

DIFFUSION OF INDIUM ALONG [001] Sn–Ge INTERPHASE BOUNDARIES: PREWETTING PHASE TRANSITION AND CRITICAL PHENOMENA

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Summary

The diffusion of indium along the [001] Sn–Ge interphase twist boundaries has been studied in the vicinity of the β – γ' transition in the Sn–In system. The temperature of the β – γ' transition in the interphase boundaries is lower than that in the bulk and depends on the boundary misorientation angle. Strong violations of the Arrhenius law were observed at the Sn–Ge interphase boundaries near the temperature of the β – γ' boundary transition. Such violations were not observed in the twist boundaries in tin. The critical index for the $D'\delta$ product above T_c^B was calculated using the thermodynamical theory. The theoretical value is in good agreement with experimental values. The model of heterophase fluctuations and the idea of the prewetting phase transition enabled us to explain the observed value of the critical index for $D'\delta$ below T_c^B .

1. Introduction

In a previous work [1] we have found that in the Sn–In system the β – γ' phase transition in grain boundaries takes place at a lower temperature than in the bulk. The temperature of the β – γ' phase transition in the bulk and in the boundaries respectively was determined from the discontinuities in the temperature dependences of the coefficients of bulk and grain boundary diffusion at indium concentrations between 2 and 8 at.%. It was found that the temperature of this grain boundary phase transition in the Sn–In alloy depends on the grain boundary misorientation angle. This dependence is explainable under the assumption that the β – γ' transformation (a “weak” first-order phase transition) occurs in the grain boundaries analogous to the prewetting phase transition on external surfaces [2–4].

Various theories [4] predict that the details of wetting and prewetting transitions depend strongly upon interatomic potentials and the atomic structure of interfaces. We consider a lattice gas model of the following kind (according to Pandit *et al.* [5]): atoms occupy the sites of a semi-infinite homogeneous lattice placed on a substrate. We denote the potential of the nearest neighbour inter-

actions by V , whereas the potential of attraction of the atomic layer next to the substrate by the substrate is denoted by U . Under some circumstances, such a model undergoes a wetting transition. If the condition $0.7 \leq U/V \leq 0.9$ is satisfied, the wetting transition is of first order and the corresponding prewetting transition also exists. When the ratio U/V decreases (*i.e.* a lowering of the attractive potential of a substrate) then the temperature T_w of the wetting transition increases. If $U/V \leq 0.7$, a second-order wetting transition occurs, with a strongly developed fluctuation phenomenon.

In our previous work [1] we investigated grain boundaries in tin. The tin bicrystal may be considered as a semi-infinite single crystal placed on a substrate (formed by another single crystal) misoriented with respect to the first one. In such a presentation, the potential U is strong enough to be comparable with the energy of interatomic interaction in a lattice. Indeed, the temperature of the grain boundary phase transition was found to be considerably lower than that for the bulk, the temperature dependence of the grain boundary diffusion coefficient exhibiting large gaps. The latter circumstance indicated quite definitely that we are dealing with the first-order transition.

It would be very interesting to investigate either the second-order phase transitions on interfaces or the first-order transitions which are close to them. In such a transition, strongly developed fluctuations may lead to interesting physical effects. It is clear from the above that such a transition may be observed in systems with a low U value, *i.e.* when the atomic interaction with the substrate is weak. In our experiments, we chose the Sn–Ge interphase boundaries. The absence of any solubility in the Sn–Ge system means that the potential of the Sn–Ge interaction is considerably lower than that of the Sn–Sn or Ge–Ge interactions [6]; *i.e.* the ratio U/V is low. In addition, the absence of solubility means that germanium has no influence on the bulk thermodynamical properties of Sn–In alloy (indium is used as a diffusant) so that the binary phase diagram Sn–In obtained in our previous work [1] may be used instead of the ternary diagram.

