

MICROSCOPIC STUDY OF EXTENDED DEFECTS RELATED TO NON STECHIOMETRY IN ZINC OXIDE SINGLE CRYSTALS

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In the present paper it is shown that precipitates of excess zinc in the zinc oxide crystal lattice occur on the $(10\bar{1}\bar{1})$ and $(\bar{1}01\bar{1})$ faces. Depending on the concentration of excess zinc we obtain various forms of microstructure — disks, or, perhaps, thin needles. It is also shown that Zn_i atoms lead to a change of interplanar spacing d in the mother lattice, as well as in the precipitate. Comparing our results with those of Azaroff [8] we can suppose that precipitates of Zn_i atoms are probably formed in an oxide constituting a hitherto relatively unknown permanent hexagonal lattice with, possibly, a different stoichiometric composition.

1. Introduction

In the interpretation of measurements, especially electric measurements, it is important to know the degree of defectiveness of the crystal structure of a given semiconducting compound, especially the concentration of excess and impurity atoms as well as the density of dislocations. While the excess and impurity atom concentration can be estimated with a certain degree of accuracy by the method of measuring the Hall coefficient, it is difficult to say anything about the distribution of these atoms in the crystal lattice of a given compound.

In the present paper an attempt is made to study this problem.

The studies were conducted on thin crystals of zinc oxide with a relatively high degree of defectiveness using a transmission electron microscope.

2. Obtaining of highly defective crystals of zinc oxide

Highly defective crystals of zinc oxide were obtained in a high temperature X-ray camera, by sublimation of polycrystalline zinc oxide at a temperature about 1473°K, during irradiation of the sample with an X-ray beam. Pair condensation took place on the

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walls of the camera at a temperature not exceeding 573°K, in the form of small crystals. The crystals obtained were in the shape of thin platelet about $0.2 \times 0.5 \text{ mm}^2$ in area and 1000 Å in thickness. Among them some whose thickness exceeded 1000 Å could be found.

The method described made possible the sublimation of ZnO at a temperature around 500° lower than the temperature of sublimation of zinc oxide at 1 atm of pressure (sublimation temp. = 1993°K). It is an interesting question why the sublimation temperature of ZnO decreases so considerably under the influence of X-rays. Research into a detailed explanation of the process suggested is in progress and will be the subject of a separate publication.

Preliminary observations of zinc oxide crystallites under a polarising microscope with crossed nicols indicated that their crystal lattice was plastic strain. This type of deformation was observed in the form of bands of varying colour. Such crystals were not subjected to relaxation, rather they were immediately observed under a transmission-electron microscope.

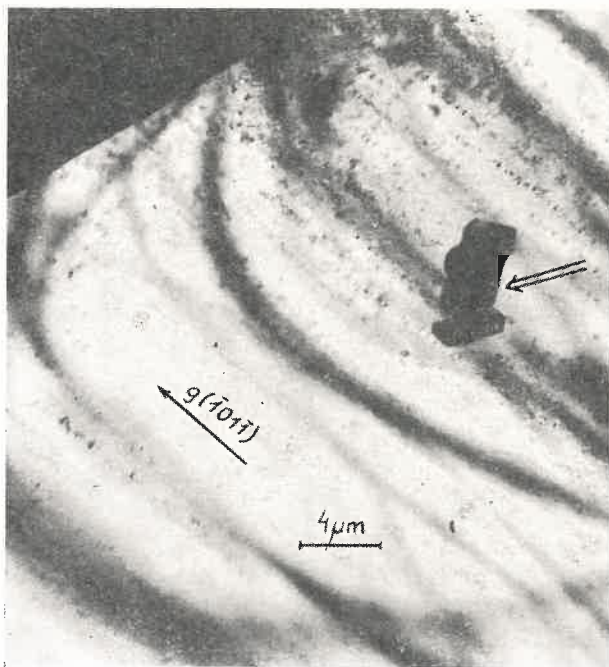
The spectrographic analysis conducted showed that the crystals contain a slight amount of Mg and Pb impurity totaling of a 0.001 to 0.01% of the weight.

