

## ON THE KINETICS OF THE PHASE TRANSFORMATION OF CsCl CRYSTALS II\*

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The kinetic curve of the  $B_2 \rightleftharpoons B_1$  phase transformation observed during uniform heating may be divided into three different stages. In the first stage disk-like nuclei are formed which grow rapidly along the  $B_2$  phase boundaries. In the second stage no nuclei are formed and the growth takes place normal to the original grain boundaries. Finally, the decrease of the transformation rate in stage III may probably be associated with the Clausius-Clapeyron type decrease of the driving force. In the framework of this visualization of the kinetic curve some previous results are also interpretable.

### 1. Introduction

The (CsCl type lattice)  $\rightleftharpoons$  (NaCl type lattice) phase transformation in CsCl is connected with a pronounced change in the electrical conductivity [1, 2, 3, 4, 5] which gives a good opportunity to investigate the kinetics of this transformation [5, 6]. The conductivity of various sintered Johnson—Matthey specpure CsCl samples was found to be a well-defined function<sup>1</sup> of time when heating the samples at a constant rate above the equilibrium temperature of transformation ( $T_c = 726^\circ\text{K}$ ) (Fig. 1 [6]). The aim of this paper is to present the experimental data in terms of the formal theory of phase transformation.

It will be assumed that the  $B_1 \rightleftharpoons B_2$  transformation is of the nucleation and thermally activated growth type, i.e. the volume fraction of the stable phase ( $\xi$ ) is given by the equation

$$\xi(t) = 1 - \exp \left[ \int_0^t \left( \prod_{i=1}^3 \int_{\tau}^t V_i(T(t')) dt' \right) I(T(\tau), \tau) d\tau \right], \quad (1)$$

\* Dedicated to Prof. P. GOMBÁS on his 60th birthday.

<sup>1</sup> It should be noted that the data were corrected for various experimental errors.

where  $T(t)$  is the temperature programme of heating,  $I(T(t)t)$  is the temperature and time-dependent rate of nucleation and  $V_1, V_2, V_3$ , denote the growth velocities in three mutually perpendicular directions. The growth velocity is determined by the phase boundary mobility,  $B$ , and the driving force,  $\Delta G : V = B\Delta G$ . The mobility depends on the temperature, concentration of dissolved impurities and the relative orientation of the adjacent phases. The temperature dependence of the mobility is characterized by an energy of activation denoted by  $E_M$ . The driving force is given by the free energy difference between the adjacent phases along the phase boundary and by the curvature and free energy of the migrating boundary (see e.g. [7]).

## 2. Relation between conductivity and the transformed volume

Debye—Scherrer patterns obtained by electron diffraction prove that the  $B_1$  and  $B_2$  phases form a two-phase aggregate in the course of the  $B_1 \rightleftharpoons B_2$  transformation [8]. There are many formulae to determine the effective electrical conductivity of two-phase aggregates [9]; we used the formula of ODALEVSKI [10] and LANDAUER [11]

$$\left( \frac{\sigma_1 - \sigma_{eff}}{\sigma_1 + 2\sigma_{eff}} \right) x_1 + \left( \frac{\sigma_2 - \sigma_{eff}}{\sigma_2 + 2\sigma_{eff}} \right) x_2 = 0, \quad (2)$$

where  $\sigma_1, \sigma_2$  are the  $B_1$  and  $B_2$  phase conductivities, respectively,  $x_1, x_2$  are the volume fractions of the component phases. This equation is valid for random geometry, since it was derived from the assumption that the mean electric and current field in the constituent 1 (or 2) might be determined by considering a sphere 1 (or 2) embedded in an infinite conducting medium.<sup>2</sup>

LANDAUER [11] has shown that Equ.(2) accounts quite fairly for the observed conductivities in equiaxial two-phase matrices even when  $\sigma_1$  and  $\sigma_2$  differ by a factor of 10. However, it should be emphasized that this statement is limited to random geometry. Model experiments show that for disk-like second phases perpendicular to the mean direction of the current the experimental results may deviate from the values calculated with Equ. (2) by a factor of 30 if  $\sigma_1/\sigma_2 \gg 1$  [12].

