TRIMORPHISM IN ZINC SULFIDE*

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Abstract

Experimental evidence was found for the existence of a third polymorphic modification of zinc sulfide. In addition to β zinc sulfide (zincblende or sphalerite) and α zinc sulfide (wurtzite) structures, a three-layer rhombohedral structure was found to occur in the temperature range of approximately 600° C. to 1020° C. This structure is similar to the zincblende structure referred to hexagonal axes wherein the c and a dimensions are slightly altered. In conformity with conventional nomenclature it is designated γ-zinc sulfide.

The experimental evidence for the existence of rhombohedral zinc sulfide is the fine structure of cubic (111) x-ray reflections as observed with high resolution spectrometer studies on pure zinc sulfide heated for various temperatures and quenched.

The role of the rhombohedral phase in the sphalerite-to-rhombohedral-to-wurtzite transformation has been studied.

Introduction

Zinc sulfide has been known to exist in the two polymorphic forms, zincblende (β-ZnS) and wurtzite (α-ZnS), and in a series of multilayered structures.[1] Two of the latter are based on wurtzite lattice with 4- and 6-ZnS layers stacked in the [001] direction, and the other on a rhombohedral lattice, which, when referred to hexagonal axes, has 15 layers. Natural 2-layer wurtzite is the prototype of the wurtzite lattice polytypes (*4H* and *6H*) because it is the simplest close packed hexagonal unit cell. The simplest unit cell in the rhombohedral lattice (expressed on hexagonal axes) is a 3-layer cell *3R*. A *3R* zinc sulfide has not been previously observed. It is difficult to distinguish from face centered cubic zincblende by x-ray methods. The purpose of this paper is to present experimental evidence for the existence of a *3R* polymorph of zinc sulfide (γ-ZnS), to describe the behavior of its lattice constants c and a (referred to hexagonal axes) in the temperature range 600° C.–1100° C., and to discuss the rôle of γ-ZnS in the transformation $\alpha\text{-ZnS} \rightleftarrows \beta\text{-ZnS}$.

Experimental

For some time the mechanism of the transformation from the zincblende to wurtzite structures has been a matter of interest, and it was in this realm of study that we obtained the experimental evidence for a 3-layered rhombohedral structure existing in the temperature range from

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[1] Frondel, C., and Palache, C., *Am. Mineral.*, **35,** 29–42 (1950).

the zincblende to wurtzite transition temperature (1020° C.) down to about 600° C. In conformity with conventional nomenclature, it is designated γ-zinc sulfide. The evidence for the existence of the 3-layered rhombohedral structure was found in the fine structure of the (111) cubic reflection. Normally, zinc sulfide has a (111) cubic *d*-spacing of 3.12 Å and the half width (width in angular separation at half a maximum intensity) is about $\frac{1}{3}$ degree 2*θ*, where *θ* is the Bragg angle. However, it was found that when samples of zinc sulfide powder were heated to temperatures near the transition temperature, the (111) cubic peak separated into several narrow distinct peaks with separations of the order of magnitude 0.1 degree or less. Figure 1 shows one of these split peaks,

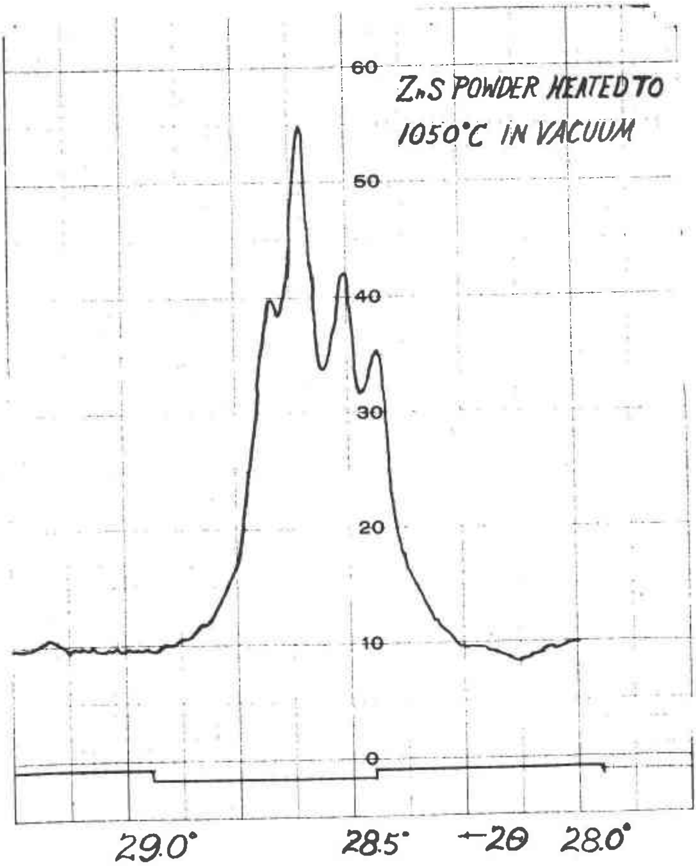

FIG. 1. Example of (111) cubic *x*-ray diffraction peak splitting recorded by Norelco *x*-ray diffraction spectrometer.

