THE AGEING OF A SUPERSATURATED SOLID SOLUTION OF NaCl + BaCl₂ I

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The ionic conductivity of single crystals of $NaCl + BaCl_2$ has been measured as a function of annealing time at different constant temperatures. The samples of crystals were treated differently thermally and mechanically before annealing. $BaCl_2$ was found to be of low solubility and forming a supersaturated solid solution in NaCl. The solubility determined on the basis of ageing is lower than that determined in the usual way from the plot of $\log \sigma$ vs $1/T$. On the other hand, a higher enthalpy of solution was found.

INTRODUCTION

Very small amounts of impurities dissolved in crystals decide often about their properties. In the alkali halides namely the divalent impurities play an important role. They are incorporated substitutionally in small amounts and form with the matrix a solid solution. These solid solutions prepared at a comparatively high temperature become easily supersaturated at lower temperatures because the solubility decreases with temperature. This leads to the precipitation of a separate phase of impurity. The diffusion of impurity ions, the rate of which decreases exponentially in the first approximation with increasing reciprocal temperature, plays a dominant role in the precipitation. Therefore, the „freezing-in“ of impurities in the solid solution can occur at concentrations which exceed the solubility and the non-equilibrium concentration of impurity can cause a considerable distortion of the dependence of different quantities — such as conductivity, diffusion and likewise — on concentration and temperature. Because, moreover, comparatively little is known about laws of solubility and precipitation of impurities in alkali halides, these effects require a more detailed study.

As to the solubility of divalent impurities, mostly only experimental data on the solubility of free unassociated impurities are published (Haven [2], Rolfe [3], Rothmann, Barr et al. [4], Brown and Hoodless [5], Trnovcová [6] and others). However, it was already shown by Haven [2] and

Lidiard [7] that the total solubility is in fact a higher one. It is due to the formation of complexes, or higher complexes of impurities. The total solubility was determined only for $ZnCl_2$ (Pauliny-Tóthová and Popeliš [8]).

As it was noted by Kessler [1], on the basis of comparison of his conductivity measurements of $NaCl + CaCl_2$ with Beans measurements [9], a supersaturated solid solution is apparently relatively easily formed. This is recognized by a „virtual" maximum in the plot of σ vs c, $T = $ const, i. e., for c smaller than its maximum value. As seen in the results of Fröhlich and Hensel's measurements [10] and others, it occurs in several different systems.

If the solubility is determined from the respective knee in the conductivity isotherms $\sigma = f(c)$, $T = $ const. (or from the respective knee in the plot of $\log \sigma$ vs $1/T$), the freezing-in can lead to both erroneous data of the free energy of association of complexes [1] and incorrect conclusions regarding the solubility of free unassociated impurities.

To verify experimentally the idea of the freezing-in of impurities, i. e., of the formation of a supersaturated solid solution and to utilize it to check the solubility, crystals doped by barium were grown. The ionic radius of Ba^{2+} is namely larger than that of Na^+. Therefore we can expect a low solubility and a low diffusion coefficient. These should favour to form a supersaturated solid solution. On the other hand, barium can be built-in into NaCl in a relative great concentration. If we deal indeed with a supersaturated solid solution we can expect that the surplus of impurities will precipitate through convenient ageing, which should be evident also by a decrease in conductivity.

THEORY

As shown by Lidiard [11], the following is valid for the free-impurity solubility

$$c_f x_1 = \exp(-\Gamma/kT) = \exp(\eta/k)\exp(-\chi/kT),\qquad (1)$$

where Γ is the Gibbs free energy of dissolution needed to transfer one molecule of impurity from its matrix crystal phase to the alkali halide lattice, η and χ are the entropy and enthalpy associated with the dissolution; c_f and x_1 are the free-impurity solubility and the concentration of cation vacancies, respectively (expressed in molar fractions). However, the relations expressing the solubility product of vacancies and the condition of electroneutrality have still to be fulfilled for x_1 and c_f

$$x_1 x_2 = x_0^2,\qquad (2)$$

$$x_1 = c_f + x_2,\qquad (3)$$

where x_2 is the concentration of anion vacancies and x_0 is the concentration of thermal vacancies (in molar fractions). As long as $x_0 \gg c$, it follows from (2) and (3) that $x_1 \sim c_f$, so that we obtain from (1)

$$c_f = \exp(-\Gamma/2kT).\qquad (4)$$

If the formation of thermal vacancies cannot be neglected, substituting into (3) from (1) and (2) we obtain

$$c_f = \frac{\exp(-\Gamma/2kT)}{\{1 + x_0^2 \exp(\Gamma/kT)\}^{1/2}}.\qquad (5)$$

It is evident from what has been said that the formation of thermal vacancies decreases the free-impurity solubility.

