

## Oriented Growth and Crystal Structure of Phases Precipitated in $\text{Eu}^{2+}$ -doped NaCl Single Crystals

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### Abstract

X-ray investigations of  $\text{Eu}^{2+}$ -rich precipitates in NaCl single crystals have revealed the presence of two phases. Phase *A* of chemical formula  $\text{EuCl}_2$  with a  $\text{CaF}_2$ -type structure and lattice parameter  $a = 6.969(2) \text{ \AA}$  preserves strictly the orientation of the matrix lattice. Phase *B* with the lattice parameter  $a = 7.47(1) \text{ \AA}$  and tentative formula  $\text{EuCl}_2 \cdot 2\text{NaCl}$ , containing  $\text{Eu}^{2+}$  ions and charge-compensating cation vacancies, is localized at subgrain boundaries and is thermally less stable than phase *A*.

### 1. Introduction

Divalent cations introduced substitutionally into the alkali halide crystal lattice show a tendency towards formation of aggregates composed of  $\text{Me}^{2+}$  and cation-vacancy dipoles (Miyake & Suzuki, 1954; Suzuki, 1955; Sors & Lilley, 1975). In some instances, at sufficiently high dopant concentration, the aggregation results in formation of precipitates large enough to induce a strong light scattering responsible for the milky appearance of the crystal.

X-ray investigations of the impurity-related precipitated phases in alkali halide crystals have been performed (Suzuki, 1955). The same author was also first to show in  $\text{Cd}^{2+}$ -doped NaCl crystals the appearance of a metastable phase of composition  $\text{CdCl}_2 \cdot 6\text{NaCl}$  of cubic symmetry (space group  $Fm\bar{3}m$ ) and doubled lattice parameter relative to that of the NaCl matrix (Suzuki, 1961). So-called Suzuki phases of the above composition have also been found in several other doped alkali halide crystals, e.g.  $\text{LiF}:\text{Mg}^{2+}$  (Lilley & Newkirk, 1967),  $\text{NaCl}:\text{Mn}^{2+}$  (Sors & Lilley, 1975; van Loon & IJdo, 1974). A different type of precipitated phase of inverted spinel structure and doubled lattice parameter has been proposed in  $\text{LiF}:\text{Ni}^{2+}$  (Jehanno & Perio, 1968; Levelut, Lambert & Gunier, 1968). In other doped crystals, e.g.  $\text{NaCl}:\text{Ca}^{2+}$  and  $\text{NaCl}:\text{Ba}^{2+}$ , precipitation of  $\text{CaCl}_2$  or  $\text{BaCl}_2$  crystallites having the structure, except for some slight distortion, characteristic of the species obtained in the pure state was

observed (Toman, 1963; Swamy Rao & Parasnis, 1977). The form and the orientation of the precipitated phases were also examined by electron microscopy in  $\text{NaCl}:\text{Ba}^{2+}$  (Vlasak & Hartmanova, 1975) and in  $\text{NaCl}:\text{Mn}^{2+}$  (Yacaman, Hobbs & Goringe, 1977).

In  $\text{NaCl}:\text{Eu}^{2+}$  the precipitation proved to be more complicated due to the existence of two precipitated phases differing in structure, distribution and stability.

### 2. Characteristics of precipitated phases

$\text{Eu}^{2+}$ -doped NaCl crystals were grown by the Bridgman method in vacuum-sealed quartz ampoules (Voszka, Tarjan, Berkes & Krajsovsky, 1966). The crystalline samples showing strong scattering of light were taken from the  $\text{Eu}^{2+}$ -rich (about 0.1 mol%) end of the crystal stored at room temperature for two years. Preliminary Laue photographs taken in the [100] direction revealed the presence of several new symmetrically distributed low-angle reflections (Stępień-Damm, Mugeński & Łukaszewicz, 1978). Subsequently, a series of oscillation and Weissenberg photographs were taken for [100] and [110] rotation directions of the sample with graphite-monochromatized  $\text{Cu } K\alpha$  radiation. Fig. 1 shows an oscillation photograph with [110] as rotation axis and

