

SUB-SOLIDUS RELATIONS IN THE SYSTEM PbS-CdS<sup>1</sup>

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## ABSTRACT

The solvus defining the solubility of CdS in galena has been determined between 500° and 900°C, and is defined by the relationship:

$$\log \text{ mole percent CdS} = 5.216 \log T_{\text{OK}} - 14.677$$

The solvus has been reversed, and is described by this function to  $\pm 0.70$  mole percent CdS ( $2\sigma$ ). The low cadmium content of natural galenas reflects the low activity of CdS in most ore fluids. Reevaluation of our earlier published relationship between unit-cell edge and composition of CdS-bearing galenas suggests that unit-cell volume, rather than unit-cell edge, is a linear function of composition. The relationship between unit-cell volume (in cubic Å) and composition is:

$$\text{mole percent CdS} = \frac{209.151 - V}{0.4389};$$

this relationship describes the data to  $\pm 0.16$  mole percent CdS ( $2\sigma$ ). Conchoidal fracture replaces cubic cleavage as the principal mechanism of fracture as CdS content increases. Compositions above 15 mole percent CdS break entirely by conchoidal fracture.

## METHOD

The sub-solidus relations in the system PbS-CdS were determined from 500° to 900°C at the vapor pressure of the system. Most of our runs were made to determine the position of the solvus defining the solubility of CdS in galena. Runs consisted of 50 to 200 mg charges of CdS+PbS or Pb+Cd+S mixtures (solution runs) or CdS-bearing galena solid solutions (exsolution runs) sealed in evacuated silica glass tubes. The compositions of the resulting CdS-bearing galena solid solutions were determined by precise, high-angle X-ray diffractometry utilizing the spacing curve published earlier (Bethke and Barton, 1961). The precision of the compositional determinations was better than 0.2 mole percent CdS (based on 2 times the standard deviation on our spacing curve). A close approach to equilibrium was demonstrated by the sharpness of the X-ray diffraction profiles at high angles and the excellent agreement between solution and exsolution runs. The lead, cadmium, and sulfur used were all of at least 99.99 percent purity. Analyses of the lead and cadmium were reported in our spacing curve paper, and that of the sulfur by Skinner, Barton, and Kullerud (1959). Temperatures of the furnaces were controlled to  $\pm 5^\circ\text{C}$ .

## RESULTS

The conditions and results of our experiments are listed in Table 1 and illustrated in Figure 1. In the inset in Figure 1, the positions of the liquidus and solidus curves, inferred from the melting points of the pure end members and the temperature of the eutectic, are indicated by dashed lines. The two phase ( $gn+gk$ ) region is highly asymmetric. We could not detect any change in the high angle interplanar spacings of

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Table 1. Results of experiments

Run	Reactants	T+5°C	Days	Mole percent CdS in galena		
				solution (a)	exsolution (a)	calculated (b)
Cd28A	Pb+Cd+S	930	47	23.46		24.63
Cd19	PbS+CdS	900	7	22.29		21.50
Cd51	PbS+CdS	860	25	17.48		17.95
Cd28B	Pb+Cd+S	820	7	14.88		14.88
Cd50A	Pb    Cd    S .837    .163	800	25		13.88	13.51
Cd16S	Pb    Cd    S .851    .149	725	9		9.01	9.26
Cd49S	Pb    Cd    S .866    .134	725	9		8.77	9.26
Cd28F	Pb+Cd+S	700	11	8.46		8.11
Cd28D	Pb+Cd+S	660	48	6.25		6.52
Cd28E	Pb+Cd+S	600	342	4.47		4.61
Cd50B	Pb    Cd    S .837    .163	600	25		4.90	4.61
Cd28C	Pb+Cd+S	540	126	3.30		3.18
Cd48A	Pb    Cd    S .929    .071	500	25		2.39	2.44
Cd48B	Pb    Cd    S .929    .071	400	142		1.31	1.19

(a)  $\pm$  0.1 mole percent; (b) from relation (1) in text

greenockite equilibrated with galena in any of our runs, indicating that the solubility of PbS in greenockite is less than 0.1 mole percent even at 930°C. On the PbS side, the solvus intersects the solidus at about 24 mole percent CdS and near 920°C. A curve described by the equation:

$$\log \text{mole percent CdS} = 5.216 \log T_{K^{\circ}} - 14.677 \quad (1)$$

was fit to the solvus data by the method of least squares. Higher order equations were tried but did not improve the fit. Equation (1) describes the data to  $\pm 0.7$  mole percent CdS in galena ( $2\sigma$ ). Runs Cd28A (930°C) and Cd48B (400°C) were not included in the curve fitting calculations. Run Cd28A probably intersected the solidus and therefore would represent the composition of galena in equilibrium with a CdS-PbS melt near the binary eutectic. Run Cd48B was discarded as being too far removed from a solution run to be considered reversed, although it lies very close to the projection of the curve.

