

On the "Average" Crystal Lattice Parameter in Decomposition of CsBr-CsJ Solid Solutions

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The true equilibrium decomposition curve has been obtained for the solid solutions CsBr-CsJ. It has been shown that the important empirical rule of the constancy of the "average" parameter of a crystal lattice is valid only in the case of a true equilibrium decomposition curve of solid solutions CsBr-CsJ. The mean value of the lattice parameter of the decomposition phases is shown to remain constant over the temperature range from 20 to 180°C. © 1987 Academic Press, Inc.

Introduction

Thermodynamical stability determined by the position of the equilibrium decomposition curve (solvus) is an important parameter for practical work with any solid solution. Almost all of the presently known experimental decomposition curves were obtained using quenching technique. Because of a number of shortcomings of a fundamental character associated with the kinetic factors (the possibility of a shift in the equilibrium upon quenching and in subsequent analysis of the sample, residual strains in the sample, and so on (1)), the quenching procedures are not certain to give true equilibrium decomposition curves. Study of the samples and determination of the solvus lines under true thermodynamical equilibrium conditions are associated with great experimental difficulties, but it is such data that would be the most reliable because of the absence of complications from the kinetic factors.

It has been shown that the equilibrium

decomposition of binary isostructural solid solutions proceeds according to an important empirical rule: the mean arithmetic parameter, \bar{a} , of the equilibrium decomposition phases is independent of temperature over the whole decomposition region: (2, 3)

$$\bar{a} = (a_{x_1} + a_{x_2})/2 = \text{const} \quad (1)$$

where a_{x_1} and a_{x_2} are the crystal lattice parameters of the phases in equilibrium at the given temperature, x_1 and x_2 are compositions of the phases. a_{x_1} and a_{x_2} were calculated according to Vegard's rule using temperature dependences, $a(t)$, of the crystal lattice parameters of pure components of solid solution.

The high accuracy ($\sim 0, 1\%$) with which the relation (1) is fulfilled greatly improves the accuracy of determination of the solid solution composition at the critical point (2, 3). Relation (1) can also be used as a criterion of the equilibrium state of the solvus curves.

Decomposition of CsBr-CsJ solid solutions has been studied by the quenching

method (4), but relation (1) was not found to hold for the solvus curve (4). The possible reasons for this may be (i) deviation of the solvus curve from equilibrium due to kinetic effects; (ii) limited applicability of (1).

The effect of the kinetic factors on the decomposition equilibrium may be different in different systems. For example, for KCl–NaCl and some other solid solutions the equilibrium of the decomposition is little affected by the kinetic factors (1, 3), whereas in other cases this effect can be large. Therefore, we studied the decomposition of CsBr–CsJ solid solutions under true equilibrium conditions using high-temperature X-ray diffractometry.

Experimental

The starting CsBr and CsJ salts (of 99% purity) were subjected to additional purification by normal freezing from the melt. The solid solutions were prepared by alloying the component in quartz ampoules under vacuum. The specimens were measured on a DRON-0.5 X-ray diffractometer (CuK_α -radiation) having a high-temperature chamber over the temperature range from 20 to 600°C. The chamber was calibrated as described in (5). The uncertainty in the determination of the true specimen temperature was less than 2°C. The crystal lattice parameter was calculated by extrapolating (by the method of Nelson-Riley (6) to the angle $\theta = 90^\circ$. The error of the a value determination did not exceed $\pm 0.002 \text{ \AA}$.