TABLE I. RHOMBOHEDRAL PHASE IN HEAT TREATED CUBIC ZnS POWDER

(Annealed samples first heated to 1050° C. and quenched)

Temperature °C.	Split cubic (111) spacings in Å (Hexagonal indices)		Rhombohedral cell in Å			From (100) spacing of hexagonal phase present a
			Hexagonal axes		Ratio c/a	
	101	003	a	c		
950	3.113	3.121	3.811	9.363	2.457	3.818
1000	3.131	3.143	3.833	9.429	2.460	3.816
1050	3.122	3.136	3.822	9.408	2.462	3.824
Annealed at						
1000	3.131	3.159	3.830	9.477	2.474	3.822
950	3.113	3.122	3.811	9.366	2.457	3.810
900	3.127	3.135	3.829	9.405	2.456	3.808
850	3.112	3.116	3.811	9.348	2.453	3.805
Cubic	(111) 3.121		3.822	[111] 9.363	(2.4495)	geometrical ratio

as recorded by a high-resolution x-ray diffraction spectrometer.

Samples of zinc sulfide powder were sealed in evacuated quartz vials and heated to the temperatures indicated in Column 1 of Table I, and quenched in water at room temperature. Also powder which had been heated to 1050° C. for $2\frac{1}{2}$ hours and quenched, was then annealed at temperatures between 1000° C. and 850° C.

In these annealed samples, the (111) cubic peak splitting remains until the temperature is lower than 850° C. The angular separation of the components of the multi-peaked reflections varied appreciably over the temperature range 850–1050° C., the spread being greater at higher temperature. The relative intensity of the minor peak components is greater at higher temperature.

Figure 2 shows the (111) planes of the zincblende structure referred to a hexagonal axis system whose base (001) plane is the (111) plane of the original face centered cubic cell and the c axis of this 3-layered hexagonally based cell is the body-diagonal of the face centered cube. To investigate the effects of temperature on the form of the x-ray diffraction reflections, we will consider two simple models. If the crystal undergoes isotropic thermal expansion, the spacings of all planes in the crystal will increase uniformly. If the rates of thermal expansion vary over a small range according to some parameter, such as position in the crystal, the diffraction line will be broadened as well as moved towards lower Bragg

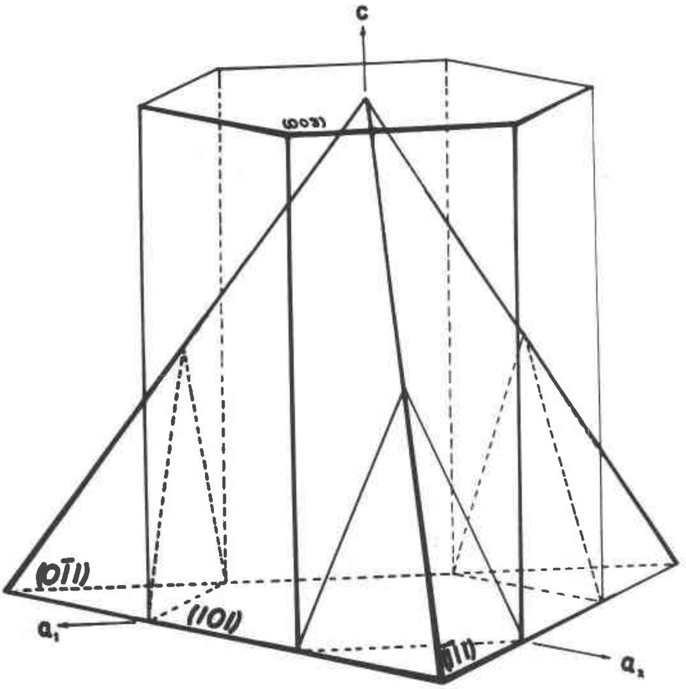

FIG. 2. (111) cubic planes referred to a 3-layer hexagonal axis system and indexed in the hexagonal system.