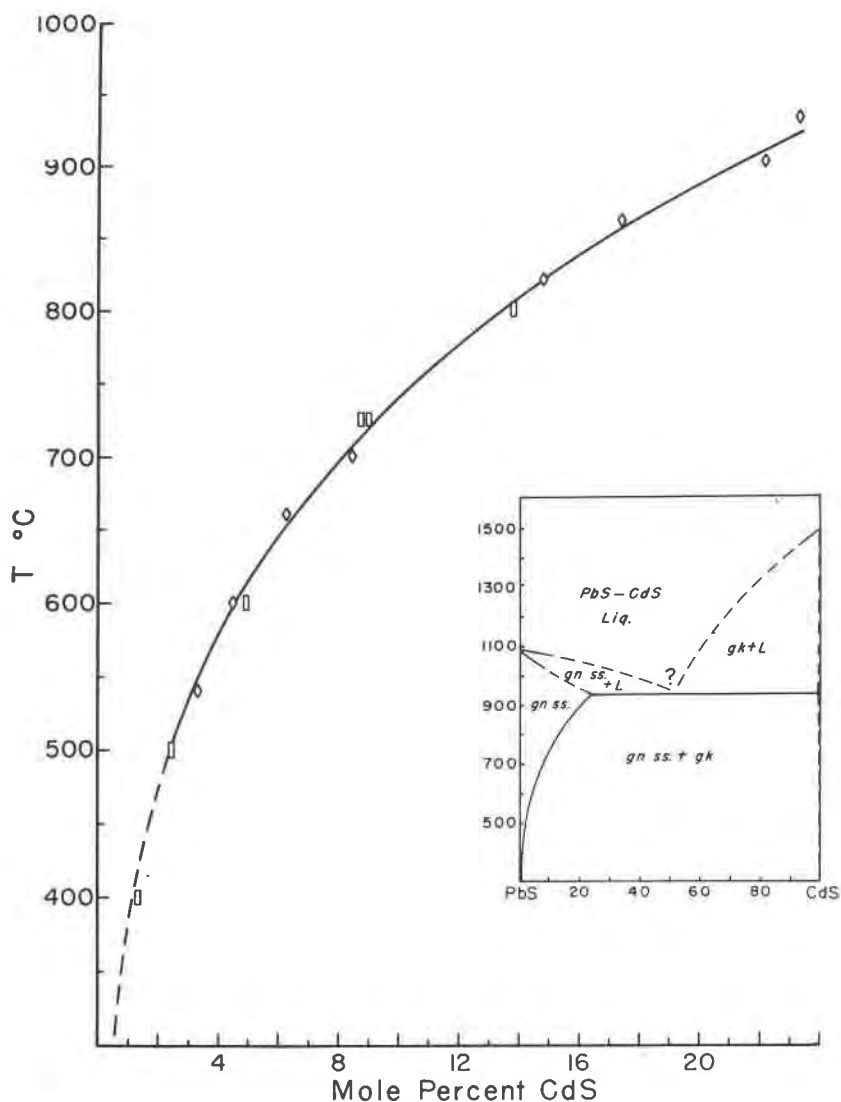


FIG. 1. Experimental determination of the solubility of CdS in galena. Diamonds indicate solution runs, rectangles exsolution runs. Dimensions of symbols indicate uncertainty in composition and temperature. Inset: complete PbS-CdS system. Dashed lines show inferred relations. Diagrams are for pressure equal to the vapor pressure of the system.  $gk$  = greenockite;  $gn$  = galena.

Extrapolation of equation (1) to lower temperatures and conversion from mole percent CdS to ppm cadmium in galena indicates maximum equilibrium Cd concentrations of approximately 300 ppm at 100°C, 1500 ppm at 250°C, and 5600 ppm at 400°C. Few reliable analyses of the cadmium content of natural galenas have been reported. The strong fractionation of cadmium toward sphalerite (Bethke and Barton, 1971) requires quantitative removal of sphalerite from the galena concentrate prior to analysis, for even very small amounts of sphalerite will add significant amounts of cadmium to the analytical results. The relatively few analyses of zinc-free galenas known to us (Fleischer, 1955; R. A. Both, written communication, 1971; W. E. Hall, written communication, 1970-1971, and M. S. Toulmin, written communication, 1965) indicate that nearly all galenas contain less than 100 ppm cadmium, the highest value found being that of Oftedal who reported 1000 ppm cadmium from a high-bismuth Norwegian galena (Fleischer, 1955). The fact that natural galenas contain cadmium in amounts far lower than the maximum solubility level is simply a reflection of the usual role of cadmium as a minor constituent in ore-forming fluids. The activity of CdS in ore fluids rarely approaches unity, as evidenced by the fact that cadmium contents of natural sphalerites and wurtzites rarely approach saturation values.