When applying Equ.(2) to evaluate  $x_1$  one has to take into account that  $\sigma_2$  and  $\sigma_1$  are inherently temperature-dependent. The actual conductivities might be determined by extrapolating from the  $B_2$  and  $B_1$  data using the relations

$$\sigma_2(T) = \sigma_2(T_2) \exp \left[ -\frac{E_2}{h} \left( \frac{1}{T} - \frac{1}{T_2} \right) \right], \quad (3a)$$

$$\sigma_1(T) = \sigma_1(T_1) \exp \left[ -\frac{E_1}{h} \left( \frac{1}{T} - \frac{1}{T_1} \right) \right]. \quad (3b)$$

<sup>2</sup> It is worth noting that the derivation of Eq. (2) makes use of the Maxwell equations and Ohm's law only and so it applies equally to metals, semiconductors and insulators.

In Equ. (3)  $T_1$  and  $T_2$  are temperatures at which CsCl exists in the  $B_2$  and  $B_1$  phase, respectively;  $E_1$  and  $E_2$  are activation energies of the conductivities in the respective phases.

At the evaluation of the conductivity values from the measured data corrections must be made to account for the volume change of the samples due to the transformation. Since the elastic moduli of  $B_1$  and  $B_2$  at the tem-

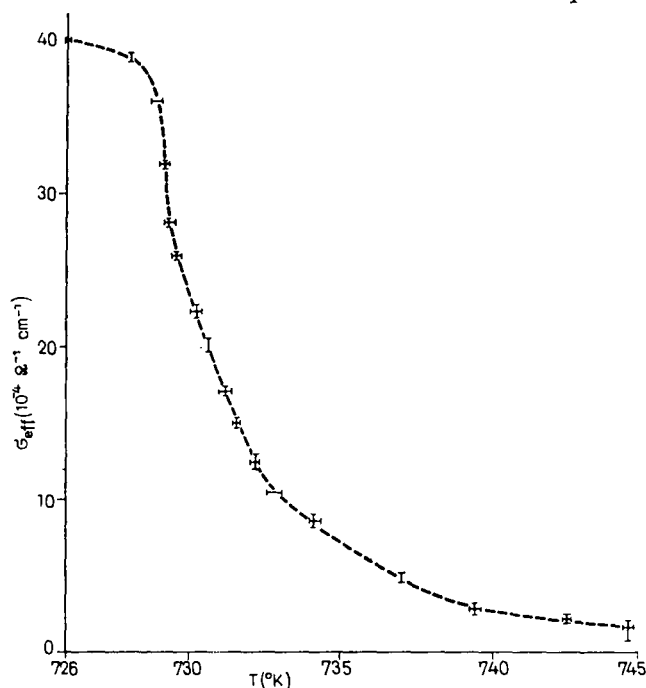


Fig. 1. The decrease of the effective conductivity in the  $B_2 \rightarrow B_1$  transition. (The measurements were carried out on 8 different samples)

perature of transformation are not known equal elastic moduli were assumed for both phases. According to this assumption [16]

$$\frac{v(x_1) - v(x_2 \approx 1)}{v(x_2 = 1)} = \frac{V_1 - V_2}{V_2} x_1, \quad (4)$$

where  $v$  denotes the volume of the sample and  $V$  the mole volume of the phase ( $V_1 - V_2/V_2 = 0.12$  [13]). Knowing the dimensions of the sample before the phase transformation ( $l_0, q_0$ ), the effective conductivity is given by the relation

$$\sigma = \frac{T}{V} \frac{1 + \Delta l/l}{1 + \Delta q/q} \cong \frac{T}{V} \frac{l_0}{q_0} \left( 1 - \frac{1}{3} \frac{V_1 - V_2}{V_2} x_1 \right). \quad (5)$$

