ELECTRON MICROSCOPIC INVESTIGATION OF THE COLLAPSE OF UNSTABLE SOLID SOLUTIONS IN $NaCl:MCl_2$ SYSTEMS

By

J. SÁRKÖZI and A. TÓTH

Department of Experimental Physics, Institute of Physics, Technical University, Budapest

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Introduction

It is a well known fact that crystals used in practice are never pure, and that the concentration and condition of impurities may seriously affect the physical properties of these materials. Consequently the investigation and understanding of the processes taking place in doped samples is of outstanding importance. Subject of the present paper is an electron microscopic study of precipitation of impurities in sodium chloride single crystal model samples doped with divalent cations *M*.

Experimental technique

In case of a relatively low impurity concentration the divalent impurities substitute Na^+ ions in the NaCl lattice thus realizing an $NaCl:MCl_2$ type solid solution [1]. By increasing the impurity concentration, part of the dopant precipitates and gradually (forming dipoles-dimers-trimers etc.) small MCl_2 precipitates will develop [1]. Of course the precipitation rate and the dimensions of the precipitates strongly depend on the temperature (diffusion processes). These precipitation processes can be studied by applying an impurity concentration fully dissolving in the lattice only at some elevated temperature and then by quenching the crystal a solid solution can be obtained. When this unstable solid solution is heat-treated at various temperatures, various precipitation stages are produced.

The precipitating processes can indirectly be followed by measuring various physical properties (e.g. electrical conductivity, dielectric loss, yield point etc.) [1], although only a few research workers investigated the precipitates directly [2, 3].

The aim of this work was a systematic electron microscopic study of the precipitates by means of the gold-decoration method [4], which consists of evaporating gold on properly prepared surfaces, the gold grains trace out the

surface irregularities (steps, defects, precipitates). The surface replicas obtained this way were electron microscopically investigated and photographed.

Specially grown OH^- free crystals were used containing practically only the impurity introduced intentionally into them [5]. One given crystal contained only one impurity type, the impurity content of the undoped (further on pure) crystals was less than 10^{-7} mol/mol. The following doped samples were used: NaCl:$BaCl_2$, NaCl:$CaCl_2$, NaCl:$MgCl_2$, NaCl:$SrCl_2$, NaCl:$PbCl_2$, NaCl:$MnCl_2$.

The heat treatment of the crystals as well as the quenching have been carried out in vacuum at 10^{-5} torr. The impurities were dissolved at 700 °C, the crystal dimensions and quenching rates were chosen so that no change of dislocation density takes place.

In order to obtain a better understanding of the processes in each experiment also the temperature-dependent electrical conductivity has been measured.

Results and discussion

The investigation of the samples containing various impurities was carried out as follows. First the samples containing the solid solution were produced by annealing at 700 °C and quenching to room temperature. After this the quenched samples were annealed at various temperatures for several hours, then decorated with gold and investigated in the electron microscope. Since with various impurities the series obtained were quite similar only a typical series of micrographs obtained with the NaCl:$SrCl_2$ system is presented (Fig. 1). Picture a) shows the initial stage (quenched from 700 °C). The dark spots are gold grains deposited on the surface either dispersed at random, or forming lines (surface steps) or clusters (precipitates). The presence of small precipitates in the starting sample is easy to explain since because of the finite quenching rate the solid solution has not become thoroughly frozen in, a small amount of precipitation has already been formed. By annealing at various temperatures T_a various types of precipitates are formed. At lower temperature a great number of small precipitates appear (Fig. 1b) whereas very large precipitates in a small amount are typical results of high temperature annealing (Fig. 1c). Above a critical temperature T_0 the impurity becomes again dissolved in the lattice and a picture very similar to the starting one is obtained (Fig. 1d). Every impurity has a characteristic temperature of annealing which yields the largest precipitates (for Sr this is depicted in Fig. 1c). This critical temperature depends on the solubility and diffusion constant of the given impurity.