2. Experimental details

In previous work [1] we have shown that the region of homogeneity of the γ' phase in the Sn–In system is situated between 0.5–2.5 and 8 at.% In (see Fig. 1). At a temperature of $179 \pm 0.5^\circ\text{C}$ the γ' phase transforms into the β phase. The γ' phase region in this part of the diagram is observed as a very flat dome and resembles the homogeneity regions of MnAu_3 in the Mn–Au system, of InMg_3 in the In–Mg system and of Cu_3Sn in the Cu–Sn system [7]. The β – γ' transition is close to a second-order transition because the thermal effect of the transition is small: the boundaries of the two-phase region ($\beta + \gamma'$) were not revealed by differential thermal analysis (DTA) in works devoted to the study of the Sn–In stable phase diagram, and the boundary of the γ' ($\gamma' + \gamma$) regions was treated as the solubility limit of indium in the β phase [8] or, in other works, the boundary was not found at all [9]. The γ and γ' phases form a eutectic ($T_c = 165 \pm 2^\circ\text{C}$). The γ phase has a simple hexagonal lattice. Analogous γ phases also exist in the Ag–Sn and

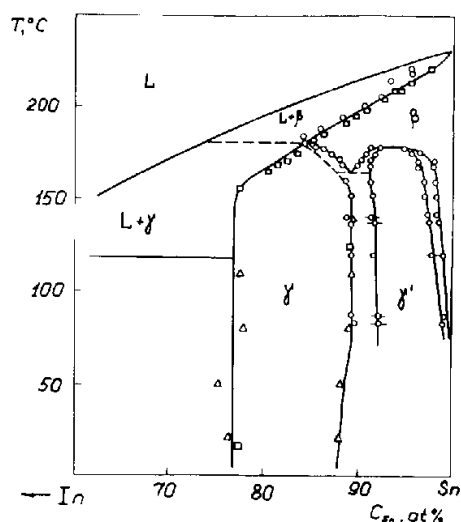


Fig. 1. Portion of the Sn-In diagram: ○, results of our previous work [1] obtained from the concentration distribution in the region of interdiffusion of tin and indium; □, DTA data [8]; △, data from X-ray structural analysis in high temperature chamber [9].

Cd-Sn systems [10]. The positions of the γ phases in the binary diagrams of B metals is determined by their electron concentration ($3.9 \text{ electrons atom}^{-1}$). The metastable γ' phases are also formed in a number of tin alloys on rapid cooling [11]. The γ' phases are observed in the In-Sn, In-Bi and Tl-Sn systems [12]. A simple hexagonal lattice of the γ phase is formed from the lattice of β -Sn through the displacement of one of the sublattices by a quarter of a period along the tetragonal axis c [13], whereas in the γ' phase lattice the analogous displacement takes place by less than a quarter of a period [12].

Thus at the β - γ' phase transition the relative position of the crystal lattice sites in the (001) plane perpendicular to the tetragonal c axis does not change. Therefore we have chosen the [001] Sn-Ge interphase twist boundaries for our studies. These boundaries are formed by tin (001) and germanium (001) planes. The misorientation angle is present by rotation about the common [001] four-fold axis. The [001] interphase boundaries possess a low energy and special properties near the misorientation angles 3° , 31° and 40° [6]. These angles are very close to the epitaxial misorientation and to the $\Sigma 17$ and $\Sigma 5$ coincidence misorientations respectively. This is explained by a small difference (approximately 3%) between the interatomic spacings in the (001) planes of tin and germanium. For our studies we have grown bicrystals with misorientation angles of 0° , 1° , 3° and $10^\circ (\pm 0.5^\circ)$. The first three boundaries have a low surface tension, while their properties (activation energy and activation volume of diffusion) differ significantly from those of general boundaries. The fourth boundary is an interphase general boundary. The regions of existence of special and general grain boundaries are covered in more detail in ref. 14.

