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Polytype Phase Transition in the Series $GaSe_{1-x}S_x$

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The structure of crystals $GaSe_{1-x}S_x$, grown by the iodine transport method, has been investigated with X-ray diffraction techniques. Between $x = 0.2$ and 0.3 a phase segregation has been found, which is indicative of the first-order nature of the ϵ to β polytype transitions, which occur in this composition region with increasing sulfur content.

Introduction

The crystal structures of the compounds GaS and GaSe are very similar to each other; i.e., a layer structure of slabs which are built from four close-packed monoatomic sheets in the sequence Se(or S)–Ga–Ga–Se(or S) (*1–3*). Since the top and bottom of the slabs are formed by a closed packing of anions, the slabs can be stacked in various ways, resulting in a large number of polytypes (*4*, *5*). The most simple polytypes are formed with a repetition of two slabs, for which theoretically three different stackings are possible (Fig. 1):

(a) Stacking sequence . . . AββA, BγγB . . . ; space group $P\bar{6}m2$, the ϵ structure, which is one of the polytypes observed in GaSe.

(b) Stacking sequence . . . AββA, BααB . . . ; space group $P6_3/mmc$, the β structure, which is the only structure observed in GaS.

(c) Stacking sequence . . . AββA, CββC . . . ; space group $P6_3/mmc$; this structure does not occur within the $GaSe_{1-x}S_x$ system.

By growing crystals of GaS and GaSe with the iodine transport process, only the β structure was found for GaS and the ϵ structure for GaSe (*6*, *7*). Higher polytypes of GaSe were only found in needle crystals grown by sublimation techniques (*5*), which is indicative of the effect that the growth process is one of the factors determining the occurrence of polytypes. It is possible to analyze the structure of polytypes in crystals, but the kinetics of the formation of polytypes or the transformation of polytypes by changing external parameters like pressure and temperature is less understood.

As it is reported (*7–10*) that GaS and GaSe form a continuous series of mixed crystals, the question arises what will be the crystal structure of intermediate compositions. A number of authors (*7–10*) reported a sharp transition ϵ to β with increasing selenium content near $x = 0.25$. An indirect investigation of the structure problem was reported by Aulich *et al.* (*12*), based on optical absorption measurements on mixed crystals grown from the melt. Evidence was found that the ϵ and β structures

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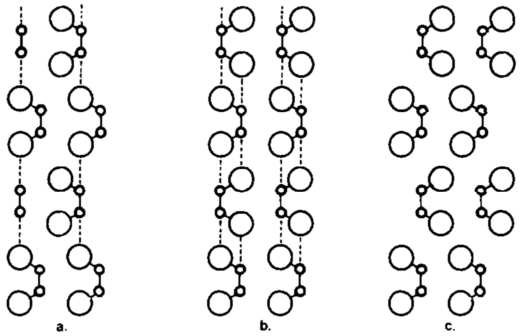

FIG. 1. Three possible two-slab stackings (a) ϵ structure, $p\bar{6}m2$; (b) β structure, $P6_3/mmc$; (c) space group $p6_3/mmc$, not present in $GaSe_{1-x}S_x$ system.

occur simultaneously in the composition range $0.2 < x < 0.4$ and that in melt-grown crystals (Bridgman technique) the higher polytype 3R (γ-structure) was also present. Since we found that in the mixed series $GaSe_{1-x}S_x$ prepared by the iodine transport process, only the two-slab polytypes were formed, we investigated the crystal structure of the mixed crystals in order to find the features of the $\beta \rightarrow \epsilon$ transition which has to occur in this system.

Experimental

Single crystals of $GaSe_{1-x}S_x$ were grown by the iodine-transport method. In sealed silica tubes ($\varnothing = 20$ mm, 8 cm length) about 2 g of mixtures of GaSe and GaS was transported from higher temperature to lower temperature; 4 mg of iodine per cubic centimeter of tube volume were added for the transport. The high temperature in the furnace was adjust to the sulfur content of the mixture and varied gradually from 800 to 930°C with increasing sulfur content, the low temperature varied from 830 to 850°C. In this way single crystals with steps in the composition $\Delta x = 0.1$ were grown.

