

## The crystal structures and compressibilities of layer minerals at high pressure. I. $\text{SnS}_2$ , berndtite

ROBERT M. HAZEN AND LARRY W. FINGER

*Geophysical Laboratory, Carnegie Institution of Washington  
Washington, D. C. 20008*

### Abstract

Unit-cell dimensions of synthetic berndtite ( $\text{SnS}_2$ , hexagonal, brucite-type structure) have been measured at 1 atm and 12, 20, and 30 kbar, and complete structure refinements have been determined at 1 atm and 12 and 30 kbar from three-dimensional X-ray diffraction data. Sulfur-sulfur Van der Waals bonds between adjacent layers compress ten times more than sulfur-sulfur and sulfur-tin bonds within an octahedral layer.

### Introduction

Physical properties of minerals are a direct consequence of bonding within the minerals. Differences in interatomic forces in different directions within minerals may result in anisotropic physical properties. Layer minerals possess perhaps the most anisotropic bonding characteristics of all known structures, and therefore should display strongly anisotropic physical properties as well. The present study describes linear compressibility and high-pressure structure data for hexagonal  $\text{SnS}_2$ , berndtite, a mineral with the brucite-type structure.

### Experimental

#### *Specimen description and room-pressure data collection— $\text{SnS}_2$*

Single crystals of pure synthetic one-layer hexagonal  $\text{SnS}_2$  were kindly provided by Dr. Martin Powell, Department of Physics, University of Cambridge, England. The crystals are transparent and have a golden-brown color due to a strong absorption edge in the ultraviolet. Most specimens had obvious bends, internal strain, or edge defects, as is common with crystals of layer minerals. A thin rectangular plate approximately  $250 \times 150 \times 10 \mu\text{m}$  was selected for room-pressure X-ray examination, and X-ray photographs reveal the crystal to be significantly less deformed than other available material.

Unit-cell dimensions were determined from least-squares refinement of twelve diffraction maxima positions on an automated four-circle diffractometer us-

ing the method of Tichý (1970). Peaks were broad, and relatively large uncertainties in measured peak positions resulted in significant errors in calculated cell constant. Unit-cell dimensions of hexagonal  $\text{SnS}_2$  at 1 atm are  $a = 3.638 \pm 0.003$  and  $c = 5.88 \pm 0.01 \text{ \AA}$  ( $V = 69.5 \pm 0.2 \text{ \AA}^3$ ).

Intensity measurements were made on an automated four-circle Picker diffractometer with Nb-filtered  $\text{MoK}\alpha$  radiation, using the constant precision intensity technique described by Finger *et al.* (1973). All reflections in one hemisphere of reciprocal space from  $0.1$  to  $0.55 \sin \theta/\lambda$  were collected, including 81 symmetrically nonequivalent observed ( $I > 2\sigma$ ) reflections. Observed intensities were corrected for absorption ( $\mu_t = 91.0 \text{ cm}^{-1}$ ), and refinement was accomplished using program RFINE (Finger and Prince, 1975). Neutral scattering factors of Cromer and Mann (1968) and the corrections of the scattering coefficients for anomalous dispersion of Cromer and Liberman (1970) were used.

#### *High-pressure data collection— $\text{SnS}_2$*

The crystal of  $\text{SnS}_2$  was mounted in a miniature diamond-anvil high-pressure cell (Merrill and Bassett, 1974), with an Inconel type 750X (International Nickel Company, Inc.) gasket and glycerin as the hydrostatic pressure medium. Procedures for centering the crystal, measuring unit-cell dimensions, and collecting X-ray diffraction intensities with an automated four-circle diffractometer are described by Finger and King (1978). Unit-cell dimensions were measured at 12, 20, and 30 kbar; pressure was cali-

Table 1. Refinement conditions and refined parameters

	1 atm	12 kbar	30 kbar
Number of independent observed ( $I > 2\sigma$ )	81	50	53
Weighted $R$ ,* observed data (%)	10.3	2.8	3.4
$R$ ,** observed data (%)	6.3	3.8	5.3
$Z$ coordinate of sulfur	-0.25(1)†	-0.259(1)	-0.271(2)
$B$ of Sn (Å)	1.4(6)	1.7(4)	1.9(5)
$B$ of S (Å)	1.8(6)	1.3(4)	2.1(5)

$$*\text{Weighted } R = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

$$**R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

†Parenthesized figures represent *esd*'s of least units cited.

brated using the shift in the  $R_1$  fluorescence line of 10  $\mu\text{m}$  ruby crystals in the cell. It was observed that diffraction maxima became significantly sharper at elevated pressure, thus facilitating data collection of X-ray intensities. All accessible reflections in one hemisphere of reciprocal space from 0.1 to 0.7  $\sin \theta/\lambda$  were collected, including 50 and 53 observed non-equivalent reflections at 12 and 30 kbar, respectively. Because of the pressure annealing of this crystal, this is the first instance in which the high-pressure structure refinements were found to be superior to the room-pressure results.