ARENDS and NIJBOER [2] have found that  $E_{B_2}$  and  $E_{B_1}$  are 1.35 eV and 1.65 eV, respectively.  $\sigma_{B_1}$  (744.5) and  $\sigma_{B_2}$  (729) amount to  $0.16 \cdot 10^{-5} \text{ Ohm}^{-1} \text{ cm}^{-1}$  and  $40 \cdot 10^{-5} \text{ Ohm}^{-1} \text{ cm}^{-1}$  (Fig. 1). With these data  $x_1$  was calculated from

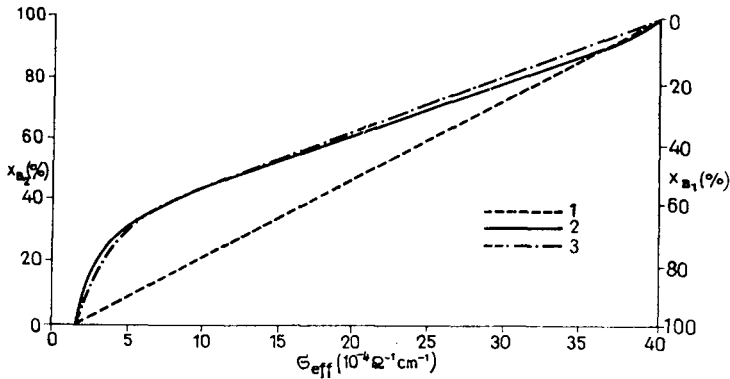


Fig. 2. Effective conductivity as a function of  $x_{b_2}$  or  $x_{b_1}$  (Curve 1 visualizes the conductivity by linear interpolation. Curve 2 was calculated from (2), (3) and (5) with temperature corrections, Curve 3 was calculated without any temperature correction

Equ. (2), (3) and (5) (Fig. 2). Since there is some disagreement in the literature about the activation energy values  $E_2$  and  $E_1$  those  $x_1$  values are also given in Fig. 2 which were calculated without any temperature correction.

### 3. The interpretation of the kinetical curve

In Fig. 3  $\log 1/1-x_1$  is plotted against  $T-T_c = a \cdot t$ . The curve has three quite well separated stages. The first is parabolic, the second linear, and the third begins with a significant decrease of  $\log 1/1-x_1$  with time (or with  $T-T_c = a \cdot t$ ).

Let us first consider the second stage. It is clear that  $I(T(t), t) \geq 0$ , and if it is assumed that the growth velocity is not a decreasing function of  $T-T_c = a \cdot t$ <sup>3</sup> the linearity of the kinetical curve leads to the conclusions that in this stage: i) the growth of the equilibrium phase grains is restricted to one special direction only, their growth in the other two directions being vanishingly small; ii) no new nuclei are formed; iii) the driving force is constant. This means that:

$$\log \frac{1}{1-x_1} = \text{constant} \left( \int_0^t M_0 e^{-E_M/kT} dt \right). \quad (6)$$

In good approximation

$$\frac{1}{T} = \frac{1}{\left(1 - \frac{at}{T_c}\right)} = \frac{1}{T_c} \left(1 - \frac{at}{T_c}\right) \quad (7)$$

<sup>3</sup> The mobility of the grain boundaries is an increasing function of the temperature, and so the quasi-constant velocity of the phase boundary migration needed to explain the linearity of stage II would mean a compensation of the  $E_M$  determined increase of the mobility by the Clausius-Clapeyron type decrease (see later) of the driving force. At present, we do not think there is any support for such kind of assumption.