By chemical analysis it was found that the overall composition of the transported $GaSe_{1-x}S_x$ crystals was identical with the starting mixtures of GaSe and GaS, within an accuracy of ±0.5 at.%.

The crystal structure of the mixed crystals was investigated by means of X-ray techniques. The structure of the polytypes was determined with Weissenberg techniques, whereas the lattice parameters were more accurately determined on powdered single crystals by means of an X-ray diffractometer using Cu$K\alpha$ radiation.

Whitehouse and Balchin (*9*) reported that at $x \approx 0.25$ a discontinuity in the c parameter occurs, which points to a sharp transition from the β to the ϵ structure with increasing Se content. However, the X-ray measurements were carried out with a photographic method by which line-broadening is not accurately analyzed. Moreover, the abrupt transition is in contradiction with the interpretation of the above-mentioned optical absorption measurements (*12*), from which evidence is found of a coexistence of the β, ϵ, and γ structure in one crystal.

In a preliminary electron microscopy study (*11*) of this transition, we found in crystals (dimensions <10.000 Å) in the critical composition range, networks of partial dislocations together with isolated partials, pointing to the coexistence of the β structure (extended ribbons) and ϵ structure (isolated partials).

Results and Discussion

The results of our lattice parameter measurements on powdered single crystals are presented in Fig. 2 and Fig. 3. Figure 2 shows that the c value has a positive deviation of Végard's law, attended with a dip between the compositions 0.2 and 0.3. The a value, however, follows within the experimental error Végard's law as is shown in Fig. 3, although near $x = 0.25$ an irregularity just somewhat larger than the experimental error has been observed. A detailed analysis of the X-ray powder diagrams

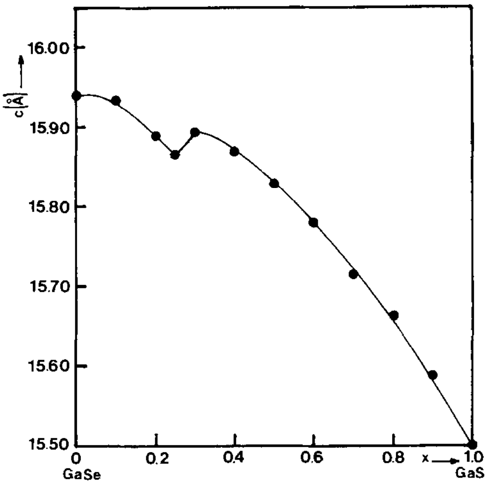

FIG. 2. Lattice parameter c of the mixed series $GaSe_{1-x}S_x$.

proofs further a structural change at $x \approx 0.3$. For $x > 0.3$ the powder diagrams show sharp reflections, identical with the powder diagram of GaS, while for $x < 0.3$ some reflections are broadened. The broadening of the reflections is caused by stacking faults, dominantly formed in the ϵ structure by powdering, which is explained by the relatively low stacking fault energy in the ϵ structure compared with the stacking fault energy of the β structure of GaS (*11*).

The line-broadening also has an effect upon the accuracy of the lattice parameter determination. For $x > 0.3$ the accuracy in the a and c parameters is high (± 0.002 Å) because the X-ray diagrams show sharp reflections. For $x < 0.3$ only the c parameter can be determined accurately from the (00.1) reflections, which are sharp and in general not effected by the stacking faults. The reflections (hkl) with $h - k \neq 3n$, and to a lesser extent those with $h - k = 3n$ are strongly broadened. This implies that for these compositions the stacking faults are mainly made in the [110] direction and that the a parameter is less accurately determined than the c parameter.

