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A New Polytype of Zinc Selenide Crystal

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A new polytype structure of zinc selenide crystal was found in crystals grown from vapor. The crystal structure was found to be eight layered ZnSe lattice having Z(11 21 12), *i.e.* the packing Aα Bβ Aα Bβ Cγ Bβ Cγ Bβ.

INTRODUCTION

Zinc selenide has been known to have zincblende- and wurtzite-structure,[1] although considerable polytype structures are known about similar compounds, *e.g.* zinc sulphide and silicon carbide.

In the course of the electron microscopic study of the growth of zinc selenide crystals from vapor, a new polytype structure was found. The crystal structure of the new polytype and the irregularities in the structure were studied by electron microscopy and diffraction.**

CRYSTAL STRUCTURE OF POLYTYPE OF EIGHT ZN-SE DOUBLE LAYERS

The crystals of zinc selenide were grown from their vapor at 1000°C. Most of the crystals were either zincblende- or wurtzite-structure as has been reported.[2,3]

In some of the crystals it was found that there are regions where the crystal structure is different from their surrounding regions of wurtzite structure. This region is a long band parallel to the $[10\bar{1}0]$ direction of the wurtzite structure. Periodic fringes parallel to the (00, 1) planes of the wurtzite structure, *i.e.* parallel to the close-packed planes, were observed in this band as shown in Fig. 1. The spacing of the regular fringes was 25.0 ± 1.0 Å, which is equal to four times as large as the lattice constant c_0 of the wurtzite structure.

Figure 2 shows the electron diffraction pattern of the region shown in Fig. 1. The extra spots other than those due to the wurtzite structure are observed and correspond to the spacing of the fringes observed in the micrograph. Thus zinc selenide in this band has the structure having eight Zn-Se double layers in the unit cell. Based on this long periodicity in the direction perpendicular to the close-packed plane, the diffraction spots are indexed as shown in Fig. 2. It was difficult to obtain the diffracted intensities reliable to use for the structure analysis, because of the multiple scattering of the Bragg diffraction. However, the fact that the diffracted intensities are zero at $10,4n+2$ spots (n; integer) can be used for the analysis.

It is easy to find that there are six possible ways of packing of eight close-packed double

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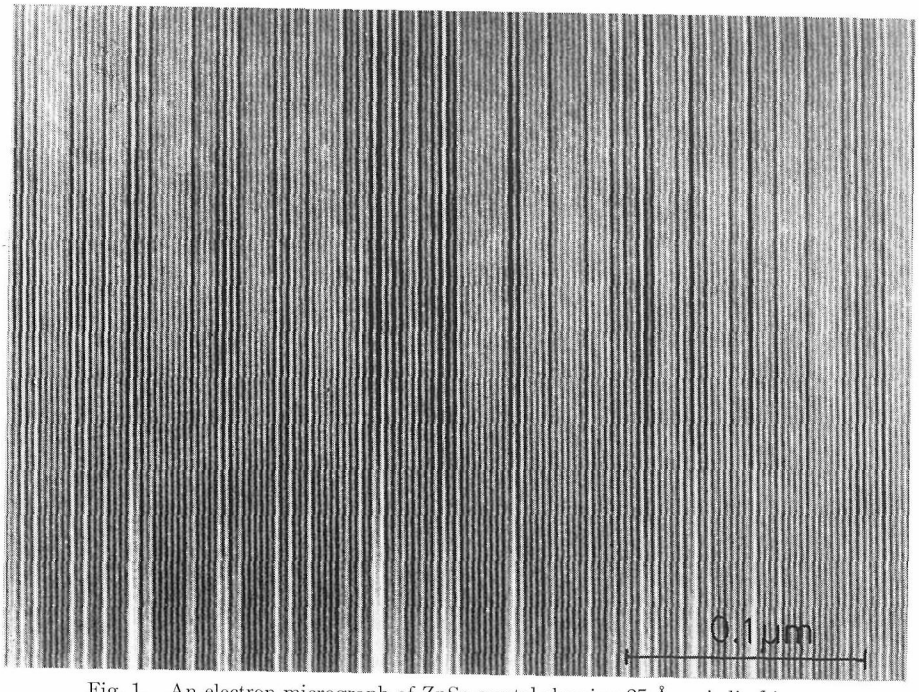

Fig. 1. An electron micrograph of ZnSe crystal showing 25 Å periodic fringes.