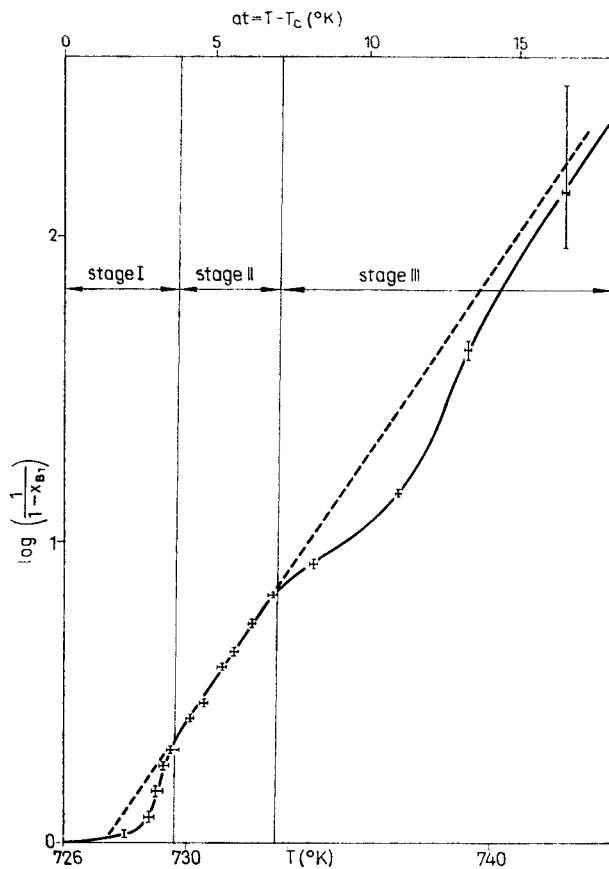


Fig. 3. The kinetic curve (the maximum possible error in  $\log 1/1 - x_1$  and  $\Delta T$  is marked by +)

because in the investigated temperature interval

$$\frac{\Delta T}{T_c} = \frac{at}{T_c} \leq 0,15.$$

Putting (1) into (6) and assuming that

$$\frac{E_M}{kT_c} \cdot \frac{\Delta T}{T_c} \ll 1$$

the expansion into power series yields

$$\frac{1}{1-x_1} = \text{const } \Delta T \left( 1 + \frac{E_M}{kT_c} \cdot \frac{\Delta T}{k} \right). \quad (8)$$

This equation accounts for the observed linearity if

$$\frac{E_M}{kT_c} \frac{\Delta T}{T_c} \ll 1.$$

The observed deviation from exact linearity gives an upper limit 0.6 eV for the activation energy of the phase boundary mobility. By supposing the two conductivity values to be slightly more accurate than was actually found in the experiments one obtains the value 0.2 eV for  $E_M$ . These values (0.6—0.2 eV) are quite reasonable, since the activation energy of the grain boundary migration was found to be equal or lower than that of vacancy migration in the cases investigated [14].

At first sight it appears that, in spite of our suggestion, the driving force of the phase boundary migration ought to be an increasing function of  $T - T_c = a \cdot t$ , since the free energy difference between the stable and unstable phase increases with increasing  $T - T_c$ . One has, however, to keep in mind that the phase transformation connected with a volume change gives rise to accommodation stresses. This stress field cannot be fully relaxed by plastic deformation, since the flow stress has a finite value and only the shear components of the stress tensor can initiate the flow. According to the Clausius-Clapeyron equation the stress field is connected with a change in the equilibrium transition temperature in the following way [15]

$$T_c - T_{c_0} = \frac{u_{ik}(B_1) u_{ik}(B_2)}{T_{c_0} \Delta H}. \quad (9)$$

In the formula,  $T_{c_0}$  and  $T_c$  are the equilibrium transition temperatures in the stress-free state and in the elastically distorted state, respectively.  $u_{ik}$  denotes the stress tensor at the phase boundary and  $u_{ik}(B_1)$  and  $u_{ik}(B_2)$  are the components of the distortion tensor at the  $B_1$  and the  $B_2$  side of the phase boundary. (The stress tensor and the displacement vector are measured with respect to the single phase matrices in the stress-free state.)  $\Delta H$  amounts to 7.5 K/mole [17].