In order to investigate the irregularity of the lattice parameters in the mixed series between $x = 0.2$ and 0.3 more precisely with an X-ray diffractometer, additional batches of crystals were grown with starting compositions between $x = 0.2$ and 0.3 with a composition interval of $\Delta x = 0.01$ and the composition $x = 0.15$ and 0.35. The powder diffractograms of these batches showed in addition to the above-mentioned broadening of the reflections $h - k \neq 3n$, a complex form of the reflections (00.1), which is caused by the presence of two phases with slightly different lattice parameters. In Fig. 4 the (00.14) reflections for the batches $x = 0.20$, 0.26, 0.27, and 0.30 are shown. It can be seen that these reflections, in addition to the $K\alpha_1$ and $K\alpha_2$ splitting, consist of two or more or less overlapping peaks. With increasing sulfur content the intensity of the peak with the highest c value increases gradually with the parameter x while the intensity of the peak with the lowest c value decreases. Because of the line-broadening in the other reflections ($h \neq 0$, $k \neq 0$, l) this effect cannot be observed for the a parameter. The two c parameters are now determined from a number of (00.l) reflections for all the composition between $x = 0.15$ and $x = 0.35$ and plotted in Fig. 5.

A remarkable effect is that the c parameters seem to be independent of the overall

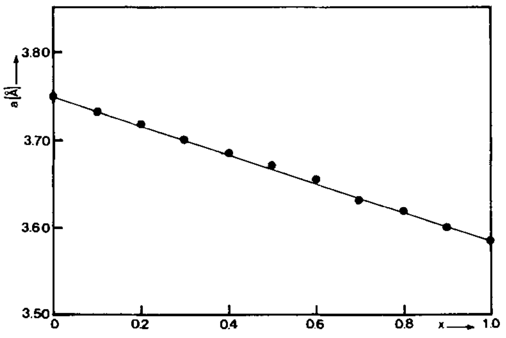

FIG. 3. Lattice parameter a of the mixed series $GaSe_{1-x}S_x$.

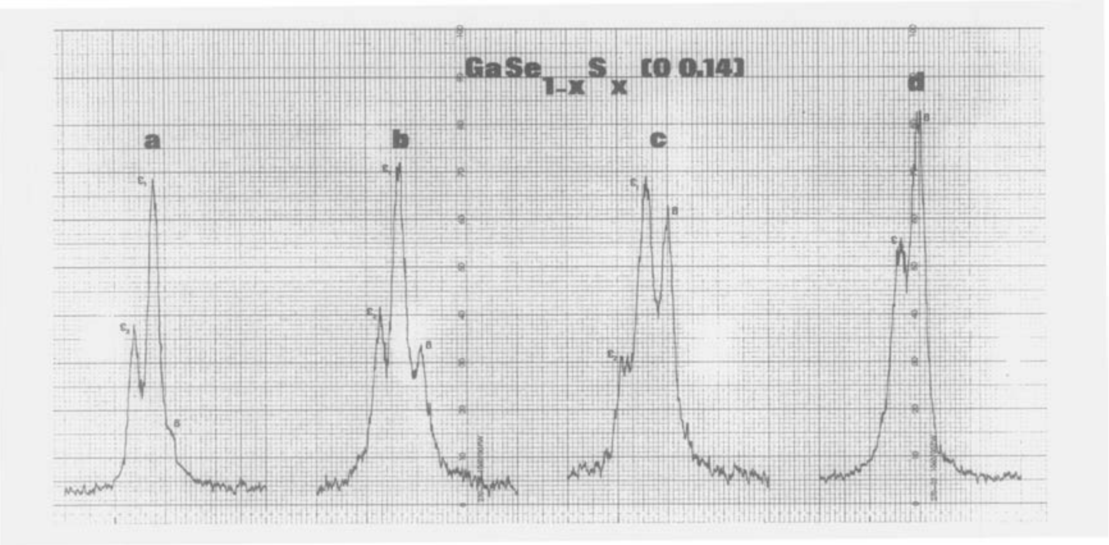

FIG. 4. X-Ray reflection (00.14) for batch compositions $GaSe_{1-x}S_x$ with (a) $x = 0.20$, (b) $x = 0.26$, (c) $x = 0.27$, and (d) $x = 0.30$.

composition of the batch, which points to a separation into two phases during the growth process of the crystals. It is obvious to conclude that the phase segregation is due to the coexistence of the β and ϵ structure in this composition range.

