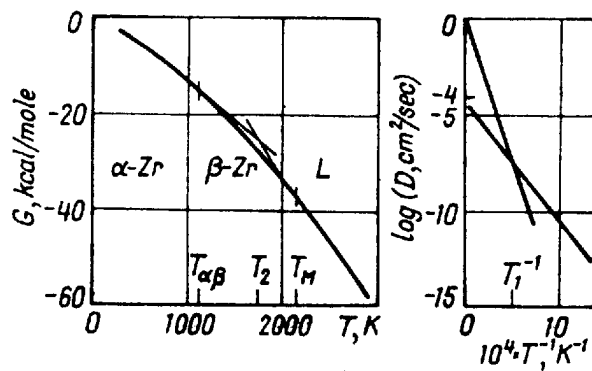


FIG. 9

FIG. 9. Temperature dependence of free energy  $G$  ( $T = 1750$  K) and coefficient of volume diffusion ( $T_1 = 1850$  K) for Zr [7, 12].

is a relation between diffusion and phase transitions [11]. That correlation is destroyed in systems with allotropic transformations, which typically have an anomalous temperature dependence of the diffusion coefficient, but it is observed if the allotropic transformation temperature is substituted for the melting point (Fig. 7). As we have mentioned, we have discovered that volume diffusion of indium in tin follows an anomalous temperature dependence.

Thus, in the range of temperatures close to the melting point the elementary diffusion event is connected in some way with melting, and near the allotropic transformation point with that transformation. It is reasonable to suggest that the major contribution to diffusion is made by "reversion" to the more stable of the two "competing" phases, given that both phases are metastable. Figure 8 shows a schematic temperature curve of free energy  $G$  for a system with two phase transitions. The dashed lines show the respective metastable continuations of  $G(T)$  for adjacent phases. If the hypothesis is valid, the transitional region on the anomalous  $\ln D$  vs.  $1/T$  curve should lie near the point of intersection of those dashed lines. Our analysis of self-diffusion in zirconium (Fig. 9) confirms that deduction.

## CONCLUSION

Our results, together with analysis of published data, show that the elementary diffusion act in solids can be associated with phase transformations in the system (melting and the allotropic transformation). It can be suggested that it is connected with the formation of heterophase fluctuations in the system.

That can be used to explain and predict anomalies of the temperature curve of diffusion coefficients, calculate the position of the transitional range (see Figs. 9 and 4) and estimate the diffusion activation energy on the basis of the correlation with the allotropic transformation point.

A clear indication of a relation between diffusion and phase transformations in the system is the compensation effect, which we consider to be not an artefact, but rather to be associated with the physical nature of diffusion events.

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