The degree of the achieved equilibrium was checked as follows. While the specimen was maintained at a predetermined temperature the diffractograms were taken at regular intervals. These data were then used for plotting the lattice parameter as a function of time (kinetic curve) at the fixed temperature. Figure 1 shows examples of kinetic curves. In this figure instead of the lattice parameter the difference between

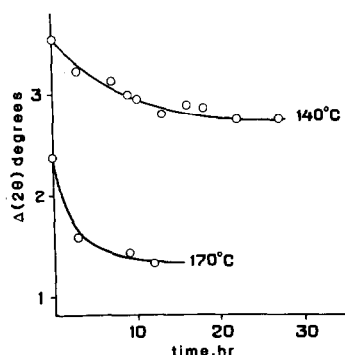


FIG. 1. Kinetic curves for a specimen of the composition 40 mol% CsJ.

the 2θ values of the diffraction peaks having the same indices but belonging to different phases are plotted on the ordinate axis. This increases the sensibility of the kinetic curves since the changes in 2θ of the two phases during the decomposition have opposite directions. The horizontal parts of the curves correspond to the equilibrium state. Figure 1 shows that the time required for the equilibrium to be established is strongly temperature-dependent.

At temperatures of 120° and below this time becomes prohibitively large. Therefore at temperatures from 20 to 120° the specimen preparation procedure was as follows. The diffractometer chamber was heated to the required temperature. A concentrated aqueous solution of required composition was prepared and deposited onto a special cell arranged in the diffractometer chamber. After complete evaporation of the moisture, the diffractograms were taken at the same temperature and the kinetic curves plotted. Such a procedure leads to a considerable reduction of the time needed for the establishing of the equilibrium since, according to the phase diagram, isothermal evaporation of an aqueous solution gives rise to a solid solution which is in equilibrium at the temperature of evaporation (7).

Most of the measurements were per-

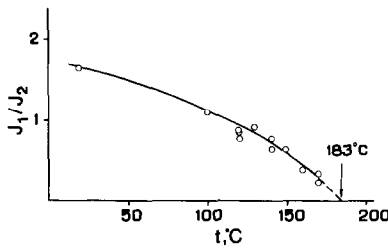


FIG. 2. The intensity ratio of the diffraction lines belonging to different phases as a function of temperature. Given is the mean value of three pairs of lines with identical indices.

formed on specimens of composition 40 mol% CsJ since such a composition was shown (4) to be near the critical point of the solvus. Accordingly, the critical decomposition temperature, t'_k , for this composition (the temperature at which the line for this composition intersects the solvus curve) lies near the critical temperature of the solvus, t_k . In view of the special importance of this point the value of t'_k for CsJ 40 mol% was determined as follows. The intensity ratios of the diffraction peaks (I_1/I_2) having

the same indices but belonging to different phases in equilibrium states were measured for this composition over the temperature range from 20 to 160°C. As the temperature was increased, the relative amounts of the phases changed according to the lever rule, and I_1/I_2 was proportional to the ratio of the amounts of the equilibrium phases. At $t = t'_k$ one of the phases disappears completely and $I_1/I_2 \rightarrow 0$ at $t \rightarrow t'_k$. Figure 2 shows I_1/I_2 as a function of t for the composition 40 mol% CsJ. By extrapolating the curve for this composition the value $183 \pm 5^\circ\text{C}$ for t'_k was obtained (indicated by the arrow). This value seems to almost coincide with the critical temperature of the solvus, t_k , since all of the compositions investigated were already homogeneous at 190°C.

Results and Discussion

Figure 3 shows the overall plot of the crystal lattice parameter against temperature for the subsolidus region of CsBr-CsJ solid solutions. In the homogeneous part of