The order of magnitude of the Clausius-Clapeyron effect can be estimated with the help of the following model. Let a spherical  $B_2$  phase be surrounded concentrically by a spherical  $B_1$  phase, and let the boundary between them be an incoherent one. Assuming that no plastic flow takes place, and using the well-known stress field values [15, 16] one gets 100 °K for  $T_c - T_{c_0}$ . When plastic deformation relaxes the stress field to the value of the flow stress ( $\sim 1 \text{ hg} \cdot \text{mm}^{-2}$  [18]) the change in the transformation temperature is 5 °K. According to these considerations a constant driving force results owing to an interplay between the Clausius-Clapeyron type change in the equilibrium

transformation temperature and the restricted plastic deformation of the matrix. The one-dimensional growth may be explained in the following way: in the first stage disk-like nuclei are formed in the grain boundaries of the polycrystalline  $B_2$  phase; these nuclei grow rapidly along the  $B_2$  phase grain boundaries; during this growth the thickness of the  $B_1$  phase grains remains as small as that of the nuclei. At the end of the first stage the area of the original  $B_2$  grain boundaries is covered with  $B_1$  phase grains, whose slow growth normal to the surface of the original  $B_2$  phase is considered to account for the one dimensional growth characteristic of the second stage.

If the nucleation rate were constant during stage I,  $\log 1/1-x_1$  would be a third order parabola. If the nucleation rate were a rapidly decreasing function of time, owing to the decrease of the grain boundary area of the  $B_2$  phase,  $\log 1/1-x_1$  would be a second order parabola. A numerical test has shown that the experimental curve has an intermediate position between these two extreme possibilities.

It should be noted that the formation of disk-like nuclei in the original grain boundaries is favoured by two effects: i) disk-like nuclei indicate the smallest possible accommodation energy in the two phase aggregate, as was shown by NABARRO [19]; ii) the rapid growth along the grain boundaries might be associated with the Clausius-Clapeyron type change in the equilibrium transition temperature. (The plastic relaxation is certainly favoured by the plastic shear of the grain boundaries. This gives rise to a rather easy stress relaxation which in consequence makes the Clausius-Clapeyron type decrease of the driving force less effective in the direction parallel to the grain boundaries than in the direction normal to it.)

The decrease of the transformation rate in stage III may probably also be associated with the Clausius-Clapeyron type decrease of the driving force. To show this, let us assume that the plastic flow resulting from the accommodation stress has exhausted the lower yield point region of the matrix, and now work hardening becomes a dominant factor. When the rate of recovery does not compensate the hardening in exactly the same rate as the phase transformation goes on, a decrease or an increase might both be observable. This depends only on the relative rate of these two reactions.

#### 4. Discussion

Let us now discuss some other experimental results supporting the model suggested.

One of us described some isothermic conductivity measurements carried out slightly above  $T_c$  [6]. The change of the conductivity was not a monotonic function of time; an increasing transformation rate was followed by a consider-

able slowing down after which the transformation rate increased again. This process which was repeated several times seems to be very similar to the "fine structure" of phase transformation observed by ARENDS [20]. These effects may be associated with the Clausius-Clapeyron type changes in the driving force (see stage III). The internal stress field which played an important role in the suggested model appears directly in the anomalous change of the lattice parameter of the phase during phase transformation observed in [8]. From the amount of the anomalous change in the lattice parameter a value of several degrees arises for  $T_c - T_c$ .

In another set of experiments, published earlier, it was shown that the transformation process is extremely structure-sensitive which means that the transformation kinetics depends strongly on the defect state of the lattice [5]. The experimental facts can easily be explained with our suggested model by considering three effects of a heat treatment slightly above  $T_c$ : i) some  $B_1$  grains are formed; ii) the grain size of the  $B_2$  grains decreases as a result of the driving force brought about from the decrease of the total grain boundary area; iii) the overall dislocation density decreases by annihilation, and the density of movable dislocation decreases by impurity reactions. If, after the heat treatment at the equilibrium temperature of transformation, the sample is quenched and then warmed up again (as they actually were in the experiments described in [5]), the nucleation and two dimensional growth along the grain boundaries will cover a smaller total grain boundary area than before the heat treatment. Consequently, the rate of transformation decreases. A second effect in the same line arises from the fact that plastic deformation becomes more difficult after heat treatment. This should be expected because an increase of the yield stress makes the Clausius-Clapeyron type decrease of the driving force more effective. When the increase in yield stress is extremely large the rate of transformation may become vanishingly small before obtaining a single phase matrix.