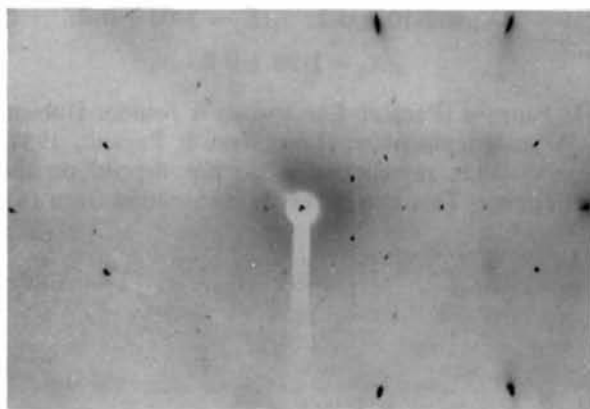


Fig. 1. Oscillation photograph. Rotation axis [110],  $\text{Cu } K\alpha$  radiation, time of exposure 12 h.

Fig. 2 a Weissenberg diagram of the  $hk0$  layer. In these diagrams one can ascertain, except for Bragg reflections originating from the NaCl matrix, the presence of two kinds of additional reflections pointing to the existence of two different precipitated phases. Reflections of the first kind can be ascribed to a cubic structure with  $a = 6.969(2) \text{ \AA}$  (phase A). Reflections of the second kind resulting from phase B appear at lower angles and are located symmetrically on each side of the main symmetry axes  $h00$ ,  $hh0$ ,  $hhh$  of the host crystal.

A distribution of  $\text{Eu}^{2+}$  ions was additionally examined with an electron microscope (JEOL) with freshly cleaved crystalline samples. As shown in Fig. 3 one can distinguish also two types of  $\text{Eu}^{2+}$ -rich precipitates. Larger ones of 1.6 to 2.0  $\mu\text{m}$  diameter, denoted as phase A, are distributed at random while the smaller ones of diameter not exceeding 0.2  $\mu\text{m}$ , denoted phase B, seem to be localized at the subgrain boundaries in the crystal. In samples heated at 873 K for 2 h the

smaller precipitates disappear and in the X-ray diagrams no reflections ascribed to phase B can be detected. In a few samples with high  $\text{Eu}^{2+}$  concentration phase A only could be detected. Phase A disappears in samples heated at 873 K for 60 h.

### 3. Phase A

The reflections of phase A were strong enough to be measured in a routine way on a single-crystal diffractometer. The measurements of a  $[110]$ -oriented sample  $0.3 \times 0.5 \times 1 \text{ mm}$  were performed on a two-circle automatic diffractometer STOE with graphite-monochromated  $\text{Mo } K\alpha$  radiation. The intensities of reflections of the matrix NaCl crystal and precipitated phase A were recorded for the same sample, which allowed us to estimate the amount of A phase in the sample to be about 0.03 wt%. The main crystallographic directions of the NaCl matrix and of the precipitated phase were found to be exactly parallel to each other. For phase A we measured 118 reflections of which 56 were symmetrically independent. Similar results were obtained for two other samples. The intensities were corrected for Lorentz and polarization factors. An absorption correction (North, Phillips & Mathews, 1968) was also applied.