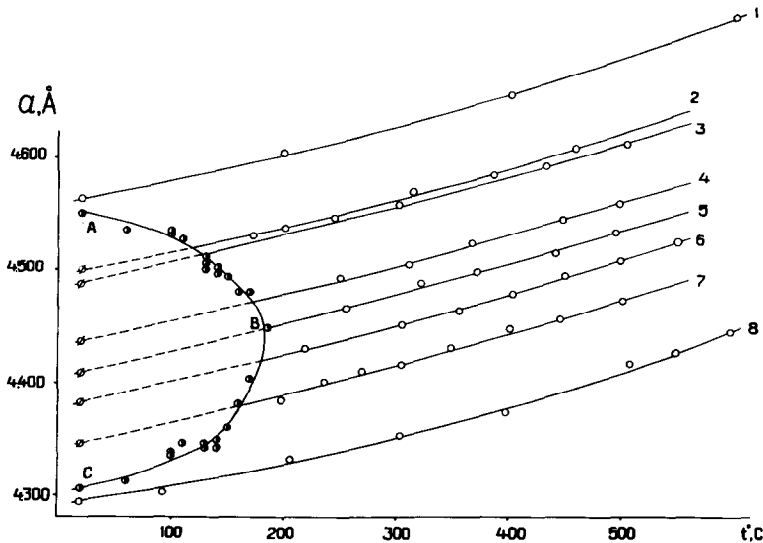


FIG. 3. Temperature dependence of the crystal lattice parameter for Cs(Br_{1-x}J_x) solid solutions. (1) $x = 1$, (2) $x = 0.7$, (3) $x = 0.685$, (4) $x = 0.5$, (5) $x = 0.4$, (6) $x = 0.3$, (7) $x = 0.2$, (8) $x = 0$. ○, A single-phase equilibrium specimen; ∅, a single-phase quenched specimen; ●, a two-phase equilibrium specimen.

the plot the curves $a(t)$ are nearly parallel, and the extensions of these curves contain the points for the samples homogeneous at 20°C (prepared by quenching). The region of the equilibrium decomposition is determined by the ABC curve. Point B represent the temperature t'_k obtained by extrapolating the curve in Fig. 2. The mean deviation of the experimental points from the graphically averaged ABC curve $\delta a = 0.004 \text{ \AA}$. The increase in δa exceeding the measurement error can be accounted for by small deviations from the equilibrium state.

From curves 1 to 8 in Fig. 3 Vegard isotherms were plotted for different temperatures (Fig. 4). The maximum positive deviations from additivity showed a regular increase from 0.12% at 20°C to 0.18% at 500°C.

Figure 5 shows the equilibrium decomposition curve obtained from the experimental data in Fig. 3. The points on the decomposition curve were obtained in two ways:

(1) The equilibrium decomposition temperature for this composition was determined as the point of intersection of the $a(t)$ curve for a homogeneous specimen of this composition with the ABC curve. The error of the composition determination did not exceed 0.05% (weighing errors). The er-

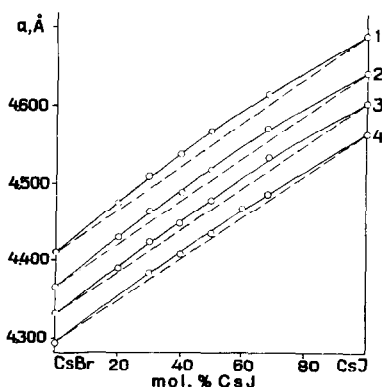


FIG. 4. Vegard's isotherms for homogeneous solid solutions CsBr-CsJ. (1) 500°C, (2) 350°C, (3) 200°C, (4) 20°C.

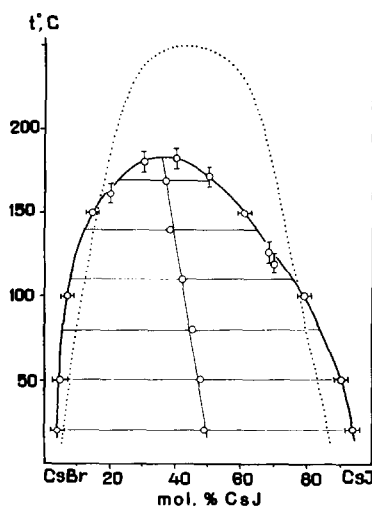


FIG. 5. The equilibrium decomposition curve of CsBr-CsJ solid solutions. The dashed line is the decomposition curve obtained in (4).

ror of the equilibrium temperature determination was estimated from the value of δa , taking into account the slopes of the curves in Fig. 3, and did not exceed 6°C in the temperature range from 120 to 180°C (vertical bars in Fig. 5).