Finally, it should be mentioned that the simplest direct test of the suggested model should be given by the micrographic investigation of the phase transformation. We hope to present some results in this line in due time.

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#### REFERENCES

1. W. W. HARPUR, R. L. MOSS and A. R. UBBELOHDE, Proc. Roy. Soc., A **232**, 310, 1955.
2. I. M. HOODLESS and J. A. MORRISON, Phys. Chem., **66**, 557, 1962.
3. J. ARENDS and H. NIJBOER, Solid State Communications, **5**, 163, 1967. Phys. Stat. Sol., **26**, 537, 1968.
4. P. J. HARVEY and I. M. HOODLESS, Phil. Mag., **16**, 543, 1967.
5. Z. MORLIN, Acta Phys. Hung., **21**, 137, 1966.



6. Z. MORLIN, *Acta Phys. Hung.*, **24**, 277, 1968.
7. J. W. CHRISTIAN, *The Theory of Transformation in Metals and Alloys*, Pergamon Press, Oxford, London, Edinburgh, New York, Paris, Frankfurt, 1965. pp. 471—489.
8. Z. MORLIN and J. TREMMEL, *Acta Phys. Hung.*, **21**, 130, 1966.
9. J. A. REYNOLDS and J. M. HOUGHT, *Proc. Roy. Soc.*, **B70**, 769, 1957.
10. V. I. ODALEVSKI, *J. Tech. Phys. (UdSSR)*, **21**, 667, 678, 1379, 1951.
11. R. LANDAUER, *J. Appl. Phys.*, **23**, 779, 1952.
12. I. GAAL and L. URAY, *Phys. Stat. Sol.*, **29**, K163, 1968.
13. Gmelins Hdbch der Anorganischen Chemie, Band 25, p. 145, Verl. Chemie Gmbh. Weinheim, Berstr. und Berlin.
14. P. GORDON and R. A. VANDERMEER, *Recrystallization, Grain Growth and Textures* (ed. H. Margolin) 205—266, American Society for Metals, Metals Park, Ohio, 1966.
15. L. D. LANDAU and E. M. LIFSHITZ, *Theory of Elasticity*, Pergamon Press, London, Paris, New York, Los Angeles, 1959, pp. 9, 20.
16. J. D. ESHELBY, in *Solid State Physics* (ed. by F. SEITZ and D. TURNBULL) Vol. 3. pp. 79—107, Academic Press, New York, 1956.
17. W. AUER, in *Landolt Börnstein Zahlenwerte und Funktionen*, Bd 2. Teil 14. p 207. Springer, Berlin, Göttingen, Heidelberg, 1959.
18. W. L. PHILLIPS, *J. Trans AIME*, **218**, 947, 1960.
19. F. R. N. NABARRO, *Proc. Roy. Soc.*, **52**, 90, 1940.
20. J. ARENDS, private communication.

## О КИНЕМАТИКЕ ФАЗОВОГО ПЕРЕХОДА КРИСТАЛЛОВ CsCl II

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### Резюме

Кинетическая кривая фазового перехода  $B_2 \rightleftharpoons B_1$ , наблюдаемого при равномерном нагреве, может быть разделена на три разные фазы. В первой фазе формируются дискообразные ядра, которые быстро растут в направления фазовых граничных линий  $B_2$ . Во второй фазе ядра не образуются и рост протекает в направления, перпендикулярные к контурам первоначальных зерен. Наконец, уменьшение скорости перехода в третьей фазе вероятно можно связать с уменьшением возбуждающей силы типа Клаузиуса—Клапейрона. В рамках данного представления кинетической кривой имеется возможность для объяснения некоторых ранних результатов.