3. Studies of precipitates of excess zinc in the zinc oxide lattice using a transmission electron microscope

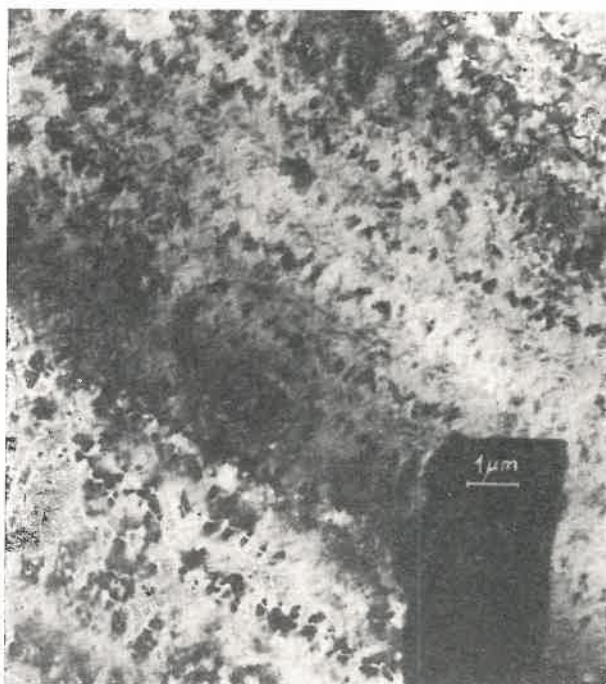
In Fig. 1 we present the microstructure of a zinc oxide crystal, on which black "dots" are visible, presumably arising from excess zinc precipitates aligned in the $[\bar{1}01\bar{1}]$ direction. On this figure one can also see lines of thermal stress as well as grains indicated by an arrow. The identification of these grains, performed by means of selective electron diffraction has shown that their lattice and its orientation coincides with the lattice and orientation of the base. It seems that the dark contrast suggesting foreign grain in nothing else but a relatively thick epitaxial nucleus which absorbs electron rays to a greater degree than the base itself. Figure 1b shows an enlargement of the microstructure of the excess around the nucleus.

As a result of the bombardment of the crystal surface with electron rays during a time of around 30 minutes, there is a change in the pattern observed in Fig. 1. In some crystals the black dots grow, taking on shapes of disks (Fig. 2 and 3), or of needles (Fig. 7), depending on the concentration of excess zinc. In other crystals the number of "dots" in the $[\bar{1}01\bar{1}]$ direction stays at a certain level (Fig. 4a + b).

The electronograms of the microstructures observed are the same and they correspond to zinc oxide crystallising in a hexagonal system. Fig. 5 shows one of the electronograms on which reflexes of zinc oxide in hexagonal system (as described) and of the superstructure are to be seen. Reflexes of the superstructure-type in crystals, those taken for observation in the electron microscope, are not observed. They appear only as a result of the ordering of atoms in octahedral vacancies [1]. The agglomeration of excess Zn atoms in the octahedral vacancies of the zinc oxide lattice produces new coherent phases. The electronogram produced by means of selective diffraction (Fig. 6) from the precipitate obtained under the electron microscope has shown that it is a crystalline phase possessing a definite



a



b

Fig. 1. Array of excess zinc precipitates in a ZnO crystal (at start of observations)

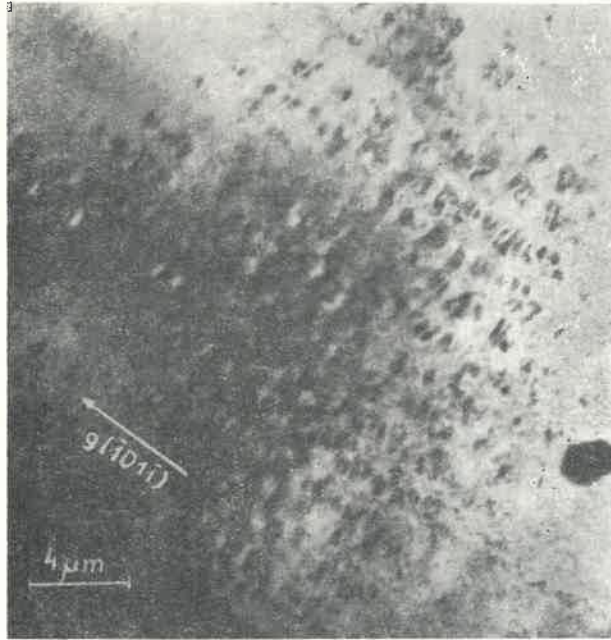


Fig. 2. Array of excess zinc precipitates in ZnO crystal, observed after around 30 minutes of irradiating the crystal with an electron beam in an electron microscope