The habit of the obtained crystals is also indicative of this coexistence. Triangles are formed on surfaces of GaSe crystals indicating the trigonal symmetry of the β structure, whereas on GaS crystals, hexagons are formed pointing to the hexagonal structure. In the intermediate composition both triangles and hexagons are observed (Fig. 6).

However, a straightforward proof we found with the X-ray measurements, using the Weissenberg technique. In Figs. 7 and 8 two typical Weissenberg photographs are shown. These photographs proof that we are dealing here with the two-slab structures only. In all batches of $GaSe_{1-x}S_x$, prepared with the iodine transport technique, we did find only these two-slab structures; higher polytypes as reported in (*4*, *5*) are not present.

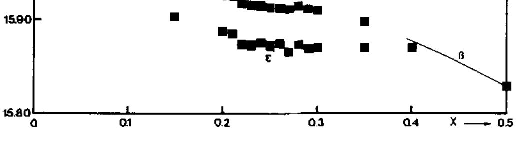

FIG. 5. Lattice parameters c as function of the batch composition x.

The Weissenberg photographs shown in Figs. 7 and 8 are zero-layer photographs with symmetrical (10.*l*), (20.*l*), and (30.*l*) festoons. For a number of reflections we have calculated the relative intensities for the three possible two-slab structures, mentioned in the introduction. The result of this calculation is partly given in Table I. Comparison of the measured intensities with the calculated intensities makes it possible to discriminate between the three possible stackings that may occur in the mixed series.

In Table I, the results are given for the calculation using the scattering factor of Se. In calculations for the mixed crystals an effective scattering factor between the factor of sulfur and selenium has been taken,

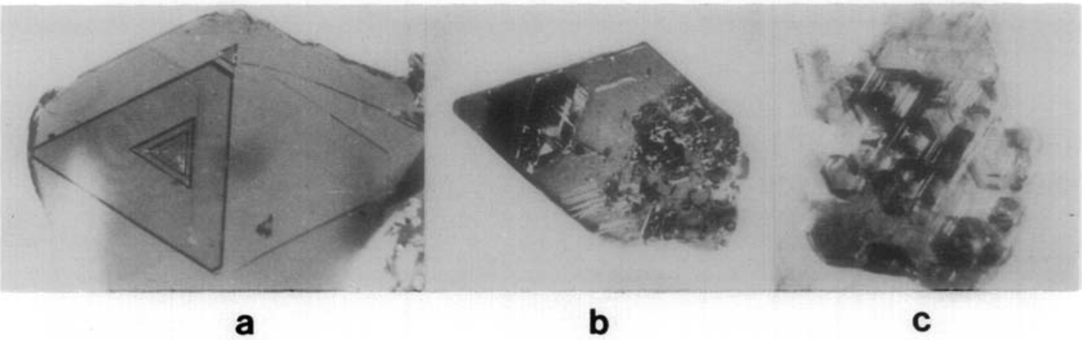

FIG. 6. Photographs of surfaces of crystals $GaSe_{1-x}S_x$ grown by the iodine transport method. (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.5$.

in accordance with the observation that sulfur and selenium are statistically distributed in the crystals (*13*).

The first result of the Weissenberg X-ray work is now that the third polytype *c* (Fig. 1) . . . AββA, CββC . . . , did not occur in the crystals we have investigated. This is obvious because in this structure the Ga–