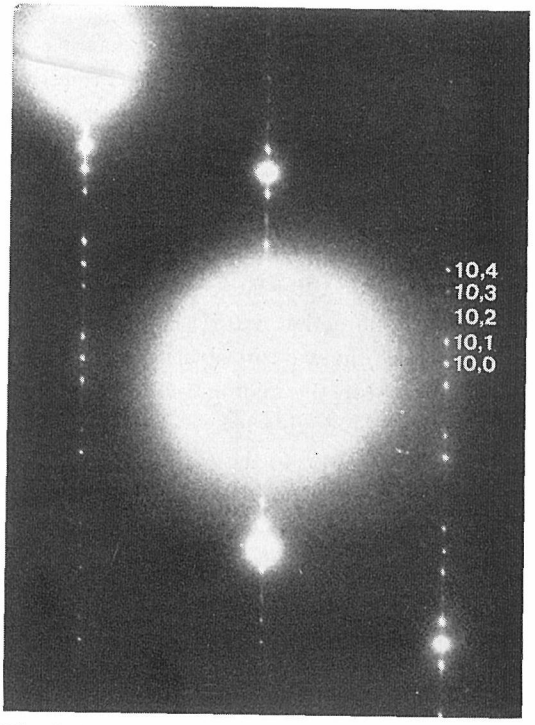

Fig. 2. The electron diffraction pattern from the crystal shown in Fig. 1.

layers of Zn and Se atoms to form $4c_0$ periodicity of hexagonal symmetry (c_0 is the lattice constant of wurtzite structure of ZnSe). They are, following Zhdanov symbol[4];

Z(11 11 22)	Aα Bβ Aα Bβ Aα Bβ Cγ Bβ
Z(11 21 12)	Aα Bβ Aα Bβ Cγ Bβ Cγ Bβ
Z(11 33)	Aα Bβ Aα Bβ Aα Cγ Bβ Cγ
Z(12 32)	Aα Bβ Aα Bβ Cγ Bβ Aα Cγ
Z(17)	Aα Bβ Aα Bβ Cγ Aα Bβ Cγ
Z(44)	Aα Bβ Aα Cγ Bβ Aα Bβ Cγ,

where Aα, Bβ, Cγ show the packing positions of Zn-Se double layer. The crystal structure factors for the diffraction of electrons of these possible structures were calculated for (10, l). The atomic scattering amplitudes for electrons tabulated in the International Tables for X-ray Crystallography were used in the calculated.[5] The results are shown in the Table I. In order to compare the observed intensity distribution and the calculated ones, it was assumed that the $|F_{hkl}|^2$-law is a good approximation. The structure which has zero or negligible values of $|F_{10,l}|^2$ for $l=4n+2$ was searched. Fortunately it was only Z(11 21 12) structure that satisfies the condition.

The most probable structure is, therefore, Z(11 21 12). The unit cell of this polytype is hexagonal and the lattice constants are;

$$a_0=4.00\pm0.04\ \text{Å}, \qquad c_0=26.1\pm0.3\ \text{Å}.$$

This polytype structure is different from the corresponding eight layered polytype Z(44) found in SiC and ZnS crystals.

Table I. $|F_{10,l}|^2$ of Six Possible Structures (Å^2)

Structure	indices 10, l								
	10, 0	10, 1	10, 2	10, 3	10, 4	10, 5	10, 6	10, 7	10, 8
Z (11 11 22)	626	266	258	247	3015	215	197	179	348
Z (11 21 12)	358	531	0	493	2784	430	0	358	199
Z (11 33)	89	421	258	1088	1624	949	197	284	50
Z (12 32)	89	669	69	970	2088	319	736	12	50
Z (17)	89	177	965	3617	232	86	53	45	50
Z (44)	89	46	775	1439	696	1255	591	31	50