angles. However, if the crystal enlarges in a preferred direction, a reduction of symmetry will occur, causing degenerate reflections to be separated into component reflections whose interplanar spacings have different expansion coefficients. Such a case is the system of (111) cubic planes in face centered zinc sulfide. Referring to Fig. 2, if the enlargement is greater in the [003] direction than in the other three ([101], [$\bar{1}$11], [0$\bar{1}$1]), the interplanar spacing of the (003) planes will increase faster than those of the (101), ($\bar{1}$11), (0$\bar{1}$1) planes thus producing two distinct interplanar spacings where there was formerly one for all (111) cubic planes. This transformation can be described by an elongation of a cube along its body diagonal. When the structure is cubic, the angle between the shortest rhombohedral axes is 60°. When the figure undergoes the elongation, these angles decrease from 60°.

Table I shows that at temperatures above 850° C. the (111) cubic line resolves itself into 3 peaks and at temperatures above 1000° C., becomes 4 peaks; also, the (100) hexagonal line is resolved into 2 peaks in this temperature range. This indicates the concurrent existence of both normal (room temperature) cubic zinc sulfide and a structure which, when referred to the hexagonal system, has a $c{:}a$ ratio greater than 2.4495 (that of a perfect face centered cube), where the a value is slightly smaller than that of natural zinc sulfide and the c axis is larger. This latter structure is, therefore, rhombohedral whose interaxial angle is slightly less than 60°.

The third split (111) "cubic peak" mentioned above corresponded to some undistorted cubic zinc sulfide which either reverted to its original form within the quenching time allowed, or never had time to make the transformation to rhombohedral. The other two (111) "cubic peaks" corresponded to the reflections from the $(\bar{1}11)+(0\bar{1}1)+(101)$ and the (003) *3R* planes (Fig. 2). The (003) *3R* plane corresponds with the smaller Bragg angle peak. Since the planes (003) cut only the c axis of the *3R* cell, the length of the c axis is simply equal to three times the spacing of this reflection. Then, since the (101) type planes all cut both the c and a axes of the *3R* cell (referred to hexagonal axes), it was possible to compute the length of the a axis using the value of the c axis obtained above from the (003) spacing. This a axis value could not be compared with one determined directly from (100) spacings, since this is an extinction in a 3-layer structure (rhombohedral or cubic on hexagonal axes) but it was compared with the a axis spacing determined from (100) reflections of hexagonal (2H) structure present in the same powder samples. The a axis values for the hexagonal phase were all lower than those for the rhombohedral phase; meaning that the rhombohedral to hexagonal phase is accompanied by further shrinkage of the a axis. All of these changes, except the 950° C. annealed sample, are greater than the experimental peak splitting resolution of 0.002 Å. The c/a ratio for the rhombohedral phase increases with temperature above the equivalent cubic value 2.4955 as shown in Table I.

It was not known whether the cubic to rhombohedral transition was a phenomenon occurring within the powder particles or a phenomenon associated with recrystallization from the vapor phase. To investigate this the apparatus in Fig. 3 was built. The system was pumped to a vacuum of about 10^{-1} mm. Hg. This reduced the chance of ZnO formation and the effect of impurities acting in the recrystallization process. The zinc sulfide is heated in boat #1 to 1050–1100° C. and recrystallization, if any, occurs on boat #2 due to its lower temperature. Since the vapor pressure of zinc sulfide climbs rapidly above 1000° C., it was not surprising that much recrystallized zinc sulfide was found in boat #2. The powder left in boat #1 was examined under the microscope and in several cases recrystallized zinc sulfide was noticed. Figure 4 shows the interplanar spacings calculated from the (111) cubic diffraction component peaks for recrystallized zinc sulfide for four experiments varying the temperature of the boat upon which the crystals formed. Again, the angular spread between peaks is an increasing function of temperature. The largest peak remained in the *d* (111) cubic position, and as temperature rose, peaks spread out in both larger and smaller *d*-spacing directions.