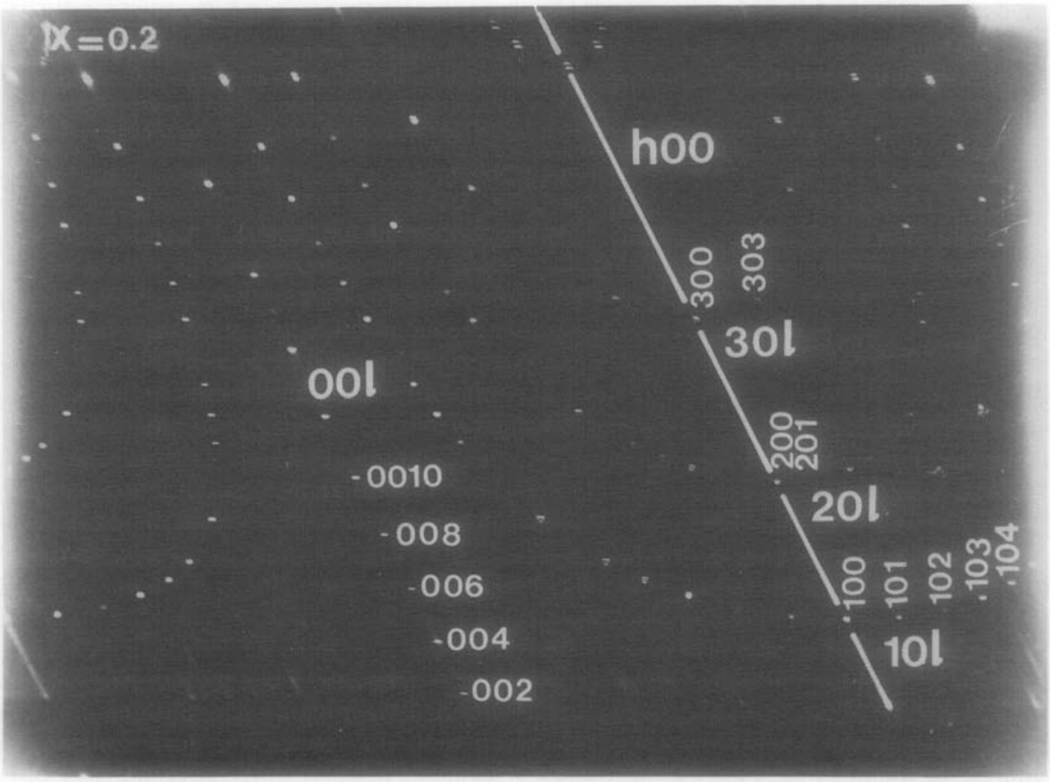

FIG. 7. Zero-layer Weissenberg photograph of a crystal from batch composition $GaSe_{0.8}S_{0.2}$; β structure.