Sn-Ge bicrystals were grown by directed crystallization from tin (purity, 99.999%) and antimony-doped semiconducting germanium with a specific resistance of $5 \Omega \text{ cm}$ (the growth technique has been described in ref. 6). The indium layer was electrolytically deposited on the bicrystal surface. Diffusion anneals were

carried out in an atmosphere of high purity argon in a special furnace consisting of a thermostat furnace and 12 small furnaces, where different temperatures were held [15]. The distribution of indium concentrations was determined by X-ray microanalysis from the intensity of the $\text{In } L\alpha$ line at an accelerating voltage of 15 kV. The product of the interphase boundary diffusion coefficient and the boundary width $D'\delta$ was found by using the Fisher method. In this case we took into account that at the annealing temperatures the diffusion flux of indium atoms from the interphase boundary is directed toward the tin bulk only, since both the solubility and the diffusion coefficient of indium in germanium are negligible [16]. The validity of the application of the Fisher formula as an asymptotic form of the Whipple solution has been analysed using the Le Claire criteria [17].

3. Results

Figures 2 and 3 show the dependence of the concentration C_v in the interphase boundary on the penetration depth plotted in Fisher's coordinates for boundaries with various misorientation angles and different temperatures. The temperature dependences of the product $D'\delta$ are shown in Fig. 4 for the four

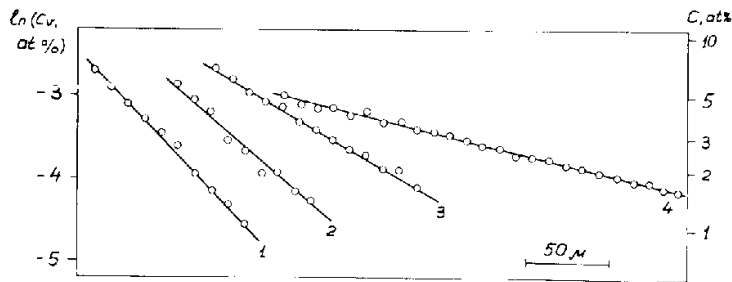


Fig. 2. The dependence of the logarithm of the boundary concentration on the distance from the surface for twist Sn-Ge interphase [001] boundaries with a misorientation angle of 3° : 1, 161.3°C , 240 h. 2, 162.7°C , 240 h. 3, 168.3°C , 240 h. 4, 173.6°C , 125 h.

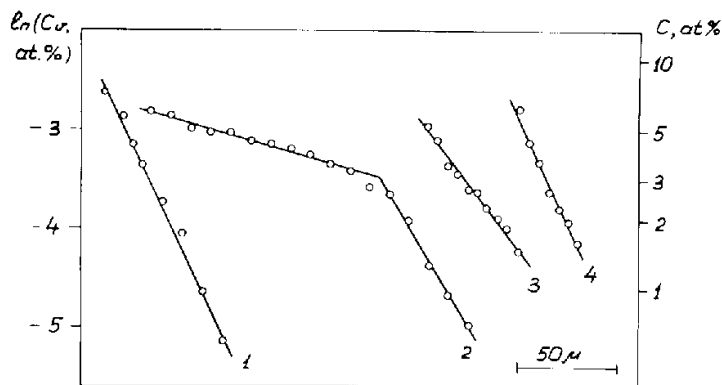


Fig. 3. The dependence of the logarithm of the boundary concentration on the distance from the surface for twist Sn-Ge interphase [001] boundaries with a misorientation angle 0° : 1, 168.3°C . 2, 162.6°C . 3, 141.7°C . 4, 133.6°C . The annealing time was 240 h.