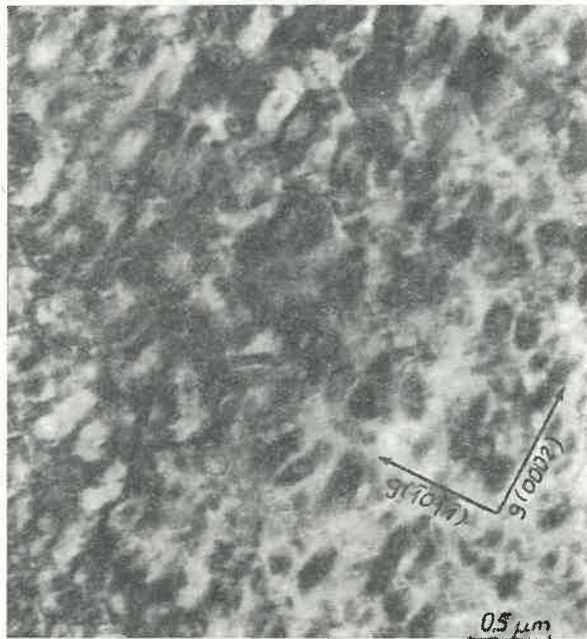
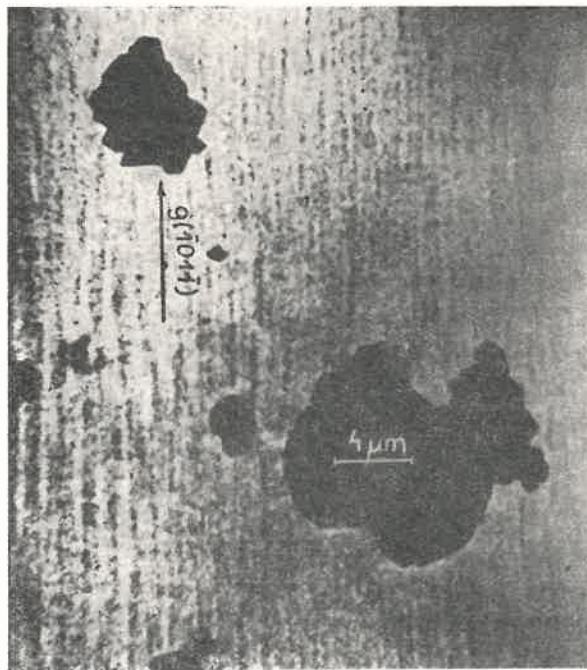


Fig. 3. Excess zinc precipitates, observed after around 30 minutes of irradiating the crystal with electron rays in an electron microscope