If complexes of divalent impurities and vacancies are formed in the crystal, then the ratio of equilibrium concentrations of free unassociated ions and complexes is given by the equation [11]

$$\frac{c_k}{c_f x_1} = 12 \exp(\xi_k/kT),\qquad (6)$$

assuming that the entropy of association is close to zero; c_k is the concentration of complexes and ξ_k is the enthalpy of association of complexes. It follows from (6), for the solubility of complexes, that

$$c_k = 12(c_f x_1)\exp(\xi_k/kT) = 12c_f^2 \exp(\xi_k/kT),\qquad (6a)$$

and for the total solubility c_T according to (5) and (6a) we have

$$c_T = c_f + c_k.\qquad (7)$$

As it is known from papers of Cook and Dryden [12] and others, different types of higher aggregates of impurity are formed as a step preceding the precipitation in the crystal; it is, e. g., in the form of trimers (3 complexes = = 1 trimer) and then higher complexes.

If we write for the equilibrium between trimers and complexes the corresponding relation according to the mass action law, whereby we assume the equilibrium constant in the form $K_t(T) = A_t \exp(\xi_t/kT)$, ξ_t is the enthalpy of association of trimers, then

$$c_t/c_k^3 = A_t \exp(\xi_t/kT),\qquad (8)$$

where c_t is the concentration of trimers; in this way we have for the solubility

of trimers using (6a),

$$c_l = c_k^3 A_t \exp(\xi_l/kT).$$ (8a)

It is to note, cf. (4) and (5) that the free-impurity solubility is not dependent on the solubility of complexes and the next higher complexes. The solubility of complexes is no doubt dependent on the free-impurity solubility, however it is not dependent on the solubility of higher complexes, etc.

EXPERIMENTS and THEIR RESULTS

As already mentioned in the introduction crystals of NaCl + BaCl₂, partly with high doping of impurity, were grown from the melt by the Kyropoulos method. In Fig. 1a is shown the conductivity isotherm of these crystals for 550° C and the values of crystals chosen for ageing experiments marked.

It was shown by ageing at an optimal temperature [13] that the conductivity of samples 1, 2, 3 decreases to the value of sample 5 and 4, the conductivity of which is no more changed by ageing. In this an isotherm which corresponds to the theoretical expectation, i. e. $\sigma \propto c$, $c \leqslant c_f$ and $c = $ const., $c > c_f$ was
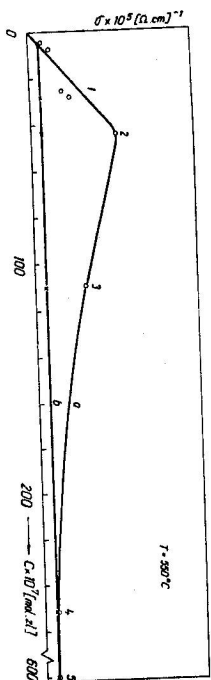
Fig. 1a. The variation of conductivity with impurity concentration for NaCl crystals doped with barium at temperature 550 °C: a — fresh grown crystals, b — aged crystals.
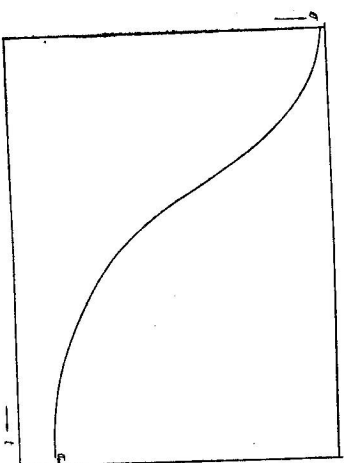
Fig. 1b. The typical decrease in conductivity σ to the equilibrium value $\sigma_{-\infty}$ with time t at constant temperature.

obtained. It can be observed that during ageing the conductivity begins to decrease after some starting time to reach finally a stable value, cf. Fig. 1b. An electronmicroscopic study of thermally etched surfaces of aged crystals (Vlasák [14]) showed that these samples contain a great number of precipitates which are formed by BaCl₂, in accordance with the X-ray structural analysis.