(2) At temperatures below 120°C Method 1 leads to substantial errors because the ABC curve becomes nearly parallel to the temperature axis. In this case the points on the curve of Fig. 5 were obtained by determining the compositions of the equilibrium phases. The lattice parameters of the decomposition phases in equilibrium at a given temperature were obtained from the ABC curve in Fig. 3. Then, using the data in Figs. 3 and 4 for this temperature, an auxiliary Vegard's isotherm was plotted from which the compositions of the equilibrium phases were obtained. The error of the composition determination by this method was 2 mol% or less (horizontal bars in Fig. 5).

Thus, in Method 1 all the errors are referred to those of the temperature determination, while in Method 2 they are referred to the composition determination errors.

TABLE I
THE CONSTANCY OF THE "AVERAGE" CRYSTAL LATTICE PARAMETER OF THE DECOMPOSITION PHASES FOR THE CsBr–CsJ SOLID SOLUTIONS

$t(^{\circ}\text{C})$	x_1 (mol% CsJ)	x_2 (mol% CsJ)	a_{x_1} (Å)	a_{x_2} (Å)	$\bar{a} = (a_{x_1} + a_{x_2})/2$ (Å)
20	4	94	4.306	4.548	4.427
40	4.5	92	4.311	4.546	4.429
60	5	89	4.316	4.542	4.429
80	6	84.5	4.322	4.534	4.428
100	7	79	4.329	4.524	4.426
120	8.5	72.5	4.337	4.510	4.424
140	12	64.5	4.350	4.493	4.421
160	18	56	4.371	4.474	4.423
180	28.5	44.5	4.404	4.447	4.426
183 ± 5 (t_k)		36		4.426	4.426
				Mean value	4.426
				Mean deviation	$\pm 0.003 \text{ \AA}$

According to the data of Fig. 5, the critical temperature of the solvus $t_k = 183 \pm 5^{\circ}\text{C}$ and the critical concentration $x_k = 36 \text{ mol\% CsJ}$. The equilibrium decomposition curve closely follows the rule of linear diameter, i.e., the node centers lie on the straight line.

The equilibrium decomposition curve enables us to check the validity of rule (1) for CsBr–CsJ solid solutions. The results are presented in the table, in which the data were obtained as follows. The concentrations x_1 and x_2 of the equilibrium phases were determined from the curve of Fig. 5 for various temperatures. The crystal lattice parameters for these phases, a_{x_1} and a_{x_2} , were determined according to Vegard's rule from the temperature dependencies of the crystal lattice parameters of pure CsBr and CsJ (Fig. 3). As is seen from the table, the "average" crystal lattice parameter of the equilibrium decomposition phases, \bar{a} , remains constant to $\pm 0.003 \text{ \AA}$ at temperatures from 20 to 180°C . It is essential that the crystal lattice parameters of the pure components increases in this temperature range by about 0.030 \AA .

It can be seen from Fig. 5 that the decomposition curve obtained in (4) using quenching technique shows considerable deviations from the equilibrium curve (by 70°C and 6 mol% for the critical point). This means that for the CsBr–CsJ solid solutions the effects of kinetic factors cannot be neglected. Besides, the data in the table and in Fig. 5 shows that relation (1) can be used as a criterion of the equilibrium state of the experimental solvus line.

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References

1. YU. I. VESNIN AND S. P. ZAKOVRYASHIN, *Solid State Commun.* **31**, 635 (1979).
2. YU. I. VESNIN AND YU. V. SHUBIN, *Mater. Res. Bull. (USA)* **19**, 1355 (1984).

3. YU. I. VESNIN, *Dokl. Akad. Nauk USSR* **275**, 1428 (1984).
4. M. AHTEE, *Ann. Acad. Sci. Fennicae A* **6**, N312 (1964).
5. YU. I. VESNIN AND S. P. ZAKOVRYASHIN, *Pribori i tekhnika eksperimenta*, No. 6, p. 128, 1979.
6. J. B. NELSON AND D. P. RILEY, *Proc. Phys. Soc.* **57**, 160 (1945).
7. V. YA. ANOSOV, M. I. OZEROVA, AND YU. YA. FIALKOV. "Osnovy fiziko-khimicheskogo analiza," p. 295, Nauka, Moscow, 1976.