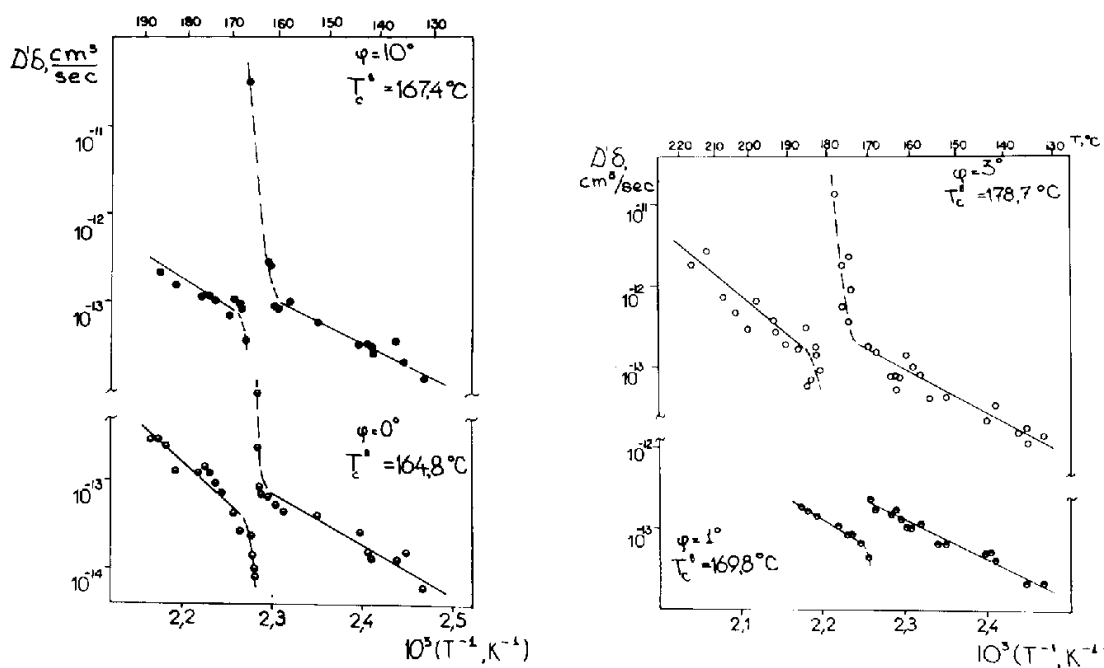


Fig. 4. The temperature dependence of the product of the boundary diffusion coefficient of indium and the boundary width $D'\delta$ for four twist [001] Sn-Ge interphase boundaries. The misorientation angles and temperatures of the β - γ' phase transitions on the boundaries are shown.

interphase twist boundaries studied. Each of these dependences exhibit a discontinuity at T_c^B . These temperatures differ for different boundaries. On approaching the T_c^B temperature from below, the values of $D'\delta$ deviate considerably upwards from the Arrhenius plot. For the boundary with $\varphi = 3^\circ$ it can be seen in Fig. 2 that the slope of the Fisher lines increases on approaching T_c^B from the region of low temperatures. Figure 3, where the Fisher lines are given for a boundary with $\varphi = 0^\circ$, shows how $D'\delta$ abruptly falls when passing over T_c^B from low towards high temperatures. At a temperature slightly below T_c^B the Fisher plot exhibits two regions: with a small slope within the concentration range 3.5–5 at.% In and with a steep slope at concentrations below 3.5 at.% In. For $C_B < 3.5$ at.% In, the slope of lines differs insignificantly both at 162.6 and 168.3°C. This means that at $T = 162.6^\circ\text{C}$ the β and γ' phases are in equilibrium in the interphase boundary at 3.5 at.% In. The $D'\delta$ values are given in Fig. 4 for the concentration range 2–8 at.% In.

All the temperature dependences of $D'\delta$ in Fig. 4 deviate from the Arrhenius law near T_c^B . On approaching T_c^B from the low temperature region the diffusion coefficients deviate greatly upwards from the Arrhenius plot, whereas on approaching T_c^B from high temperatures they deviate downwards. The deviations are observed within the temperature range $T_c^B \pm 5^\circ\text{C}$. This behaviour of the diffusion coefficient may be attributed to critical phenomena in the vicinity of the β - γ' phase transition in the bulk and in the boundaries. This can be compared with the critical behaviour of the coefficient of bulk and grain boundary diffusion in the vicinity of the "ferromagnet-paramagnet" transition [18].

