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THE ROLE OF DISLOCATIONS IN THE AGEING OF NaCl + SrCl₂ CRYSTALS

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Résumé. — Le vieillissement des cristaux de NaCl, SrCl₂ déformés à des degrés divers a été examiné à l'aide de mesures de conductivité électrique à 500 °C. Il s'est avéré que les impuretés de strontium (le plus vraisemblablement des inclusions en phase suzuki) forment des agrégats dans tout le volume du cristal hôte et pas particulièrement sur les dislocations de bord. Les résultats quantitatifs s'accordent bien avec la théorie simple de Cottrell. Au cours de cette expérience, nous avons trouvé un coefficient de diffusion $D_{Sr} = (2,43 \pm 0,7) \cdot 10^{-11} \text{ cm}^2/\text{s}$ pour le strontium en impureté.

Abstract. — The ageing of NaCl + SrCl₂ crystals deformed to various degrees has been investigated by means of electric conductivity measurements at 500 °C. It has been found that the aggregation of strontium impurity (most likely the Suzuki phase inclusions) takes place in the whole volume of the host crystal, not especially on the edge dislocations. The results are in a good quantitative agreement with the simple Cottrell theory. The diffusion coefficient of the strontium impurity in this experiment was found to be $(2.43 \pm 0.7) \cdot 10^{-11} \text{ cm}^2 \text{ s}^{-1}$.

1. Introduction. — It is well known that foreign impurities may be incorporated into a host lattice only up to a definite concentration. The solubility of divalent and polyvalent metal ions in alkali halide crystals is restricted and increases with increasing temperature (cf. e. g. [1]). When the impurity concentration exceeds the solubility limit, impurities leave the solid solution and build up aggregates or segregated phases in the crystal. In the case of divalent impurities built-in into a monovalent ionic crystal it is possible to investigate the precipitation process, by observing, e. g. the change in electric conductivity. This change is due to a change in the concentration of the charge carriers, which (cf. e. g. [1]) depends on the amount of substitutionally built-in divalent impurities.

The precipitation may occur either in the whole volume of the host crystal, for example CaCl₂ in NaCl [2], or, if the crystal structure of the secondary phase differs considerably from that of the host crystal, it takes place on lattice imperfections, such as grain boundaries, stacking faults and dislocations.

The possibility of impurity precipitation on dislocations due to elastic interaction between the impurity and the dislocation was pointed out, e. g. by Cottrell and Bilby [3]. The rate of precipitation depends on the diffusion coefficient of the impurity, on the temperature and the magnitude of the interaction. The selective precipitation on dislocations is used to make dislocations visible with the so-called *decoration technique* [4, 5]. In this paper some results concerning the dependence of the precipitation rate of strontium impurity in NaCl on the dislocation density are reported.

2. Experimental results and their discussion. — Samples suitable for conductivity measurements were cleaved from an NaCl single crystal doped with 240 ppm SrCl₂ in the crystal. The crystal was grown by the Kyropoulos method at Sektion Physik, Martin Luther Universität, Halle. The samples were first annealed for 16 hours at 650 °C in an argon atmosphere and then air-quenched at room temperature. The ageing was observed by measuring the change in conductivity with time at 500 °C. This particular temperature was chosen because at this temperature the rate of precipitation was found to be the highest.

The ageing was followed on samples deformed to different degrees. The deformations of the samples and the corresponding dislocation densities ρ established by etching are shown in table I. ρ_{rel} in table I is the ratio of the dislocation density of the deformed samples to that of undeformed ones.

TABLE I

Sample	Deformation(%)	$\rho(\text{cm}^{-2})$	ρ_{rel}
1	0	3.29×10^6	1
2	1	2.01×10^7	6.11
3	1.8	2.97×10^7	9.03
4	2.5	3.14×10^7	9.54
5	4	7.07×10^7	21.49

FIG. 1. — Dependence of the conductivity σ on the time t for variously deformed samples of NaCl + 240 ppm SrCl₂.