Fig. 2a. The dependance σ_∞ vs $1/T$ determined from equilibrium values of σ obtained by ageing of crystals at temperatures; 0 — 1 (slowly cooled); $\times$ — 2 (slowly cooled); Δ — 2 (quenched, deformed); $\bullet$ — 4 (quenched, slowly cooled); $\blacktriangle$ — 2 (slowly cooled, deformed); $\triangle$ — 4 (quenched, σ vs $1/T$), σ vs $1/T$); $\square$ — 5 (slowly cooled, σ vs $1/T$); $\odot$ — 5 (slowly cooled, σ vs $1/T$).
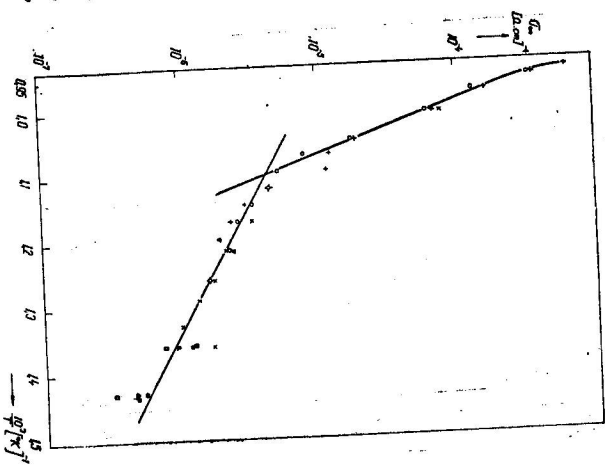
Finally, we denote by σ_∞ the conductivity values of aged crystals, which do not change any more their conductivity at the chosen temperatures with further ageing. As seen from Fig. 2a, where $\log \sigma_\infty$ vs $1/T$ is shown, these values dependent practically on temperature only: the ageing was carried out with samples of different impurity concentration, including the sample with maximum concentration [13] further with differently deformed samples, the precipitation of which takes place at a rate dependent on the dislocation density and with a different number of nuclei of precipitation [15]; finally samples, the conductivity of which did not change during ageing, were used as well.

ANALYSIS of RESULTS

The temperature dependence of concentration of free-cation vacancies x_1

can be determined from log σ_∞ vs $1/T$ by means of the known temperature dependence of vacancy mobility μ [16, 17] (Fig. 2b).

It is evident from the plot of x_1 that beyond the knee in the log x_1 vs $1/T$ curve towards higher temperatures the number of thermal vacancies will no more be negligible, compared with vacancies due to impurities. We can express explicitly c_f from (3)
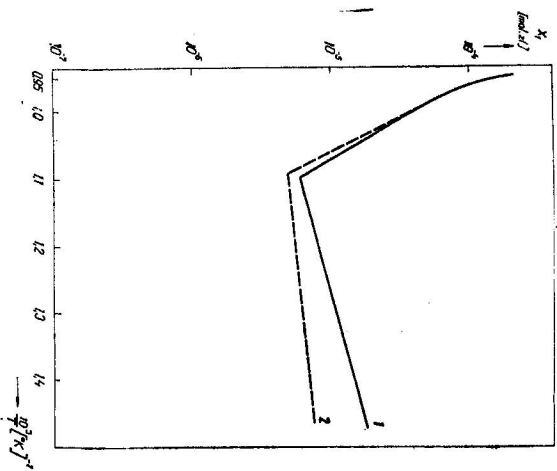

Fig. 2b. The dependence of concentration of free cation vacancies x_1 on temperature determined from plot of σ_∞ vs $1/T$ by means of mobility established by Bizouard et al. [16] – 1 by Trnovcová et al. [16] – 1 by Trnovcová [17] – 2.

$$c_f = \frac{x_1^2 - x_0^2}{x_1} \qquad (9)$$

and calculate c_f. The temperature dependence of x_0 was determined by Etzel and Maurer [18]. The use of these values of x_0 leads to negative values of c_f. The preexponential factor of x_0 was therefore adjusted to secure $c_f > 0$. As seen from Fig. 3, the dependence of log c_f vs $1/T$ is a straight line (except for highest temperatures). The half of the enthalpy of solution of free impurities of Ba^{2+} determined from the slope of the linear section is $\frac{1}{2}\chi = 1.90$ eV.

