

the investigation of oriented transformations during heat treatment, the essential geometrical relations between the various individual components is more important than their lattice dimensions. A study of the oriented transformation of calcite to CaO during heat treatment is to be reported shortly.

ACKNOWLEDGMENTS

One of the authors (Rao) is thankful to the National Research Council of Canada for the award of Postdoctorate fellowship and to the Director, Indian Institute of Technology, Kharagpur (India) for sanctioning him leave to take up this award. He is also thankful to Dr. T. C. Bagchi of the same Institute for the continued encouragement he has given the author in the pursuit of mineralogical studies.

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THE AMERICAN MINERALOGIST, VOL. 50, JULY-AUGUST, 1965

P-T DEPENDENCE OF THE SPHALERITE \rightleftharpoons WURTZITE INVERSION
IN ZnS

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In a comprehensive study designed to test the applicability of the Clapeyron relationship to various types of polymorphic transformations, the transition in ZnS has recently been reexamined. The main object in this study was to determine the p-T dependence of the sphalerite \rightleftharpoons wurtzite transition and thereby estimate the heat of transition from the p-T data employing the well known Clapeyron relationship. Kullerud (1953) has used the Clapeyron relationship to predict an increase of 20° C. in the sphalerite \rightleftharpoons wurtzite inversion temperature for every 1000 atmosphere increase in pressure. Precise measurements of unit cell parameters of the two modifications *at room temperature* and a calorimetrically determined value of 3190 cal/mole for the heat of transition obtained from the thermochemical literature provided the known variables in his estimate. However, as recent investigations of Smith (1955) and Strock and Brophy (1955) and others have shown, polymorphism in ZnS is a very com-

plicated affair and many structures intermediate between the cubic and hexagonal close packed end members have been recognized and isolated. Experiments by Müller (1952) showed that wurtzite was not stable at 905° C. but persisted at 950° C. Moreover, he records the appearance of the 4, 6 and 15 layer polytypes in the vicinity of the transition and calls this "completely inexplicable." Hill (1958) has discussed the same question of stability of these polytypes in detail.

In the present study attempts were made to measure the unit cell parameters of both forms at high temperatures by *x*-ray diffractometry

TABLE 1

Substance	Temp. (°C.)	Unit cell para.		Volume per cell (Å ³)	Volume per mol. (Å ³)	Δv (per mole)	
		<i>a</i>	<i>c</i>			(Å ³)	(c.c.)
ZnS (Sphalerite)	30	5.405		157.901	39.475		
	200	5.412		157.517	39.629		
	350	5.415		158.780	39.695		
	500	5.420		159.220	39.805		
	750	5.428		159.926	39.981		
ZnS (Wurtzite)	30	3.820	6.260	91.23	39.55	0.18 at	0.11 at
	250	3.825	6.266	91.67	37.74	1020° C.	1020° C.
	340	3.828	6.270	91.86	39.775		
	510	3.834	6.276	92.26	39.95		
	730	3.840	6.282	92.66	40.12		

in a N₂ atmosphere with a view to obtaining a more realistic value for the instantaneous volume change attendant on this transition. Unfortunately, the upper temperature limit had to be fixed at about 750°, well below the inversion temperature, as the samples showed definite signs of oxidation (a very small amount of air entrapped in the sample was probably responsible for this) at higher temperatures. The results are shown in Table 1.

As can be seen from Table 1, present measurements after extrapolation yield a value of 0.11 cc/mole for the volume change at 1020° C. (reputedly the inversion temperature) which is about twice the value of 0.05 cc/mole used by Kullerud in his calculation. Even if the value for the heat of transition is taken as reliable, use of the present Δv term alters the dp/dt term as estimated by Kullerud by more than a factor of two and demonstrates very clearly the limitation of the Clapeyron method for such transitions where the Δv term is very small.

TABLE 2

Starting Material	Pressure	Temp. (°C.)	Time	Products
ZnS sphalerite wurtzite ¹	1 atm.	955	4	sphalerite
Zns sphalerite wurtzite ¹	1 atm.	960	4	polytypes
Zns sphalerite wurtzite ¹	1 atm.	1000	4	polytypes
wurtzite ¹	1 atm.	980	24	polytypes, more cubic than the starting material
wurtzite ¹	1 atm.	980	5 min	polytypes, more cubic than the starting material
wurtzite ¹	1 atm.	970	<1 min	polytypes, more cubic than the starting material
sphalerite wurtzite ¹	680 atm. ± 5 atm.	955	2	sphalerite
sphalerite wurtzite ¹	680 atm. ± 5 atm.	960	2	polytypes, peaks other than 100, 002 and 101 are of very low intensity, if not absent, in the region $2\theta=31-35^\circ$ (CuK α)
sphalerite	680 atm. ± 5 atm.	970	2	polytypes, peaks other than 100, 002 and 101 are of very low intensity, if not absent, in the region $2\theta=31-35^\circ$ (CuK α)
sphalerite	1000 atm. ± 5 atm.	955	4	sphalerite
sphalerite	1000 atm. ± 5 atm.	960	49	polytypes, peaks other than 100, 002 and 101 are of very low intensity if not absent in the region $2\theta=31^\circ-35^\circ$ (CuK α)
sphalerite	1000 atm. ± 5 atm.	1000	49	polytypes, peaks other than 100, 002 and 101 are of very low intensity if not absent in the region $2\theta=31^\circ-35^\circ$ (CuK α)

¹ Substance much closer to 2H than to 3C structure.

