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**On precipitation of metastable centres in solid solutions NaCl-CaCl<sub>2</sub>.** By SHIZUO MIYAKE and KAZUO SUZUKI, *Tokyo Institute of Technology, Oh-Okayama, Tokyo, Japan*

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In the course of X-ray study on mixed crystals of metallic halides, we have obtained a characteristic diffuse pattern from solid solutions of NaCl and CaCl<sub>2</sub>. Single crystals used in the experiment were made by cooling the melt of the mixed salts. They were always perfectly transparent when the content of CaCl<sub>2</sub> was less than 4 moles per cent. The specimens subjected to X-ray examination were thin crystals parallel to (010), about 0.1 mm. in thickness. On keeping either a [001] or a [101] direction of the crystal vertical, and varying successively the azimuthal angle, a series of stationary-crystal photographs was taken on cylindrical or flat films with a specimen-to-film distance of 4 cm. In most cases filtered Cu and Mo radiations, and in some cases crystal-monochromated Cu K $\alpha$  radiation were used.

An example of the series of photographs for a crystal containing 2 moles per cent of CaCl<sub>2</sub>, rotated around [001], is shown in Fig. 1, in which one may see many Laue spots and, in addition, the extra diffuse reflexion com-

posed of streaks and spots. The pattern resembles those obtained from some alloys at a certain stage of the precipitation process (Preston, 1938; Guinier, 1938, 1952; Barrett & Geisler, 1940; Geisler & Hill, 1948). The displacement of the diffuse spots with the change of azimuthal angle reveals the existence of 'rods' in reciprocal space passing through certain lattice points along  $\langle 111 \rangle$  and  $\langle 310 \rangle$  directions. On the other hand, by the use of the crystal-monochromated X-rays, most of the streaks are found to be due to the continuous X-rays.

When the specimen was reheated to 400° C. and then quenched to room temperature, the diffuse spots disappeared but reappeared gradually within a month. Recovery to a similar extent occurred when the quenched specimen was kept at 100° C. for 1 hr., though there were some differences between this case and that at room temperature with respect to the intensity and sharpness of the spots and the relative rate of recovery of the  $\langle 111 \rangle$  and  $\langle 310 \rangle$  rods. When the temperature was kept

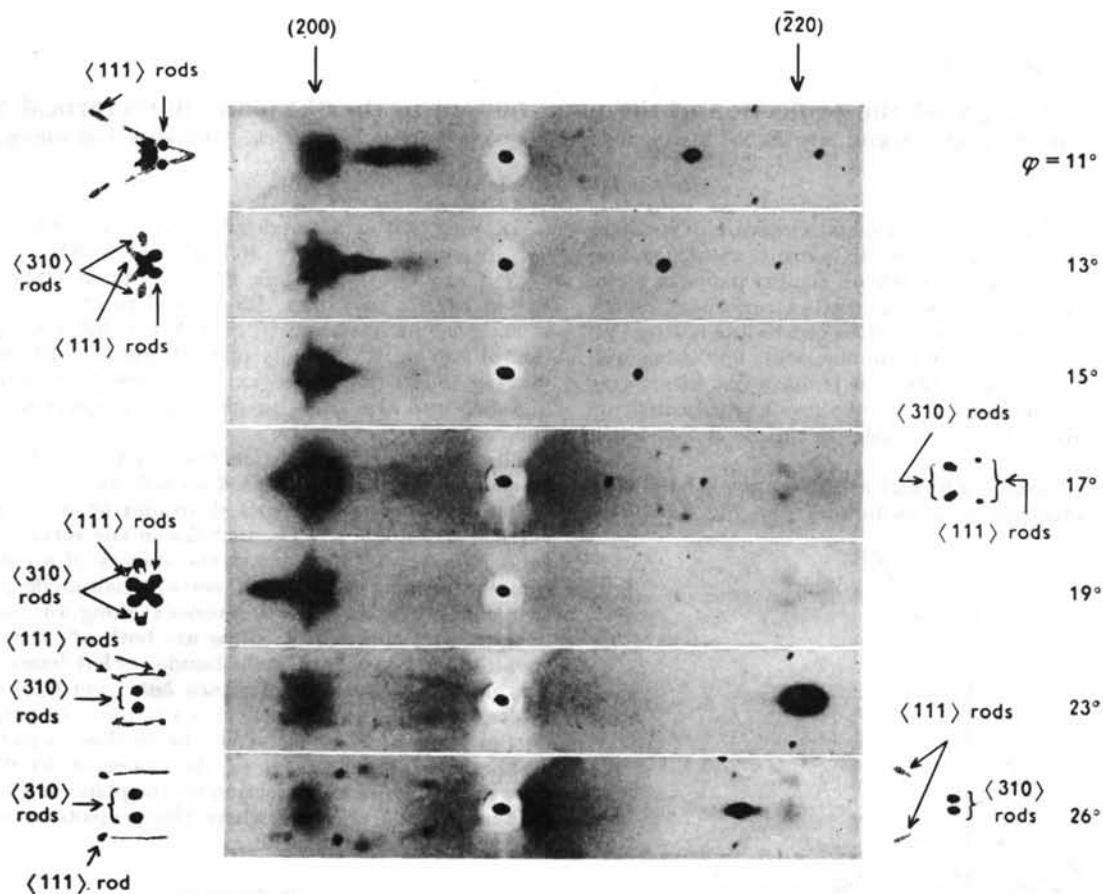


Fig. 1. Series of photographs obtained by successive rotation around [001] of mixed crystal NaCl+2% CaCl<sub>2</sub>. Orientation of the crystal is given by the angle between [010] and the direct beam. Filtered Cu radiation. 40 kV., 10 mA., 10 hr.

at 200° C. for 1 hr., all the rods disappeared again, and a new kind of spotty pattern began to appear. This disappeared at 400° C. by reheating.