Figure 5 illustrates the dependence of T_c^B on the difference $[\varphi - \varphi_\Sigma]$. Here φ is the misorientation angle of the interphase boundaries studied and φ_Σ is the angle at which the minimum surface tension of Sn-Ge boundaries and the extremum

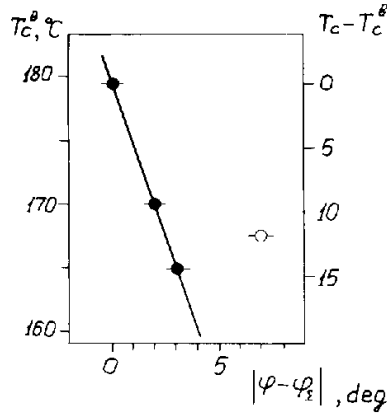


Fig. 5. The misorientation φ dependence of the β - γ' phase transition temperatures on the twist $[001]$ Sn-Ge interphase boundaries; $\varphi_{\Sigma} = 3^{\circ}$, at $\varphi = 3^{\circ}$ the interphase boundaries possess the minimum surface tension and extreme properties: T_c , the β - γ' bulk phase transition temperature; ●, special boundaries; ○, general boundaries.

diffusion parameters are observed. The transition temperature is maximal at $[\varphi - \varphi_{\Sigma}] = 0$ and decreases as the difference $[\varphi - \varphi_{\Sigma}]$ increases.

The temperature T_c^B of the β - γ' phase transition at grain boundaries in tin also decreases as the difference $[\varphi - \varphi_{\Sigma}]$ increases.

For a general interphase boundary with a misorientation angle of 10° ($[\varphi - \varphi_{\Sigma}] = 7^{\circ}$) the transition temperature is higher than from the extrapolation of the dependence $T_c^B(\varphi)$ for special boundaries to $\varphi = 10^{\circ}$. Figure 5 depicts the difference between the transition temperatures $T_c - T_c^B$ in the bulk and in the boundaries. This difference varies from 0 to 14°C .

4. Discussion

As the misorientation of the interphase boundaries deviates from φ_{Σ} , the temperature of the β - γ' phase transition in these boundaries also decreases as in the grain boundaries in tin. In a previous paper we have explained such behaviour of T_c^B in terms of the prewetting phase transition in the boundaries. However, in the grain boundaries there were no anomalously strong deviations of the diffusion coefficient from the Arrhenius law. How can we explain these critical phenomena at the interphase boundaries?

The coefficient of interdiffusion in the two-component solid solution can be represented as [19]

$$D = \frac{C_1 C_2}{RT} (C_1 D_{*2}^* + C_2 D_{*1}^*) \frac{\partial^2 F}{\partial C^2} \quad (1)$$

where C is the concentration of components; $D_{*1,2}^*$ is the coefficient of self-diffusion, F is the free molar energy of the solution. The deviations of the interdiffusion coefficient D from the Arrhenius law near T_c and T_c^B may be the result of the singularities in the behaviour of the thermodynamic factor $\partial^2 F / \partial C^2$ as well as

the variations of $D_{1,2}^*$ associated, for example, with an abrupt change in the activation energy. Let us consider in detail both of these possibilities.

(1) On approaching the critical temperature of the β - γ' transition T_c from the region of high temperatures, the homogeneous solid solution of indium in β -Sn loses its stability. Since the β - γ' transition is a weak first-order transition, F can be written as [20]

$$F = F_0(T) + A(T)(C - C_c)^2 + B(T)(C - C_c)^4 + D(T)(C - C_c)^6 \quad (2)$$

Here C_c is the indium concentration at the top of the "dome" of the γ' phase. Here, the condition $A(T_c) = 0$, $B(T_c) = 0$ should be fulfilled. In terms of the Landau theory we restrict ourselves to the first term of expansion

$$A(T) = \alpha |T - T_c|$$

Taking into account that the interdiffusion coefficient D is measured in the vicinity of C_c , we have