a



b

Fig. 4. Two different systems of excess zinc precipitates

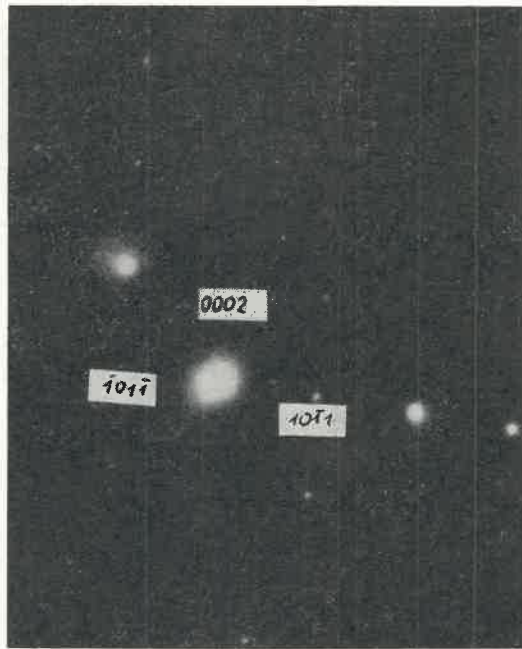


Fig. 5. Electronogram of the ZnO crystal taken around the precipitate

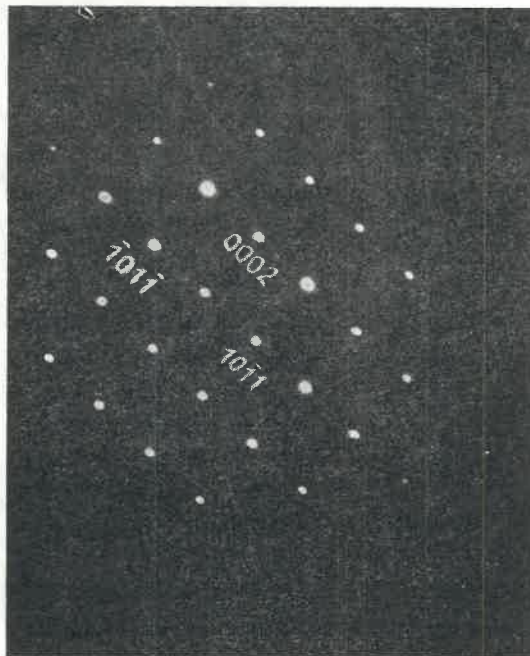


Fig. 6. Electronogram taken of the precipitate

lattice. The intensity of reflexes which, being weak were ascribed to the superstructure, now becomes comparable with that of reflexes of zinc oxide crystallising in hexagonal system. The d values enumerated from electronograms (Figs 5 and 6) show a considerable rise in interplanar spacing of the precipitate (Table I). The d values in the matrix, in turn, differ slightly from theoretical values. The ratio $d_{10\bar{1}1}/d_{0002}$ in both cases is approximately equal to one. Values of the misfit parameter ε corresponding to individual reflexes $hk\bar{l}$ are listed in Table I.

TABLE I

Listing of interplanar spacing d of the matrix and precipitate determined on the basis of the electronograms shown in Figs 5 and 6

d_{matrix}	d_{precip}	d_{calc}	$\varepsilon = d_{\text{precip}} - d_{\text{matrix}}$	$hk\bar{l}$
2.50	3.68	2.47	1.18	10 $\bar{1}1$
2.50	3.50	2.60	1.00	0002
1.81	2.50	1.47	0.69	10 $\bar{1}3$

In conjunction with the fact that a disparity exists between lattice parameters of the matrix and the precipitate, spherically strain fields appear in Figs 2 and 3. They are observed as symmetrical contrasting images. This type of contrast region, as shown by Ashby and Brown [2, 3] is a function of the parameter $\varepsilon g \varphi^3 / 8 \xi_g^2$ for a particle of a diameter φ and *in situ* misfit parameter ε . "Line of no-contrast" which are perpendicular to the vector of the reverse reflecting face lattice (0 $\bar{2}20$) also appear in Fig. 3. Characteristic "Line of no-contrast" appear in the [0001] direction.

In the case of rotation of the sample in the electron microscope by an angle of 28°, the contrast arising from the precipitate becomes poorly visible. It is then to be expected that the precipitate is rotated by an angle of 28° relative to the (0 $\bar{2}20$) face, and that it lies in the ($\bar{1}01\bar{1}$) face. The observed loss of contrast can be easily explained on the basis of a scattering amplitude analysis of electron waves in the crystal.

From the dynamical theory of electron diffraction it develops that the scattering amplitude of electron waves in a crystal containing plate precipitates can be expressed as follows [4]:

$$\frac{d\varphi_0}{dz} = \frac{\pi i}{\xi_0} \varphi_0 + \frac{\pi i}{\xi_g} \varphi_g \exp(2\pi i s z + 2\pi i g R)$$

$$\frac{d\varphi_g}{dz} = \frac{\pi i}{\xi_0} \varphi_g + \frac{\pi i}{\xi_g} \varphi_0 \exp(-2\pi i s z - 2\pi i g R) \quad (1)$$

where ξ_0 is a parameter which is inserted to make the equations dimensionally correct, ξ_g is the extinction distance which varies with the specimen, the diffraction conditions and