Three models based on space group  $Fm\bar{3}m$  were checked: two models with random distribution of  $\text{Eu}^{2+}$  ions and charge-compensating cation vacancies and one model of  $\text{EuCl}_2$  composition but of the  $\text{CaF}_2$ -type structure with  $a = 6.969(2) \text{ \AA}$ . The last model was in

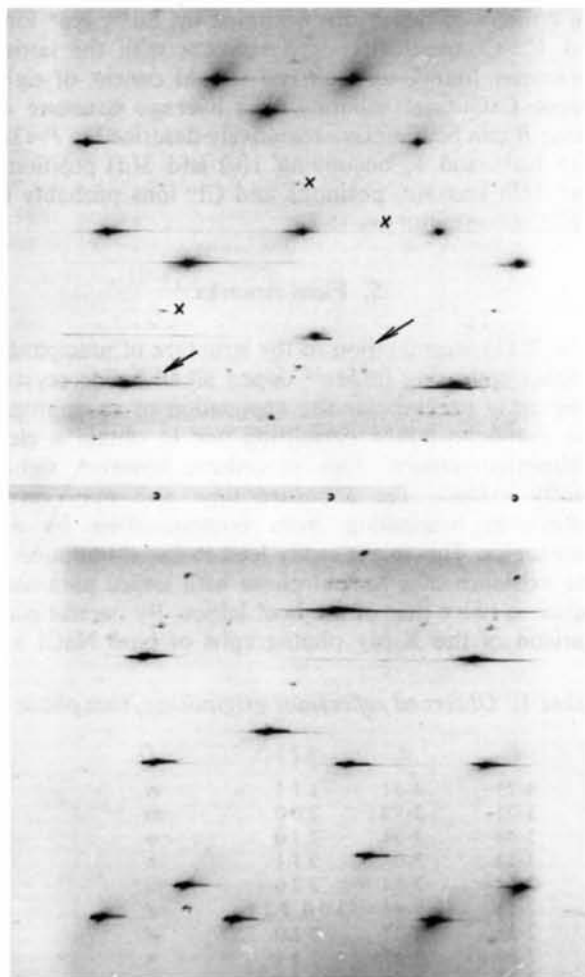


Fig. 2. Weissenberg diagram of  $hk0$  layer,  $\text{Cu } K\alpha$  radiation, time of exposure 70 h.  $\times$  Reflections originating from phase A.  $+$  Reflections originating from phase B.

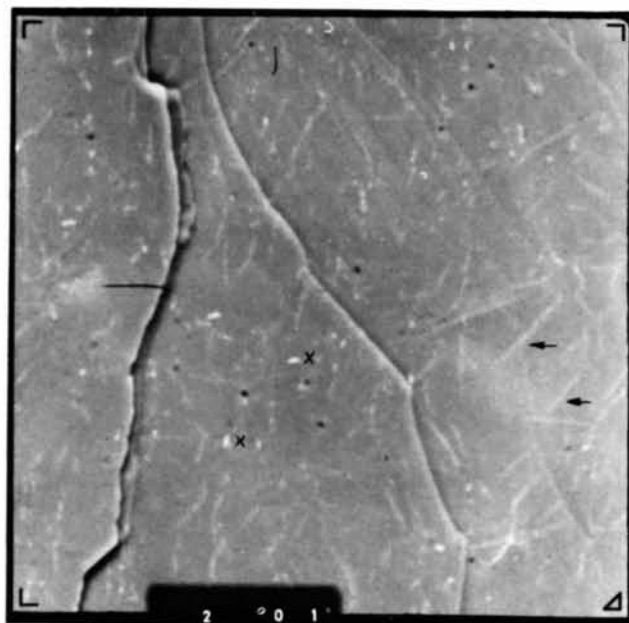


Fig. 3. Electron microscope photograph of freshly cleaved (100) surface of  $\text{NaCl}:\text{Eu}^{2+}$  crystal (Magnification  $\times 600$ ).  $\times$   $\text{Eu}^{2+}$ -rich precipitates — phase A.  $+$   $\text{Eu}^{2+}$ -rich precipitates — phase B.

best agreement with experiment. Scattering factors for Eu<sup>2+</sup> and Cl<sup>-</sup> were taken from *International Tables for X-ray Crystallography* (1974). Eu<sup>2+</sup> scattering factors were corrected for anomalous dispersion.\* The refinement of isotropic temperature and scale factors was performed with the X-RAY 70 system. After refinement  $R = 0.056$ . The isotropic temperature factors are 1.46 and 1.36 Å<sup>2</sup> for Eu<sup>2+</sup> and Cl<sup>-</sup>, respectively.