$$\left. \frac{\partial^2 F}{\partial C^2} \right|_{C=C_c} = 2\alpha |T - T_c|$$

If the phase diagram for the interphase boundary is qualitatively similar to the Sn-In bulk diagram, then analogously

$$\left. \frac{\partial^2 F_B}{\partial C^2} \right|_{C=C_c^B} = 2\alpha_B |T - T_c^B|$$

with allowance made for eqn. (1) we have

$$\ln D \approx \ln |T - T_c^B|$$

and while approaching T_c^B from the region of high temperature, the diffusion coefficient D tends to zero like $|T - T_c^B|$.

It is known from the theory of critical phenomena that in the vicinity of the second-order phase transition (particularly the ferromagnetic-paramagnetic transition) the derivatives of free energy (e.g. specific heat, susceptibility) and the connected variables depend on the temperature by the power law [21], e.g.

$$\chi \approx |T - T_c/T_c|^{-\gamma}$$

Here, γ is the so-called critical index for susceptibility χ . The critical index for the diffusion coefficient will be dealt with in an analogous fashion. It follows from above that the critical index for the diffusion coefficient near T_c^B should be equal to unity at $T \rightarrow T_c^B + 0$ (this formula means that the temperature T approaches T_c^B from the region of high temperature).

Figure 6 illustrates a log-log dependence of the coefficient of indium diffusion along the Sn-Ge interphase twist boundary with misorientation angle $\varphi = 0^\circ$ on $(T - T_c^B)/T_c^B$. The points form a straight line with the tilt angle tangent 1.0 ± 0.1 .

All this enables us to explain the anomalous lowering of the boundary diffusion coefficient at $T \rightarrow T_c^B + 0$ and predict the value of the critical index.

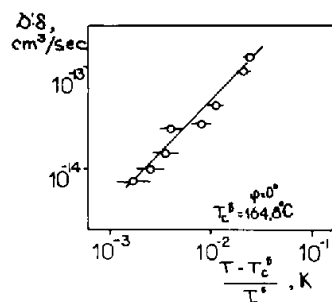


Fig. 6. The log-log dependence of $D\delta$ for an interphase boundary with $\varphi = 0^\circ$ above T_c^β on the $|T - T_c^\beta|/T_c^\beta$. The critical index for $D\delta$ is 1.0 ± 0.1 .

It should be noted that the lowering of the diffusion coefficient was also observed in the Zn–Al system at temperatures above the miscibility gap [19].

(2) Let us consider now the anomalous increase in the diffusion coefficient when approaching the temperature of the β – γ' transition from the region of low temperatures. The theory of heterophase fluctuations [22] can be used with advantage for describing the diffusion in solids. Similar theories assert that during the diffusion jump the structure of the activated complex coincides with that of a metastable phase whose free energy is the lowest [23, 24]. An indirect confirmation of the theory is the compensation effect. The compensation effect is a phenomenon observed in a wide range of metallic, biological and chemical systems. Consider the temperature dependences of some kinetic property (*e.g.* mobility) of the aggregate of similar objects. Grain boundaries with various misorientation angles may form such an aggregate. Although the activation energies E and pre-exponent factor A_0 are different boundaries, a linear dependence between E and $\lg_{10} A_0$ can be observed. Such a dependence is called the compensation effect. It follows from the relationship $E \approx \log A_0$ that all the Arrhenius plots cross each other at a single point. The corresponding temperature is the compensation temperature. The compensation temperature normally coincides with a temperature of some phase transition. The compensation effect may be explained in terms of heterophase fluctuation theory [22]. The compensation effect during the diffusion of indium along the Sn–Ge interphase boundaries has been detected in various temperature ranges [6, 15]. In the temperature range of existence of the γ' phase the compensation temperature coincides with the temperature of the α – β transition in tin [6]. The activated complex seems to have the structure of α -Sn. However, close to the β – γ' transition the situation may change. In our previous paper [1] we have assumed that the grain boundaries and secondary grain boundary dislocations are centres of β phase prenucleation which leads to the prewetting phase transition. This seems to be also true for vacancies. This means that at a temperature somewhat lower than that of the β – γ' transition the prewetting phase transition takes place in vacancies and they “put on” the “coat” of a β -like phase. In this case the structure of the activated complex differs from that of the α -Sn prenucleus. Let us consider in detail how the migration of vacancies can proceed in this case.