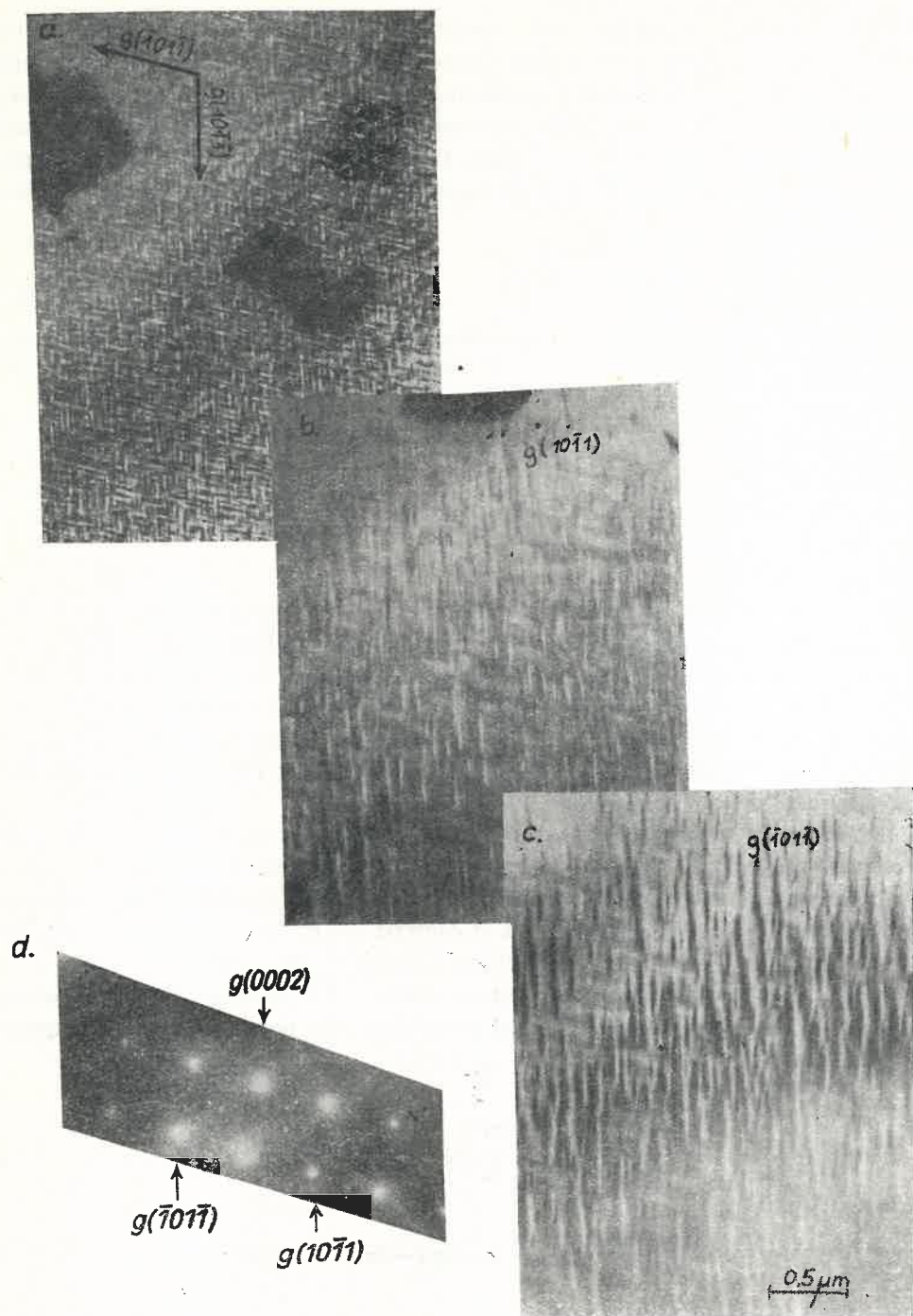


Fig. 7. System of excess zinc precipitates in ZnO crystals: a) bright field micrograph, b) dark field micrograph in the $g(10\bar{1}1)$ reflex, c) dark field micrograph in the $g(\bar{1}01\bar{1})$ reflex, d) electronogram

electron energy, R — displacement vector, g — reciprocal lattice vector, z — depth of the precipitate location in the crystal, s — deviation from the exact Bragg orientation. The contrast from the precipitate will be visible for $g \times R \neq 0$. It can be invisible for $g \times R = 0$, that is, when the new coherent phase is parallel to the incident electron beam.