#### 4. Phase B

The X-ray diffraction pattern of phase *B* is most unusual. The reflections appear only at low angles ( $\theta < 25^\circ$ ) and are weaker but very sharp compared to the reflections of phase *A*. Typical reflections are split as if they resulted from twins or slightly disoriented grains. The splitting of these reflections could be observed in both the oscillation (Fig. 1) and Weissenberg diagrams (Fig. 2). In Weissenberg photographs (rotation axes [100] and [110]) for the zeroth layer (3 mm wide slit yields an angle of  $10^\circ$  in the plane perpendicular to the rotation axis) the reflections of phase *B* are distributed symmetrically on both sides of  $h00$ ,  $hh0$  and  $hhh$  directions of the matrix (Fig. 4).

Few reflections of phase *B* are very close to the matrix or phase *A* reflections. They can, however,

\* A list of structure factors has been deposited with the British Library lending Division as Supplementary Publication No. SUP 34653 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

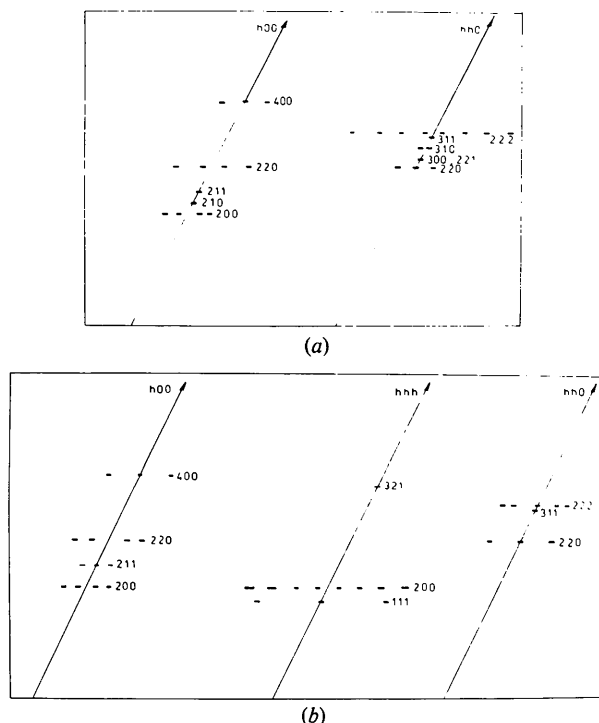


Fig. 4. Distribution of diffraction spots on Weissenberg diagrams. (a) [100] rotation axis. (b) [110] rotation axis.

easily be identified because of their shape as well as their disappearance after heating the crystal at 873 K for 2 h, which does not affect the pattern due to phase *A*.

The diffraction pattern of phase *B* was formally treated as in the case of a powder diagram. Table 1 contains the list of observed reflections, observed and calculated interplanar distances and visually estimated intensities, which were too weak to be measured on a diffractometer. Accordingly, we postulate for phase *B* a cubic symmetry with  $a = 7.47(1)$  Å.

The number of diffraction data ascribed to phase *B* is too low for an unambiguous structure determination. However, by taking into account the size of the unit cell and the condition of electrostatic compensation one can propose a model consistent with the experimental data. Accordingly, the composition of phase *B* is expected to correspond to  $\text{EuCl}_2 \cdot 2\text{NaCl}$  with an appropriate number of cation vacancies ( $V_c$ ) compensating the charge of Eu<sup>2+</sup> ions. The basic element of this assumed structure is a CsCl-type cell, the corners of which are occupied by Eu<sup>2+</sup>, Na<sup>+</sup> ions and  $V_c$ . Consequently, in agreement with the lattice parameter found, the unit cell should consist of eight simple CsCl-type subunits. The average structure of phase *B* can be therefore tentatively described in  $Pm\bar{3}m$  with Eu<sup>2+</sup> and  $V_c$  occupying 1(*a*) and 3(*d*) positions, Na<sup>+</sup> 1(*b*) and 3(*c*) positions and Cl<sup>-</sup> ions probably in 8(*g*) positions with  $x \approx 0.23$ .