The specific volume of the γ phase is larger than that of the β phase [10] and the structure of the γ' phase is intermediate between the γ' and the β phases [12].

Therefore one may believe that the specific volume of the γ' phase is larger than that of the β phase. The structure and size of the activated complex should be such that the elastic energy associated with the fluctuation nucleus becomes zero [22]. Now suppose that owing to fluctuations the “coat” of the β -like phase around the vacancy begins to increase in size. When the coat volume reaches a certain value, a second vacancy compensating the volume effect of the β - γ' phase transitions appears inside this “coat”. If the fluctuation nucleus were spherical in shape (or in the interphase boundary case a disk), the second vacancy, as follows from the symmetry reason, would appear next to the first one: in the centre of a sphere or a disk. However, near the transition temperature the fluctuation correlation radius becomes infinite: $\xi \approx |T - T_c|^{-\nu}$, where $\nu = 0.63$ for a three-dimensional case and $\nu = 1$ for a two-dimensional case. This means that on the fluctuation sphere there will be unevennesses with a characteristic size ξ . Therefore the second vacancy can arise at a distance of the order ξ from the first one. After the nucleus “collapses”, the second vacancy can remain, while the first one can vanish. Thus the vacancy will shift at a distance ξ .

This is a rather rough scheme, but it reflects the collective character of the diffusion jump near the weak first-order phase transition. The jump scheme can be represented qualitatively as follows. The first vacancy emits a soft phonon (or a packet of phonons), and gradually disappears, but at the distance of the order of the soft phonon wavelength (the latter just equals ξ) another vacancy nucleates. We can say that the first vacancy has moved a distance of the order of ξ . The pre-exponential factor of diffusion is proportional to the jump length square, therefore it is expected that the dependence of the diffusion coefficient on the temperature in the fluctuation region will take the form

$$D \approx |T - T_c|^{-2\nu}$$

The quantity 2ν varies from 1.26 for a three-dimensional system to 2 for a two-dimensional system. Figure 7 illustrates a log-log plot of the coefficient of indium diffusion along the interphase boundary with $\varphi = 3^\circ$ below T_c^B . The points form a straight line, the tangent of slope is 1.5 ± 0.2 . This means that, with respect to the

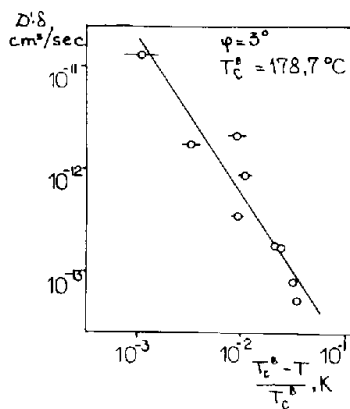


Fig. 7. The log-log dependence of $D\delta$ for an interphase boundary with $\varphi = 3^\circ$ below T_c^B on the $|T - T_c^B|/T_c^B$. The critical index for $D\delta$ is 1.5 ± 0.2 .

diffusion properties, the interphase boundaries occupy an intermediate position between the two- and three-dimensional systems.

Using the arguments given above, we can predict where the anomalous increase in the diffusion coefficient might be expected near the temperature of the phase transition. These should be systems where the second-order phase transition or a weak first-order phase transition take place, and the soft mode associated with the order parameter should interact with the acoustic phonons owing to striction, for instance. In fact, a small increase in the diffusion coefficient in the close vicinity of the Curie temperature was observed for the diffusion of zinc in α -Fe [25].

Acknowledgments

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