In order to prove that the structures depicted in Fig. 1 are actually connected with the impurities, heat treatments in accordance with the experiments of the doped samples were carried out on pure crystals. The decoration

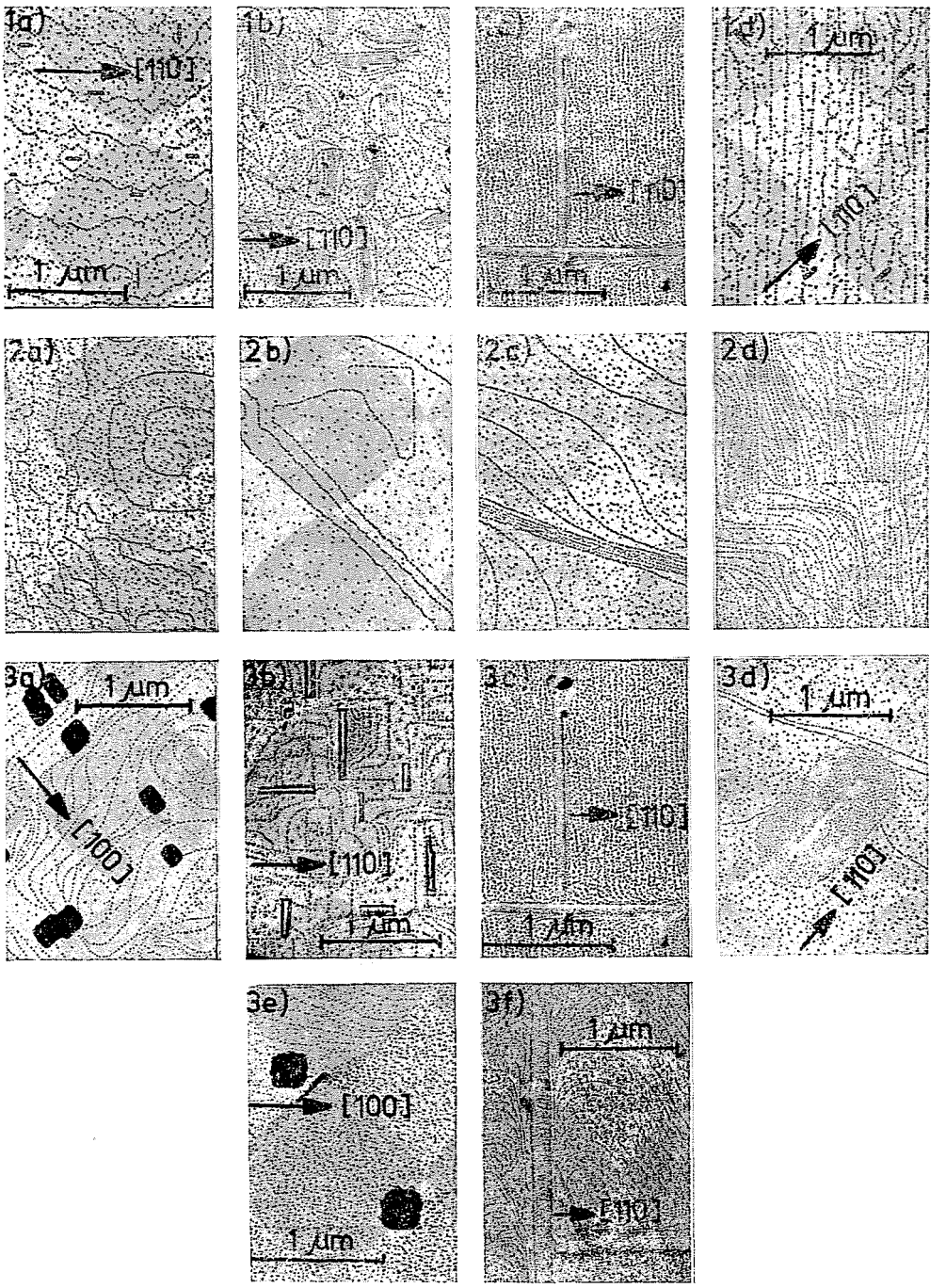

Fig. 1. Decoration electron micrograms showing the changing of the state of the $SrCl_2$ impurity in dependence of the annealing temperature T_a. a) — first stage (solid solution); b) — $T_a \approx 200$ °C; c) — $T_a \approx 300$ °C; d) — $T_a > 350$ °C

Fig. 2. Electron micrograms of pure crystals in case of the same heat treatment as applied to doped crystals. a) — first stage; b) — $T_a \approx 200$ °C; c) — $T_a \approx 300$ °C; d) — $T_a > 350$ °C

Fig. 3. Gold decoration micrograms obtained after annealing resulting in precipitates of largest dimension in case of different impurities: a) — Mn; b) — Pb; c) — Sr; d) — Ca; e) — Mg; f) — Ba

pictures obtained show — as expected — only gold grains scattered on the surface at random or arranged in lines (Fig. 2) in total absence of clusters which may refer to precipitates.