In figure 1 the observed conductivity vs. time curves are shown. It is evident that the aggregation rate increases with the dislocation density. According to [3], one may write for the early stage of the aggregation if the precipitation takes place by aggregation along dislocations :

$$\frac{N(t)}{N(0)} = \alpha \rho \left(\frac{ADt}{kT} \right)^{2/3} \quad (1)$$

where

- $N(t)$ the amount of impurity which segregates on the dislocation during the time t ,
- $N(0)$ the initial impurity concentration in the crystal,
- A a parameter depending on the elastic constant G and on the relative ratio Σ of the impurity radius r_{Sr} and the host lattice cation radius r_{Na} ,
- α a numerical factor equal to $3 \cdot \sqrt[3]{(\pi/2)}$,
- ρ the dislocation density,
- D the diffusion coefficient of the impurity,
- kT the Boltzmann factor.

The term A from equation (1) is governed by the following equation :

$$A = 4 G b \Sigma r^3, \quad (1a)$$

where for NaCl + SrCl₂

$$G = 1.49 \times 10^{11} \text{ dyn/cm}^2$$

$$b = \frac{a}{2} \sqrt{2} = \frac{5.6}{2} \sqrt{2} = 3.96 \text{ \AA}$$

$$\Sigma = \frac{r_{\text{Sr}} - r_{\text{Na}}}{r_{\text{Na}}} = \frac{1.13 - 0.98}{0.98} = \frac{0.15}{0.98} = 0.153$$

$$r = r_{\text{Na}} = 0.98 \text{ \AA}.$$

In figure 2 the quantity $1 - N(t)/N(0)$ is plotted against $t^{2/3}$. If equation (1) is obeyed, a straight line should be obtained. As seen, this is the case except for small values of t . One may conclude therefore that in NaCl + SrCl₂ precipitation takes place on dislocations according to equation (1) except for $t < 3.5$ hours. We suppose that before any precipitation occurs a certain

FIG. 2. — Relative number of aggregated Sr²⁺ ions as a function of $t^{2/3}$.

concentration of impurities must be reached, first around the dislocations. Only then can nuclei of precipitation form and the precipitation starts. During the first period the conductivity change is comparatively slow and does not agree with equation (1). Moreover, on the basis of theoretical estimates of the association and the elastic interaction energies between Sr²⁺ ions and edge dislocations, we assume that the long time ($t > 3.5$ hours) needed for the observation of the influence of the dislocation strain field is caused by the influence of the weak elastic interaction between the Sr²⁺ ions and the edge dislocations. It means that a longer time is needed to reach some concentration of impurities around the dislocations. The weak elastic interaction can also cause that the impurity precipitation does not occur directly in the dislocation core but only around the dislocations.

The rate of precipitation depends on the diffusion coefficient of the impurity, on the temperature and on the magnitude of the interaction between the impurity ions and the dislocations. We know from theoretical estimates [6, 7] that this interaction is weak in the NaCl + SrCl₂ system. The temperature at which the rate of precipitation was found to be the highest in our case is known, too. And since the dislocation density is known in our case, we can estimate the diffusion coefficient of strontium in NaCl from equation (1). We get $D_{\text{Sr}} = (2.43 \pm 0.7) \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ if we assume that one half of the total dislocation number are edge dislocations. This value is in a reasonable agreement with the experimental data obtained by the diffusion technique, which are in the interval of 1.3×10^{-11} – $3.4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ [8, 9] ⁽¹⁾. We can thus state on the basis of the mentioned changes in electric conductivity with the time that the strain field of dislocation influences the clustering of Sr²⁺ ions around the dislocations only after a longer time of ageing ($t > 3.5$ hours). In such a case the obtained results are in a good quantitative agreement with the simple Cottrell theory.