Following high-pressure data collection the crystal was reexamined at room pressure to confirm previously-determined 1 atm unit-cell dimensions. It was hoped, in addition, that the  $\text{SnS}_2$  plate retained the sharper diffraction maxima observed at elevated pressure. The crystal unfortunately displayed reflections even more diffuse than in the original room-pressure experiment. It appears therefore that the reduction of crystal imperfections observed at high pressure is not quenchable.

Table 2. Unit-cell dimensions and interatomic distances of  $\text{SnS}_2$ 

	1 atm	12 kbar	20 kbar	30 kbar
$a$ (Å)	3.638(3)*	3.616(3)	3.608(5)	3.605(2)
$c$ (Å)	5.88(1)	5.68(2)	5.55(2)	5.46(2)
$v$ (Å <sup>3</sup> )	69.5(2)	64.3(2)	62.5(3)	61.5(2)
Distance:				
Sn-S	2.56(5)	2.555(5)	---	2.55(1)
S-S(I)†	3.638(3)	3.616(3)	3.608(5)	3.605(2)
S-S(II)†	3.65(5)	3.610(5)	---	3.62(1)
S-S(III)††	3.58(5)	3.440(5)	---	3.256(9)

\*Parenthesized figures represent *esd*'s of least units cited.

\*\*Unit-cell data only.

†S-S bond within octahedral layer.

††S-S bond between octahedral layer.

## Results

Berndtite,  $\text{SnS}_2$ , is hexagonal,  $P3m1$ ,  $Z = 1$ , and has the simple  $\text{CdI}_2$  or brucite structure, in which layers of  $\text{SnS}_6$  octahedra are the principal structural elements. These layers are held together by weaker Van der Waals forces (Pauling, 1960, p. 259). Both Sn and S are in special positions with Sn fixed at the origin and S at  $(2/3, 1/3, z)$ . Refinement conditions and refined parameters at three pressures are given in Table 1, and unit-cell parameters and selected bond distances are in Table 2. Least-squares fits of unit-cell data to quadratic equations in  $P$  give

$$a = 3.638(1) - 0.0023(1)P + 4.1(1) \times 10^{-5}P^2$$

and

$$c = 5.88(1) - 0.020(2)P + 1.9(6) \times 10^{-4}P^2.$$

From these equations, linear compressibilities at room pressure parallel to the layers

$$\left( \beta_{\parallel} = \frac{1}{a} \frac{\partial a}{\partial P} \right)$$

and perpendicular to the layers

$$\left( \beta_{\perp} = \frac{1}{c} \frac{\partial c}{\partial P} \right)$$

are 600 and  $3500 \times 10^{-6} \text{ kbar}^{-1}$ , respectively.

The most striking aspect of the response of  $\text{SnS}_2$  to pressure is the extreme anisotropy of unit-cell compressibilities (Fig. 1) and observed bond compressibilities. Tin-sulfur and sulfur-sulfur bonds within the octahedral layer, *i.e.*, Sn-S, S-S(I), and S-S(II) in Table 2, compress on the order of one percent between 1 atm and 30 kbar. Similarly, the  $a$  axis compresses  $0.9 \pm 0.2$  percent at 30 kbar. Sulfur-sulfur bonds between octahedral layers, on the other hand,