The origin of the rods seems to be explained in the manner analogous to the case of alloys: at lower temperatures, the homogeneous structure is not stable for the solid solution containing a few per cent of  $\text{CaCl}_2$ , and a number of thin plate-like metastable centres may be formed in the interior of the matrix at the initial stage of the motivated precipitation. Corresponding to the two directions of the rods, there may be two kinds of plates which are respectively parallel to the  $\{111\}$  and  $\{310\}$  planes of the matrix. From the observed distribution of rods around reciprocal-lattice points, which is a superposition of rods corresponding to possible orientations of the plates, we can obtain the distribution for a single plate orientation. Fig. 2(a) and (b) shows the results concerning the  $(11\bar{1})$  and  $(031)$  plates respectively.

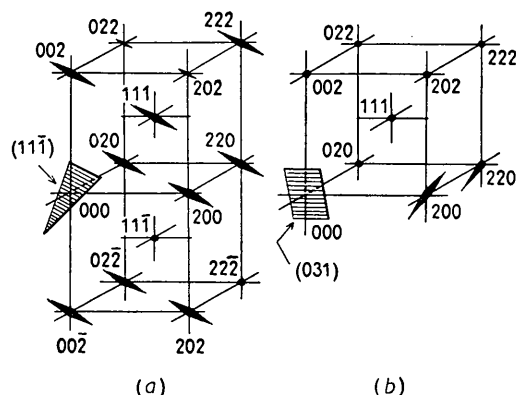


Fig. 2. Distribution of rods for a single plate orientation. (a) for the  $(11\bar{1})$  plate; (b) for the  $(031)$  plate. The hatched planes at the  $(000)$  reciprocal-lattice points indicate the orientations of plates responsible for the rods.

When calcium chloride is dissolved in sodium chloride, a  $\text{Na}^+$  ion may be replaced by a  $\text{Ca}^{++}$  ion and at the same time another  $\text{Na}^+$  ion may be removed from the crystal, leaving a vacancy. We can assume, then, that the plates are the regions where the  $\text{Ca}^{++}$  ions and the vacancies are locally concentrated. The assumption of equal numbers of  $\text{Ca}^{++}$  ions and vacancies is in accordance with the absence of any rods at the  $(000)$  reciprocal-lattice point, for all scattered waves from atoms superpose in phase to this point, while  $Z_{\text{Ca}^{++}} - 2Z_{\text{Na}^+}^+ = -2$  ( $Z$  is the number of electrons in an atom), which is very small.\* On the other hand, in order to explain the greater intensities of the rods at other reciprocal-lattice points, we must take account of displacements from the original lattice sites of  $\text{Ca}^{++}$ , vacancies, and other ions in the plate.

Since all the rods are observed only around the normal reciprocal-lattice points, one might suppose that the individual plate would possess the structure of a periodic pattern, with a primitive cell of a size equal to that of the

\* If we let  $F_s$  and  $F_0$  be the structure amplitudes corresponding respectively to the structures of a plate and of the part of the matrix replaced by the plate, then  $F_s - F_0$  is the structure amplitude contributing to the diffuse scattering (Guinier, 1952).

matrix. But such cannot be the case, because, in any kind of periodic structure containing  $\text{Ca}^{++}$ , its primitive cell should contain at least one  $\text{Ca}^{++}$  ion associated with two negative particles (including the vacancies), whereas the volume of the primitive cell of the matrix is too small to accommodate even these three. On the other hand, if we take a structure having a larger primitive cell, then rods should appear also at non-integral positions in reciprocal space, which is inconsistent with the experiment.

In order to avoid this difficulty, we assume that the plate is not an inclusion having a coherent periodic pattern, but is an assemblage of a number of thin *platelets* (or, more generally, small units of an arbitrary shape); each of them has a periodic pattern, the primitive cell of which is larger than that of the matrix—perhaps a few multiples of the latter—, containing ions ( $\text{Ca}^{++}$ ,  $\text{Na}^+$ , and  $\text{Cl}^-$ ) or vacancies co-ordinated at positions generally deviating from the original lattice sites. The lattice of each platelet is coherent to that of matrix, but, as a result of the different sizes of the primitive cells of the matrix and the platelets, it is probable that there are ‘anti-phase’ relations among platelets in a way similar to that found in the superstructure phases of alloys (Jones & Sykes, 1938). We assume, then, that the assemblage of the platelets in a plate contains nearly equal numbers of different kinds of anti-phase platelets. It is supposed that the thin space of the plate is filled densely with the platelets, but only imperfectly. The plate having a structure as mentioned above gives the rods only around the normal reciprocal-lattice points.

By adopting the above model, and assuming a suitable structure of the unit cell of the platelet, we can explain the relative intensities of the rods qualitatively. By a rough estimation, we can also confirm that they give correct order of magnitudes of absolute intensities. The total thickness of the plates, estimated from the observed length of the rods, is about 10–20 Å, so that the thickness of the platelets is supposed to be a small fraction of it. Though the unique determination of the structure of the primitive cell is difficult, we can propose some plausible models for the two kinds of rods by referring to Pauling’s rule, the relation of ionic radii, and the crystal structure of  $\text{CaCl}_2$ . For complete explanation of the phenomena, however, the lattice distortion should also be taken into account, which is actually suggested by the existence of asymmetrical rods around certain reciprocal-lattice points (Fig. 2(b)).

Though there is no exact similarity between the models for the precipitated plates in the present case and those in the case of alloys, we can say that the present model is akin to that given for alloys by Guinier (1952) rather than to that given by Geisler & Hill (1948). A more detailed report will be published at a later date.

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