This statement regarding the aggregation of Sr²⁺ ions taking place along the dislocations is also support-

(1) Grňo, J., private communication.

ed by the electron microscope investigation of the thermally etched surfaces of crystals, decorated with gold by means of a technique developed by Bethge [10]. One finds the aggregates (most likely the Suzuki phase inclusions [11] ⁽²⁾) located without exception outside the cores of the edge dislocations (none in the cores of screw dislocations), in their environment and in the whole volume of the NaCl crystal. It should be noted that no interaction is expected between screw dislocations and impurities. The assumption that the observed aggregates are the Suzuki phase inclusions is based on our recent investigations of the solubility of the associated strontium in NaCl [11], performed on the same samples as in the present paper. One can ascribe the observed ITC band at 233 K, according to its properties, to the Suzuki metastable phase. Moreover, the preliminary X-ray diffraction measurements ⁽²⁾ performed on these samples indicate the presence of an

⁽²⁾ Suszyńska, M., private communication.

ordered arrangement as expected for the Suzuki phase.

We wish to remark that the observed concentration of aggregates around the dislocations is not essentially greater than elsewhere in the crystal. It means that the precipitation of Sr²⁺ ions in NaCl is not so considerably influenced by the dislocations as it is in the case of Ba²⁺ ions in NaCl, where the precipitates of BaCl₂ are formed almost without exception in the cores of edge dislocations [12].

3. Conclusion. — The ageing of NaCl + SrCl₂ crystals takes place through the aggregation of strontium impurities (most likely in the form of Suzuki phase inclusions) in the whole volume of the host crystal. The strain field of dislocation compared with other parts of the crystal does not influence more markedly the aggregation process. This influence is in good quantitative agreement with the simple Cottrell theory. The diffusion coefficient of strontium impurity in NaCl, D_{Sr} , was found to be $(2.43 \pm 0.7) \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$.

References

- [1] LIDIARD, A. B., *Handbuch der Physik* **20** (1957) 246.
- [2] TOMAN, K., *Czech. J. Phys.* **B 13** (1963) 296.
- [3] COTTRELL, A. H. and BILBY, A. B., *Proc. Phys. Soc. A* **62** (1949) 49.
- [4] AMELINCKX, S., *Sol. Stat. Phys.* (1964) Suppl. 6, 55.
- [5] HARVEY, K., *Phil. Mag.* **8** (1962) 3.
- [6] BASSANI, F. and THOMSON, R., *Phys. Rev.* **102** (1956) 1264.
- [7] VLASÁK, G., HARTMANOVÁ, M. and MRAFKO, P., *Czech. J. Phys.* **B 26** (1976) 164.
- [8] ALLNATT, A. R. and PANTELIS, P., *Trans. Farad. Soc.* **64** (1968) 2100.
- [9] CHEMLA, M., *Ann. Phys. (Paris)* **1** (1956) 959.
- [10] BETHGE, H., *Phys. Stat. Sol.* **2** (1962) 3.
- [11] HARTMANOVÁ, M., THURZO, I. and BESEDIČOVÁ, Š., *J. Phys. & Chem. Solids*, to be published.
- [12] KUPČA, Š., HARTMANOVÁ, M. and VLASÁK, G., *Czech. J. Phys.* **B 19** (1969) 789.

DISCUSSION

F. GRANZER. — Can you exclude the precipitation of a phase along dislocations having the structure of SrCl₂ ?

M. HARTMANOVÁ. — We can not exclude this possibility in the samples with high concentrations of strontium on the basis of the presented results. However, it results from our recent investigations of solubility of associated strontium in NaCl by means of

ITC, performed also on samples with high concentration of strontium that the Suzuki phase inclusions should be play a dominant role in samples with highest concentrations too. Further experiments, concerning a detailed investigation of products of phase segregation in the system NaCl + Sr²⁺ by the electron microscope and X-ray diffraction measurements, are continued at the present.