An other possibility to establish χ is to use equation (5). We use the designation $K(T) = \exp(-\Gamma/kT)$ and rearrange eq. (5) in the form

$$K(T) = \tfrac{1}{2}c_f^2 \{1 + (1 + 4x_0^2/c_f^2)^{1/2}\}, \qquad (10)$$

which is suitable for the determination of the enthalpy of solution. Substituting

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Fig. 3. The free-impurity solubility of Ba^{2+} in NaCl: c_f (according eq. (9)), $K(T)$ (according to eq. (10)), data of Brown and Hoodless [5].
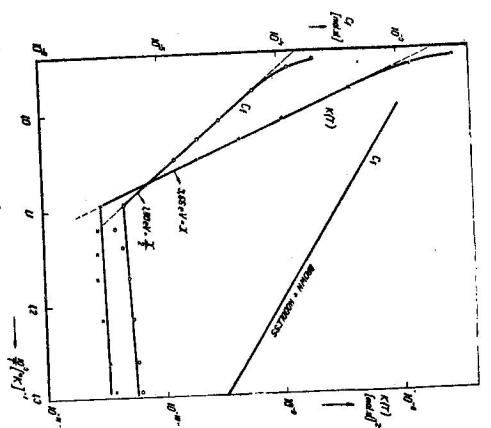
the calculated values of c_f and the corrected Etzel-Mauer values of x_0, we calculate the values of $K(T)$ for different temperatures. As seen from Fig. 3 the dependence of log $K(T)$ vs $1/T$ gives the enthalpy of the solution $\chi = 3.66$ eV ($\frac{1}{2}\chi = 1.88$ eV).

DISCUSSION

During the ageing of the crystals 1, 2, 3 precipitation sets in. This is evidenced not only by the decrease in conductivity, i. e. the decrease of incorporated free impurities, but by electronmicroscopic findings as well. From the thermodynamic point of view it is evident that the system of solid solution was not in equilibrium. If it had been in equilibrium no change would occur. On the contrary, the system achieves a stable state by ageing. This is evident from the plot of the decrease in conductivity. This stable state corresponds either to a thermodynamic equilibrium of it results from the freezing-in of some step in the precipitation process.

In accordance with the theory of solubility, the following should be valid for the conductivity isotherm: $\sigma_\infty \propto c$, $c \leqslant c_f$ and $\sigma_\infty = $ const., $c > c_f$. We see that it is exactly this condition which is almost ideally fulfilled by the aged crystals, whilst the plot of the isotherm of fresh crystals can hardly be understood otherwise than as the consequence of an unevenly progressed precipitation without achievement of the equilibrium state. Further, it was shown that the stable state depends neither on the impurity concentration nor on the precipitation rate and other circumstances but on temperature only, as expected of solubility, viewed theoretically.

From the analysis of the experimental data in the previous section it is seen that the calculated c_f values fit approximately (5) above the temperature of the knee at $10^3/T = 1.1$. There is an uncertainty, which arises from the fact that x_0^2 is not know precisely enough — the enthalpy of formation is e. g. according to Etzel and Maurer [18] 2.02 eV, according to Brown and Hoodless [5] established from the conductivity of $NaCl + BaCl_2$ 2.30 eV. But the influence of the thermal vacancies is comparatively small, as is seen e. g. from a comparison of the x_1 and c_f values in Fig. 2b and Fig. 3. From the discussion of the experimental findings it occures that below $10^3/T \sim 1.1$ c_f represents the solubility with $\chi/2 \sim 1.9$ eV, above this value the impurity is obviously frozen in.

As already mentioned in the introduction, the solubility of free Ba^{2+} ions in NaCl was determined by Brown and Hoodless [5] from their conductivity data. As seen from Fig. 3 they obtained over the whole measured range not only a higher solubility but a much lower enthalpy of dissolution. Since the ageing took place isothermally, we cannot find another reason for this difference than that (a) in the case of Brown and Hoodless the impurity was frozen in in a substitutional position by a relatively quick cooling of the crystals (in comparison with our time of annealing), or that (b) the solubility for the crystals which we used is lower, e. g. as a consequence of a different dislocation density, or likewise. However, as seen from Fig. 2a, no influence of dislocation density and deformation of crystals on solubility was evidenced. Therefore it seems to be more probable that Brown and Hoodless experimented with supersaturated crystals.

CONCLUSIONS

On the basis of the above discussion, the following conclusions have been arrived at:

1. The conclusions with respect to the formation of a supersaturated solid solution [1] were confirmed.

2. The solubility determined on the basis of ageing is lower than that determined before [5] and the enthalpy of solution is a higher one.

3. For temperatures lower than $10^3/T \sim 1.1$, i. e. 640 °C, some amount of barium (with the ionic radius 1.35 Å larger than that of natrium with 0.95 Å) remains frozen in the lattice, i. e. the casual precipitation below this temperature takes place so slowly hat it could not be observed during the time of annealing (13 hours).

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