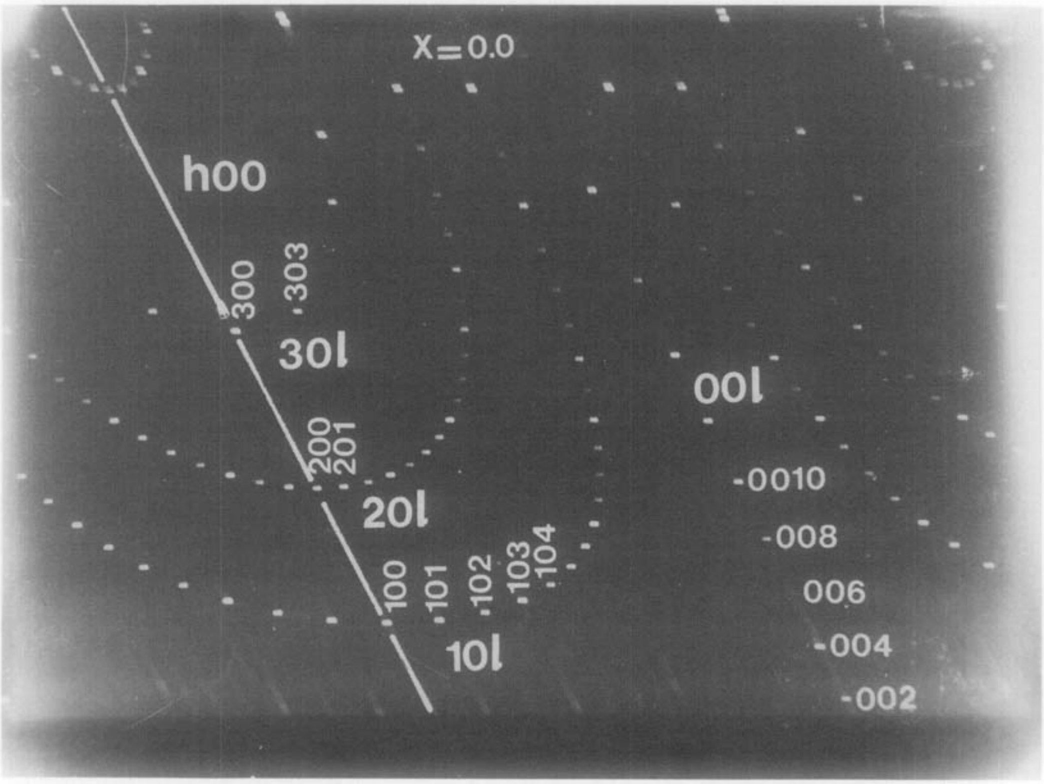

FIG. 8. Zero-layer Weissenberg photograph of a GaSe crystal; ε structure.

Ga pairs in adjacent layers are on top of each other, which is energetically very unlikely compared with the two other possible stackings (see Fig. 1). The starting point to distinguish further between the β and the ε structure is given by the weak reflections (10.2), (10.6), (20.2), and (20.6) for the β structure in comparison with the ε structure.

In Fig. 7, the photograph of a $GaSe_{0.8}S_{0.2}$ crystal shows now clearly the relatively weak characteristic reflections compared with the photograph of GaSe in Fig. 8. Also the other reflections on Fig. 7 give a good fit for the β structure, whereas the photograph presented in Fig. 8 fits the ε structure. A number of the mixed crystals were investigated with the Weissenberg technique and it turned out that above $x = 0.3$, we did find evidence of the β structure and below $x = 0.2$ only the ε structure was found. In the intermediate region $0.2 \leq x \leq 0.3$, both structures could be detected, which supports the idea that the phase segregation indicated by the powder X-ray work is indeed a segregation into the ε and β structure.

As final results of our experiments we can make the following statements.

Detailed X-ray investigation proofs that the irregularity in the lattice parameters of the mixed series $GaSe_{1-x}S_x$ is attended by a phase segregation at the growth temperature of the crystals. The irregularity in the parameters is due to a change of the crystal structure from the β polytype into the ε polytype, which takes place between $x = 0.15$ and 0.35. This polytype transition, in-

TABLE I

Reflection $h\,k\,l$	I_{calc}[a] (normalized) ϵ	β	Third structure
10.0	15.4	89.5	46.9
10.1	30.9	12.4	21.8
10.2	8.1	3.3	85.6
10.3	32.3	69.0	
10.4	4.2	13.5	0.6
10.5	16.3	15.6	4.2
10.6	16.0	0.5	113.2
10.7	50.4	100.0	15.6
10.8	6.4	4.0	34.4
10.9	2.1	0.9	16.8
10.10	2.8	7.4	0.0
10.11	8.0	5.3	0.1
10.12	2.5	2.7	0.8
10.13	5.6	0.1	7.3
10.14	1.3	9.0	17.3
20.0	4.5	26.0	15.0
20.1	9.4	4.2	6.1
20.2	2.6	1.1	27.1
20.3	10.2	22.4	19.1
20.4	1.5	4.7	0.2
20.5	6.6	6.3	1.6
20.6	6.9	0.3	48.4
20.7	23.2	46.2	7.0
20.8	3.2	2.1	17.8
20.9	1.2	0.6	9.0
20.10	1.6	4.4	0.0
20.11	5.4	3.5	0.0
00.2			
00.4	100.0	105.1	100.0
00.6	5.0	2.9	0.4
00.8	3.4	21.6	76.8
00.10	11.4	38.3	38.7
00.12	13.8	12.3	42.0
00.14	25.7	39.1	21.8

[a] Intensities in arbitrary units.

troduced by changing the composition is a first-order transition because of the appearance of a two-phase region.

In mixed series of compounds in which polytypism occurs, anomalies in the composition dependence of the lattice parameters may, in our view, be indicative of polytypic transformations caused by a shift of the composition. Another typical example of such mixed series is the tin sulfide-selenide system, in which such an irregularity is found around the composition $SnS_{0.75}Se_{1.25}$ (*14*).

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