In cases where the concentration of excess zinc will be higher than in the examples given above, the micrograph of the precipitates will be such as is given in Fig. 7. That is, two precipitate directions appear: $[\bar{1}01\bar{1}]$ and $[10\bar{1}\bar{1}]$. In Figs 7b and c photographs are shown taken on a dark field for reflexes labelled on Fig. 7d.

On the picture (Fig. 7c) taken in reflex $g(\bar{1}01\bar{1})$ one can observe the fading of precipitates lying in the $(\bar{1}01\bar{1})$ face, in agreement with Eq. (1), with only those lying in the $(10\bar{1}\bar{1})$ face remaining. Likewise the image taken in the $g(10\bar{1}\bar{1})$ reflex, not shown in the figure, exhibits the same type of dependence. In this case the precipitates lying in the $(10\bar{1}\bar{1})$ face fade out, and only those lying in the $(\bar{1}01\bar{1})$ remain. If we take a picture in the $g(10\bar{1}\bar{1})$ reflex, for example (Fig. 7b), in which there are no precipitates, then the pattern does not fade only its contrast diminishes.

The precipitate distribution as a function of its thickness has been determined. On the basis of images taken in a dark field for reflexes $g(\bar{1}01\bar{1})$ and $g(10\bar{1}\bar{1})$. The shape

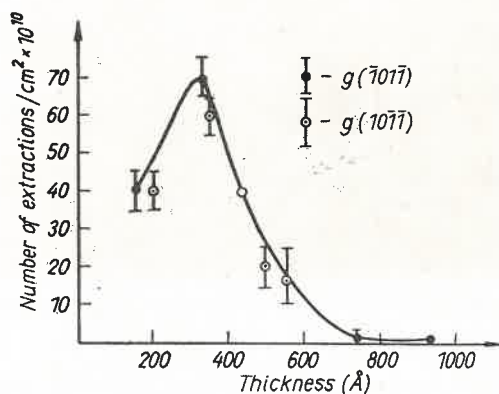


Fig. 8. Precipitate distribution curve in ZnO crystals. The values marked with circles (O) were calculated on the basis of Figs 2 and 3

of the curve presented in Fig. 8 is typical of the curves obtained in the nucleation process. The greatest number of nucleus of new phase is formed at a thickness of about 370 Å.

Knowing the magnitudes of ϵ , and g , the contrast regions determined from Figs 2 and 3, and the extinction distance for the $g(\bar{1}01\bar{1})$ reflex, equal to 585 Å and computed on the basis of reference [5], the diameter φ of the precipitate can be found. This diameter is equal to about 420 Å. Comparing then the diameter, of the precipitate computed from Figs 2 and 3 with precipitate thickness determined from Fig. 8, it can be supposed that those nucleus whose diameter is about 400 Å will be the most stable.

Fig. 9 shows the pattern of excess zinc precipitates observed upon the surface of a zinc oxide crystal under an optical microscope.

The precipitates shown in Fig. 7 were observed in many alloy systems and are relatively well described in the paper by Nicholson [7].