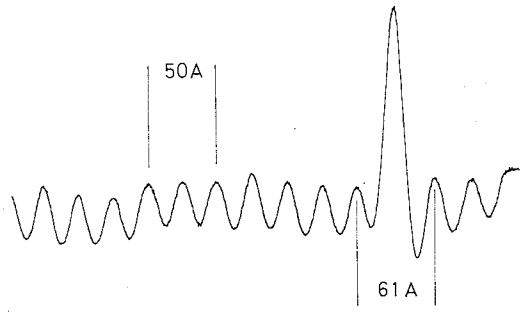

Fig. 3. An example of microdensitometer traces of the fringes.

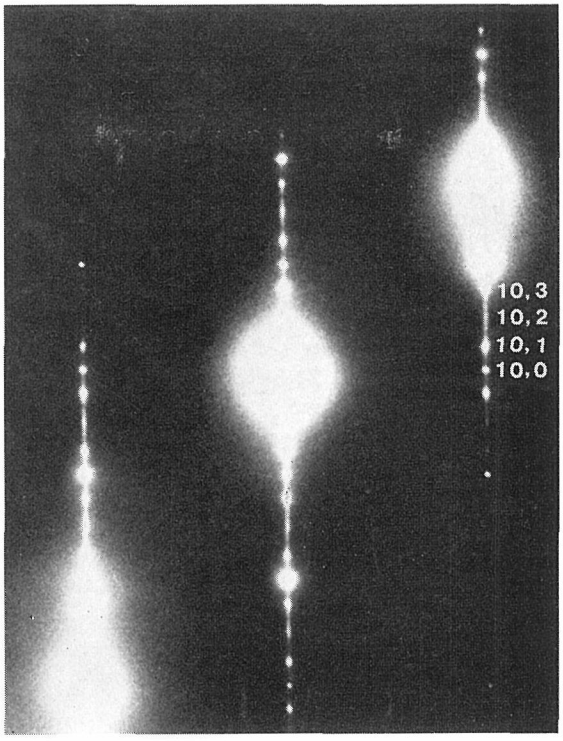

Fig. 4. The electron diffraction pattern from the crystal showing irregular fringe periodicity.

As the structure factors $F_{00,1}$ is zero for any of the possible packings of eight Zn-Se double layers, it is supposed that the periodic fringes in the electron micrographs are formed by the interference of the transmitted beam and 00,1 diffracted beam, which is formed by the effect of multiple Bragg diffraction.

IRREGULARITIES IN Z (11 21 12) STRUCTURE

The electron micrograph shown in Fig. 1 has irregularities in the fringe periodicity. Figure 3 shows an example of microdensitometer traces of the fringes. Most of the irregularities had the width 5/4 of the spacing of the regular fringes, which are equal to ten double layers. This suggests the possibility that the new polytype of ten double layered Zn-Se could be formed under this condition of crystal growth. There were other types of irregularities in the fringe spacing which were wider than ten double layers.

The electron diffraction patterns from less regular fringed region gave some anomalies as shown in Fig. 4. The broad and sometimes weak intensity distribution were observed at h0,4n+2, and h0,4$n\pm$1 spots became broad and appeared closer to the neighboring h0,4n spots. These anomalies depended on the irregularity of the fringes. These diffraction patterns can be interpreted due to the irregular packing of the close-packed planes.

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REFERENCES

(1) E. Crucianu and Y. D. Chistyakov, *Kristallografia,* **5**, 354 (1960).
(2) A. G. Fitzgerald, M. Mannami, E. H. Pogson, and A. D. Yoffe, *Phil. Mag.,* **13**, 197 (1966).
(3) A. G. Fitzgerald, M. Mannami, E. H. Pogson, and A. D. Yoffe, *J. Appl. Phys.,* **38**, 3303 (1967).
(4) F. C. Frank, *Phil. Mag.* **42**, 1014 (1951).
(5) J. A. Ibers and W. C. Hamilton, Ed., "International Tables for X-Ray Crystallography," Vol. 4, The Kynoch Press, Birmingham, 1974.