Possibly more significant, however, are the present phase data assembled in Table 2. The earlier observations of Hill (1958) seem to have been confirmed beyond doubt and persistence of polytypes at higher pressures also are very strongly indicated. The polytypes which appear above 960° C. depend markedly on the starting material—wurtzite starting material produced more complicated varieties than sphalerite. These polytypes were recognized by their *x*-ray diffraction spectra. As has been pointed out by Smith and Hill (1956) in the case of ZnS, and the present

authors in the case of AgI (Majumdar and Roy, 1959), the degree of cubicity as estimated by the relative intensities of some of the diffraction maxima are strongly influenced by grinding. As a result, some unavoidable uncertainty always remains as to the exact nature of the material *actually* produced in a run. This uncertainty has been, if only partially, guarded against by powdering the starting materials very finely, heating the samples with NaCl in sealed capsules under the desired p-T conditions and subsequently leaching the NaCl flux out of the product held on the actual glass slide used in the x-ray examination without any grinding.

The quenched charges from high pressure runs showed, on x-ray examination, that the polytypes present under these conditions are simpler than the corresponding structures obtaining at one atmosphere pressure. This may reflect the ease with which the transition from the 3C to the 2H configuration may proceed under high pressure conditions. On the other hand, in presence of NaCl flux and at atmospheric pressure, in less than the one minute which a sample takes to reach 960° C. from room temperature, 2H wurtzite is already converted partly to more cubic polytypes. The reversibility of the sphalerite \rightleftharpoons wurtzite equilibrium cannot, therefore, be studied in this way. The only temperature, therefore, that can be studied is the temperature where the sphalerite form starts to decompose into more complicated polytypic forms. This "transition" temperature has been measured at two different pressures, 680 atm and 1000 atm and no variation of this temperature outside the limits of experimental error ($\pm 5^\circ$ C.) could be detected. Meaningful calculations of ΔH are not possible.

In view of the present experimental results and similar ones due to Hill, the following conclusions may be drawn:

- a. The sphalerite \rightleftharpoons wurtzite transition is at least as low as 960° C. unless NaCl is much more soluble in wurtzite than in sphalerite.
- b. The p-T slope for the wurtzite-sphalerite transition is not known. The thermochemical value of ΔH does not (and cannot) allow for the change of heat capacity from R.T. to 960° C. A new Δv term is one half the previous value.

ACKNOWLEDGMENT

This work was supported by NSF Grant G4648 and is reported in detail in the Ph.D. Thesis by A. Majumdar, Geochemistry, PSU, 1959.

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THE AMERICAN MINERALOGIST, VOL. 50, JULY-AUGUST, 1965

SEISMIC CONTROL OF LAYERING IN INTRUSIONS

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The influence of the tectonic framework on the history of lithification of magma has been persistently ignored in the literature. The possible effects of the tectonic environment with reference to the development of small scale structures have so far not been seriously considered. The emplacement of a pluton represents a climax to tectonic activity and is therefore likely to be not only preceded but also followed by prolonged periods of intermittent seismic events of varying degrees of violence. The temporary and differential effects of the primary waves of intermittent earth tremors on the nucleation, growth and settling rates of crystalline particles of varying density and habit nucleating near the upper contact of the pluton may be profound enough to provide an efficient mechanism for the development of mineralogical as well as of textural layering.

The quantitative evaluation of the net effect would involve a large number of assumptions such as the instantaneous boundary values and the gradients of the viscosity and of the temperature of the magma, the rates of nucleation and of crystal growth as well as the respective habits of the coprecipitating solids, and the intensities of earthquakes and their frequency above the level of seismic noise. However, it is a trivial matter to demonstrate in the laboratory that a supersaturated liquid will precipitate spontaneously if mildly disturbed, and that the higher the viscosity of the liquid—that is, the lower its temperature—the higher is the degree of departure from equilibrium saturation that it is capable of accommodating in the absence of nuclei. Whether or not the continued growth of a nucleus takes place at instantaneous equilibrium, the formation of a nucleus—as distinct from its subsequent growth—requires a finite amount of supersaturation unless the liquid is mechanically agitated. In fact, a nucleus forming at equilibrium saturation near the upper contact of an intrusion would have little chance for survival and