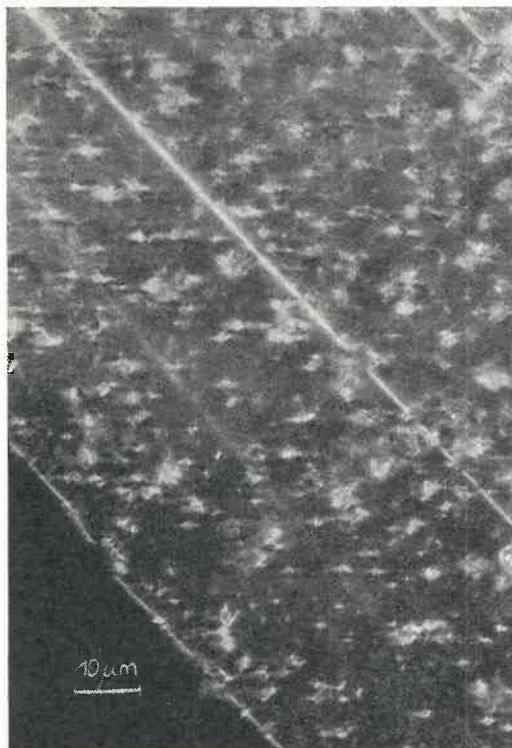


Fig. 9. Precipitate pattern viewed under an optical microscope

4. Studies of excess zinc precipitates in the zinc oxide lattice using X-ray techniques

The presence of coherent precipitates, crystallising in the same crystallographic lattice as the mother lattice (in our case, in a hexagonal system), but with a different lattice parameter gives a lauegram which is characteristic of twins, (Fig. 10).

This type of pattern can be easily observed if we superpose two stereographic projections on each other, having the same components but with different c/a ratios [6]. One then obtains double reflexes from the faces lying between the projection face (0001) and the $\{10\bar{1}0\}$ faces.

The values of the lattice constants of the matrix (labeled further on as 1) and the precipitate (labeled 2), and the c/a ratio were calculated on the basis of d and hkl values collected in Table I.

$$\begin{aligned} a_1 &\cong 3.33 \text{ \AA} & a_2 &\cong 4.99 \text{ \AA} \\ c_1 &\cong 5.00 \text{ \AA} & c_2 &\cong 7.00 \text{ \AA} \\ c_1/a_1 &\cong 1.50 & c_2/a_2 &\cong 1.40 \end{aligned}$$

The differences in c/a values confirms the assumption made above.

5. Discussion of results

From the research conducted it develops that excess zinc precipitates in the crystal lattice take place in the $[\bar{1}01\bar{1}]$ $[10\bar{1}\bar{1}]$ directions. Depending on the excess zinc concentration Zn_i , we obtain various structure types — disks or thin needles. From the microscope



Fig. 10. Lauegram taken on a crystal with precipitates

observations performed it is to be expected that disk precipitates appear for lower concentrations of excess zinc, while needle-shaped precipitates arise at higher excess zinc concentrations. The concentration of excess zinc was not determined experimentally owing to the small dimensions of the crystal, and the conclusions presented in this paper were based on qualitative arguments.

From the experiments performed it would appear that Zn_i atoms produce a change in the interplanar spacing d of the zinc oxide mother lattice and of the precipitate itself.

X-ray experiments by Mohanty and Azaroff [8], conducted in ZnO crystals highly doped with zinc have shown that the increase of excess zinc in octahedral vacancies to about 6×10^{20} atm/cm³ leads to a slight change of c/a values, from 1.6019 for weakly doped crystals, to 1.6025 for highly Zn-doped crystals. From the results quoted above one would assume these changes would be considerable. It would then appear that precipitates of Zn_i atoms do not occur in a ZnO lattice, but in a hitherto unknown permanent hexagonal oxide lattice with a possibly different stoichiometric composition. However, the determination of the chemical composition of the crystals in the presence of large amounts of Zn_i is a difficult task, whereby the problem becomes an open question.

REFERENCES

- [1] E. K. Kazenas, D. M. Chizikov, I. V. Cvetov, *Izv. AN SSSR, Metall.*, **1**, 150 (1969).
- [2] M. F. Ashby, M. L. Brown, *Phil. Mag.*, **8**, 1949 (1963).
- [3] M. F. Ashby, L. M. Brown, *Phil. Mag.*, **8**, 1083 (1963).
- [4] I. A. Belk, A. L. Davies, *Electron Microscopy and Microanalysis of Metals*, Elsevier Publ. Co. LTD, Amsterdam 1968, p. 125.
- [5] R. E. Smallman, K. H. G. Ashbee, *Modern Metallography*, Pergamon Press 1969, p. 140.
- [6] O. Johari, G. Thomas, *The Stereographic Projection and Its Applications*, Interscience Publ. 1969.
- [7] R. B. Nicholson, *Strengthening Methods in Crystals*, ed. by A. Kelly, R. B. Nicholson, Elsevier Publ. Comp. LTD, Amsterdam 1971, p. 535.
- [8] G. P. Mohanty, L. V. Azaroff, *J. Chem. Phys.*, **35**, 1268 (1961).