The most probable mechanism to explain Fig. 4 is a superposition of untransformed cubic (111) reflections and reflections from *3R* cells where again the *a* axes shrink and the *c* axis enlarges, resulting in spacings less and greater than the regular (111) cubic spacing. At 600° C. the cubic reflection and the slower increasing (101) (*3R*) reflections practically coincide; at higher temperatures the (101) *3R* spacing reflection decreases and in the 1000° C.–1100° C. sample these spacings differ by 0.10 Å, about 6 times the corresponding difference at 900° C. Thus, we see an elongation of the cell along the *c* axis and a corresponding compression of the hexagonal base varying continuously with the temperature. *X*-ray rotation photographs of single crystals grown at these elevated temperatures revealed an amount of hexagonal zinc sulfide, whose (002) reflection from our 1100° C. sample is the one with the next to largest spacing. The transformation resulting in this *2H* cell is best described in several steps:

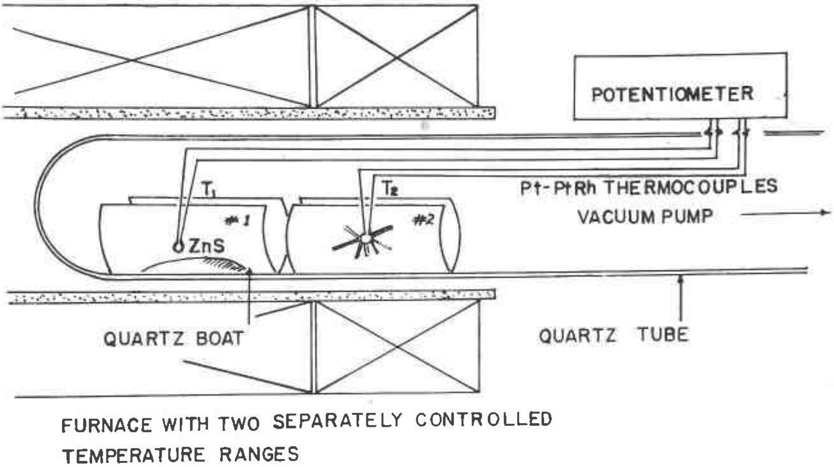

FIG. 3. Crystal growing furnace and vacuum system. ZnS powder is introduced in boat #1 and heated to temperature T_1. The vacuum is maintained until the powder has attained the temperature T_1. The pump is then shut off and the vapor pressure of ZnS at T_1 determines the pressure of the system. To quench, the furnace is slid off to left.

A differential thermal expansion occurs in one preferred of the four (111) cubic directions where zinc and sulfur ions are lined up. This direction we will call [003] in the 3-layered hexagonal structure. The sulfur presumably becomes asymmetric and orients its long axis in this pre-