The short times for the exsolution runs (Table 1) indicate that the diffusion of cadmium in galena is relatively rapid even at moderate temperatures, further emphasizing the probable infidelity of natural galenas from many ore deposits in preserving original compositional heterogeneities such as growth zoning.

In our spacing-curve paper (Bethke and Barton, 1961) we considered that the cell edge of the CdS-bearing galena solid solutions was a linear function of composition, and presented the following relationship between cell edge ( $a$ ) and composition:

$$\text{mole percent CdS} = \frac{5.9359 - a}{.004194} \quad (2)$$

This relationship described our data to  $\pm 0.0003 \text{ \AA}$  on the cell edge or  $\pm 0.16$  mole percent CdS on the composition of the solid solution (both uncertainties reported as  $2\sigma$ ). Extrapolation of this relationship to pure CdS indicated a cell edge of  $5.516 \text{ \AA}$  for CdS of the NaCl structure. This value was included in two compilations of X-ray crystallographic and molar volume data (Robie, Bethke, and Beardsley, 1967; and Robie, Bethke, Toulmin, and Edwards, 1966). Since the time of compilation Corrl (1964) and Miller, Dachille, and Roy (1966) have prepared CdS of the NaCl structure at pressures in excess of 15 bars and over a tempera-

ture range of 25 to 400°C. When quenched to room temperature and pressure these materials yielded cell edges of  $5.464 \pm .012 \text{ \AA}$  and  $5.441 \text{ \AA}$ , respectively. Although inherent strain in the quenched material inhibited precise determination of the lattice parameters, these values are clearly much lower than that obtained by extrapolation of our linear cell edge versus composition relationship. We have therefore recomputed our data on the assumption of a linear variation of unit cell volume (in cubic  $\text{\AA}$ ) with composition. The equation so derived is:

$$\text{mole percent CdS} = \frac{209.151 - V}{0.4389} \quad (3)$$

Over the compositional range of our measurements (0–16.27 mole percent), cell edges calculated using the two relationships are identical, within the precision of measurement. The calculated uncertainty ( $2\sigma$ ) on relation (3) is  $\pm 0.0003 \text{ \AA}$ , also identical to that on the linear cell edge vs. composition relationship. It is apparent that both relationships describe our data equally well.

Extrapolation of the linear cell-volume relation yields a cell edge of  $5.488 \text{ \AA}$  for pure CdS of the NaCl structure. This value is in better agreement with the direct measurements reported by Corrl and by Miller, Dachille, and Roy, and we feel that the linear cell-volume relationship is to be preferred. Corrected values for the cell edge, cell volume, molar volume, and X-ray density of CdS of the NaCl structure calculated by relation (3) listed in Table 2 are similarly preferred to those listed in Robie, Bethke, and Beardsley (1967). Below 15 mole percent CdS the two relationships yield identical values within the precision of our measurements, and the equation for the linear variation of the cell edge, which is much easier to compute, was used in the compositional analyses reported in this study.

An interesting change in the breaking characteristics of galena with

Table 2. Revised extrapolated parameters for CdS  
of the NaCl structure

unit cell edge	$5.488 \pm 0.002 \text{ \AA}$
unit cell volume	$165.29 \pm 0.18 \times 10^{-24} \text{ cm}^3$
molar volume	$24.89 \pm 0.03 \text{ cm}^3$
	$0.5949 \pm 0.0007 \text{ cal bar}^{-1}$
density (calc.)	$5.805 \pm 0.006 \text{ gms cm}^{-3}$

increasing CdS content was pointed out in our spacing curve paper. At compositions lower than about 6 mole percent CdS the galena breaks exclusively along its cubic cleavage. At higher CdS concentrations however, the cleavage is joined by a conchoidal fracture. The proportion of conchoidal fracture to cubic cleavage seen in crushed powders increases with increasing CdS content, until at compositions higher than 15 mole percent CdS, no cleavage surfaces are observed.

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