Similar observations were made with crystals containing various other dopants, however, also some deviations were revealed which are apparently connected with specific characteristic properties of the impurity atoms. The differences are properly seen in Fig. 3, which demonstrates the stages obtained after annealing resulting in very large precipitates for various impurities. There are actual differences in the separate cases with regard to the shape of the precipitates as well as to their orientation. Also the annealing temperatures resulting in these stages are different in spite of the fact that the impurity concentrations were nearly the same. This can be explained by the difference of solubility and diffusion constant of the various dopants.

The precipitation and dissolution of impurities is well known to considerably change the ionic electrical conductivity of the crystals investigated [1]. Representing the temperature T dependence of the ionic conductivity σ in $\log \sigma \cdot T$ *vs.* $1/T$, the temperature of the total dissolution of the impurity T_0 is indicated by a break in the conductivity line. Fig. 4 depicts this kind of

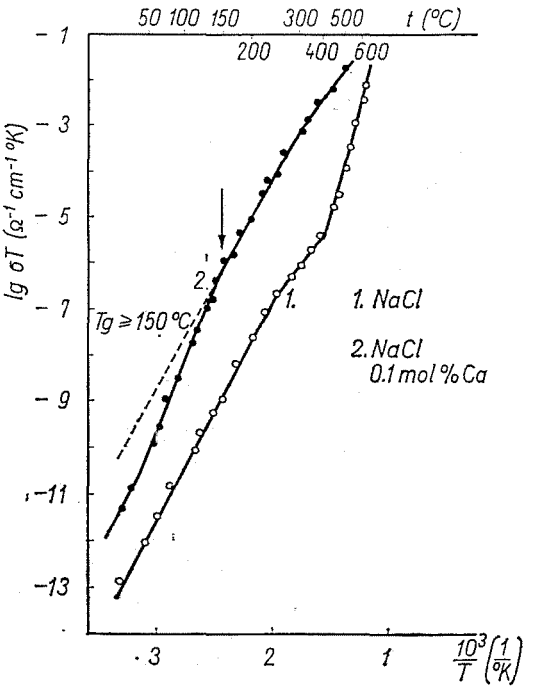

Fig. 4. Temperature dependence of undoped (pure) NaCl (diagram no. 1) and of the NaCl:$CaCl_2$ system (diagram no. 2). The dotted line indicates the conductivity of the starting (solid solution) sample

break obtained with a $NaCl:CaCl_2$ system, and indicated by an arrow. No break appears in diagrams obtained with pure crystals, which is in accordance with experience: no precipitation occurs with these crystals. Similar breaks were experienced also with the other impurities, but at different temperatures depending on their solubility.

The complete dissolution temperatures can, of course, be obtained by the electron microscopic technique discussed previously, and the results may be compared to the values obtained from the conductivity experiments:

According to the tabulated results the dissolution temperatures obtained with the two different methods are in good agreement.

Impurity atom	Ca	Mg	Mn	Pb	Sr	Ba
T_0 (°C) determined electron microscopically	140	200	300	310	340	530
T_0 (°C) obtained from conductivity measurements	150	195	310	310	335	520

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Summary

The precipitation processes of divalent cation impurities in NaCl single crystals were investigated by electron microscopy. The dimensions of the precipitates formed were found to depend upon the temperature of precipitation. Considerable differences of the shape and orientation of the precipitates for different impurities were observed at a given temperature. The complete dissolution temperature has been determined electron microscopically for various impurities. The temperatures established are in good agreement with the limiting temperatures defining the precipitation and association phases obtained by temperature dependent electrical conductivity curves.

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Dr. József SÁRKÖZI
Dr. András TÓTH
H-1521 Budapest