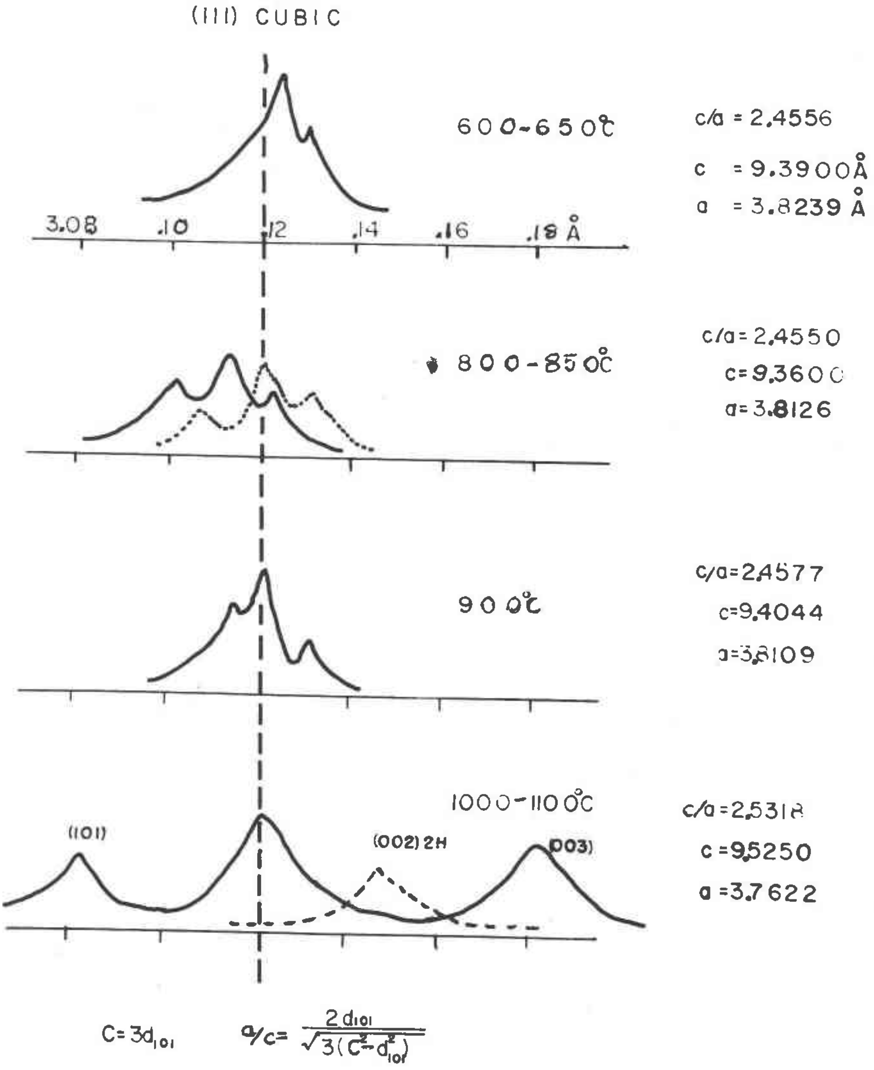

FIG. 4. Positions of (111) cubic x-ray diffraction peaks for ZnS crystals grown from the vapor phase at different temperatures of crystal growth. The dotted curve at 800–850° C. indicates correction for an unusually long quenching time. Curves obtained from powder plaque sample.

ferred [003] direction. As the expansion increases, there is a corresponding decrease in the influence of an (003) layer on the atoms settling down from the vapor phase into the second layer above the original. This causes an increasing probability of second layer atoms to land on an *AB* pair of layers forming an *ABAB* (*2H*) sequence rather than an *ABC* (*3R*) sequence. At the conventionally accepted zincblende-wurtzite transition temperature (1020° C.) this probability is theoretically unity. The *2H* cells which result from a vapor to solid phase transformation have c axes longer than that found in natural wurtzite; this is so because these crystals were quenched relatively quickly with respect to those in nature, and most of the *2H* cells are found in crystals which also have *3R* cells in them, indicating that these crystals are still strained because they were grown at a high temperature. However, some pure *2H* crystals were found from a vapor phase deposition at 1100° C. showing that the $3R \rightarrow 2H$ transition probability can be unity at a sufficiently high temperature.

The mechanism proposed above is corroborated by the study of a rotation x-ray diffraction photograph of a single crystal grown between 800° C. and 850° C. The portion of the crystal that was examined was a flat thin striated plane, and the axis of rotation was perpendicular to the striations and in the plane of the crystal. The spacings for the (003) and (101) planes in the face centered cubic, all referred to hexagonal axes, were accurately measured and found to be unequal. The spacings were:

$$d_{(003)} = 3.1399 \text{ Å}, \qquad d_{(101)} = 3.1200 \text{ Å}.$$

The length of the c-axis of this cell is 3 times the (003) spacing = 9.4197 Å, and the c/a ratio calculated from the formula

$$\frac{c}{a} = \frac{\sqrt{3}}{2} \frac{\sqrt{C^2 - d_{(101)}{}^2}}{d_{(101)}} = 2.467,$$

and the a-axis was found to be 3.8183 Å. The cell thus described was in general agreement with the cell described by the spectrometer measurements on the 800–850° C. crystal sample. Also, if rhombohedral zinc sulfide is a high temperature form, it would be expected to be metastable at room temperature to such treatments as cold working. This was found to be so; after several minutes working with the mortar and pestle, the diffraction peak splitting was completely removed from a sample of *3R* powder.

Comparison of Fig. 4 and Table I reveal an inconsistency in c/a axial ratio values at given temperatures for the heated powder samples and the crystals grown from the vapor phase. This is due to the difference in quenching times of the two types of experimental samples. The powders took about a minute to cool down to room temperature, whereas the crystals required only a few seconds to cool as they were grown on a Pt-PtRh thermocouple which cooled off quickly. The crystals then had less time to revert to lower temperature forms and they gave a more accurate picture of the structures existing at the elevated temperatures.

In case of the samples of zinc sulfide powder, heated to elevated temperatures, the vapor was continually swept away by the vacuum pump. However, some recrystallization was discovered in these samples, making it to date impossible to decide whether or not the γ-α zinc sulfide transformation occurs within the volume of the powder particles.

CONCLUSIONS

There exists a third polymorphic modification of ZnS which acts as an intermediate phase between the isometric cubic structure and the directional wurtzite structure. As the temperature increases, the inter-atomic forces become more directional and the symmetry of the structure reduces from the fourfold cubic to the threefold rhombohedral, and finally to the threefold hexagonal wurtzite. γ ZnS has been found at temperatures from 1020° C. down to 600° C. It is reasonable to expect that crystals will be found with rhombohedral structures of $c\!:\!a$ ratios ranging from the equivalent cubic value 2.4495 up to a maximum value at the rhombohedral-hexagonal transition temperature.

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