#### 5. Final remarks

The X-ray examination of the structure of precipitated phases appearing in  $\text{Me}^{2+}$ -doped alkali halide crystals frequently necessitates the application of an appropriate monochromator permitting one to obtain a clear diffraction pattern. This procedure, however, significantly extends the exposure time and may reveal reflections originating from contamination by  $\lambda/2$  harmonics. This might easily lead to the assumption of the existence of a Suzuki phase with lattice parameter equal to twice that of the host lattice. By careful comparison of the X-ray photographs of pure NaCl and

Table 1. Observed reflections originating from phase *B*

$d_o$	$d_c$	$hkl$	$I$
4.23	4.31	1 1 1	<i>m</i>
3.71	3.73	2 0 0	<i>vs</i>
3.40	3.34	2 1 0	<i>w</i>
3.12	3.05	2 1 1	<i>s</i>
2.64	2.64	2 2 0	<i>vs</i>
2.51	2.49	3 0 0, 2 2 1	<i>w</i>
2.36	2.37	3 1 0	<i>w</i>
2.22	2.25	3 1 1	<i>w</i>
2.17	2.16	2 2 2	<i>vs</i>
	2.07	3 2 0	close to 022 of NaCl
1.99	1.997	3 2 1	<i>w</i>
1.90	1.87	4 0 0	<i>m</i>

$\text{Eu}^{2+}$ -doped NaCl crystals exposed under the same conditions we could virtually exclude the existence of detectable quantities of the Suzuki phase as the intensities of reflections induced by the second harmonic wavelength were exactly the same for both materials.

In  $\text{Eu}^{2+}$ -doped NaCl crystals the precipitation results in two phases (*A* and *B*) differing in crystal structure, distribution in the host lattice and thermal stability. The crystal structure of the more stable phase *A* has been determined and described in this paper.  $\text{EuCl}_2$  precipitating in the NaCl host lattice crystallizes in the fluorite type of structure contrary to pure  $\text{EuCl}_2$  crystallizing in the  $\text{PbCl}_2$  structure (Doll & Klemm, 1939). It appears that under these conditions a new polymorphic modification of  $\text{EuCl}_2$ , perhaps contaminated by Na, can exist.  $\text{Eu}-\text{Cl}$  in this structure is equal to 3.02 Å, in good agreement with the Goldschmidt atomic radii 1.24 and 1.81 Å of  $\text{Eu}^{2+}$  and  $\text{Cl}^-$ , respectively.

Phase *B* was found to nucleate at subgrain boundaries in the vicinity of which strong distortion of the host lattice can be expected. This fact supports our speculative as well as unexpected assignment to the *Pm3m* space group and  $\text{EuCl}_2 \cdot 2\text{NaCl}$  formula. Moreover, considerably lower thermal stability of phase *B* (in comparison with phase *A*) is also in accord with the presence of charge-compensating cation vacancies facilitating the diffusion of  $\text{Eu}^{2+}$  ions and dissolution in the host matrix. It should also be noticed that phase *B* undergoes a continuous destruction under the action of X-ray photons rendering it difficult to obtain the number of data necessary for a structure determination.

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## The Scattering of High-Energy Electrons.

### II. Quantitative Validity Domains of the Single-Scattering Approximations for Organic Crystals

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#### Abstract

Two approximations that are commonly used to describe the scattering of high-energy electrons are the

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first Born approximation (kinematic approximation) and the closely related ‘weak phase-object’ approximation. The quantitative domains of validity for the use of these two scattering approximations for structural analysis of organic crystals are evaluated numerically in terms of resolution, crystal thickness and incident electron energy. The resulting calculations show how

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