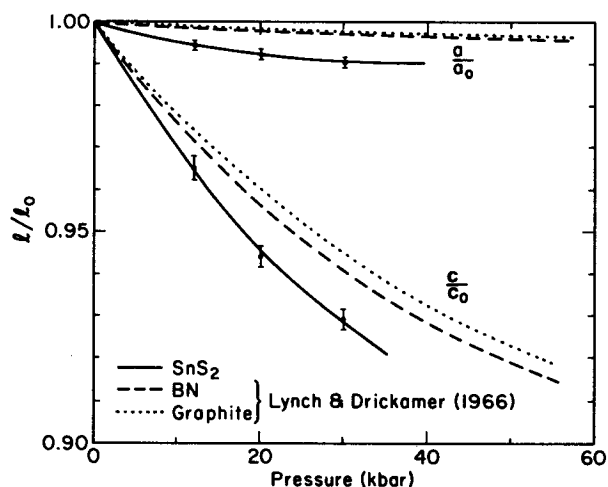


Fig. 1. Plot of  $a/a_0$  and  $c/c_0$  of graphite, hexagonal boron nitride (Lynch and Drickamer, 1966), and  $\text{SnS}_2$  (this study) vs. pressure. Curves for  $\text{SnS}_2$  represent least-squares fit of data in Table 2 to quadratic equations in  $P$ .

compress approximately 10 percent and the  $c$  axis (perpendicular to the layers) compresses  $7.1 \pm 0.6$  percent at 30 kbar. The slightly smaller compression of the  $c$  axis compared with the interlayer sulfur-sulfur bond is due to the relative incompressibility of the octahedral layer that is encompassed by the  $c$  axis but not by the interlayer bonds.

As the sulfur-sulfur interlayer distance decreases, so does the interlayer compressibility. The  $\beta_{\perp}$  decreases from  $3600 \times 10^{-6} \text{ kbar}^{-1}$  at 1 atm to  $3000 \times 10^{-6} \text{ kbar}^{-1}$  at 30 kbar. Thus, as the interlayer bonds are compressed, the strength of these bonds appears to increase. At the same time the energy associated with minor kinks and bends in the crystal probably increases, and this flattening of the  $\text{SnS}_2$  plate may explain the decrease in crystal imperfection evidenced by the observed sharpening of X-ray diffraction maxima at high pressure.

The large mosaic spread and the limited range of diffraction along the  $c^*$  axis for a cleavage fragment of  $\text{SnS}_2$  in the diamond cell are not favorable for the refinement of anisotropic temperature factors. In the present study some refinements with anisotropic temperature factors led to non-positive definite thermal ellipsoids or to ellipsoids with extreme elongation perpendicular to the layers. As a result of the observational difficulties, only isotropic temperature factors are presented (Table 1). These temperature factors have large uncertainties, and no significant variations with pressure are seen.

## Discussion

### Comparison of compression of $\text{SnS}_2$ and the graphite structure

Linear compressibilities of the closely-related hexagonal layer compounds BN and graphite to pressures over 100 kbar were reported by Lynch and Drickamer (1966). Berndtite, graphite, and boron nitride display several similarities in their structural response to pressure. Each of these hexagonal layer structures is highly anisotropic, with compression along  $c$  several times greater than compression along  $a$ . Each structure has linear compressibilities of Van der Waals bonds between layers on the order of  $3 \times 10^{-3} \text{ kbar}^{-1}$ , which are an order of magnitude greater than compressibilities of metal-oxygen bonds in many minerals (Hazen and Prewitt, 1977). Each structure shows similar decreasing  $\beta_{\perp}$  with increasing pressure (Fig. 1).

An important difference between the brucite- and graphite-type structures is the nature of the intralayer bond. Intralayer graphite and boron-nitrogen bonds are covalent (Wyckoff, 1965), and are extremely rigid with very low compressibility (as well as zero or slightly negative thermal expansion). The intralayer sulfur-sulfur bonds of berndtite are not strongly bonded, and they display compressibilities several times greater than covalent C-C and B-N. The magnitudes of linear compressibilities within the layers of graphite, boron nitride, and  $\text{SnS}_2$  are comparable to the magnitudes of linear compressibilities of diamond, cubic boron nitride, and close-packed sulfides (with sphalerite-related structures), respectively (Clark, 1966).

## Conclusions

Anisotropies in a mineral's physical properties may provide direct evidence for anisotropies in interatomic forces. The observed order-of-magnitude difference in linear compressibilities within and between layers in the brucite and graphite structures demonstrates the extreme differences in bond strengths in these two directions.

Compression behavior of these layer structures may be used as a basis for comparison with the more complex pressure responses of layer silicates, which are also expected to be highly anisotropic. These anisotropies may strongly influence the local and bulk properties of rocks with layer silicates. Therefore, an understanding of the pressure response of rock-forming layer silicates has important bearing on a variety of geological problems, such as the develop-

ment of intergranular cracks and pores, the changes of geometry of phyllites during unloading, and the density of phlogopite-bearing mantle rocks. Anisotropic compression behavior of mica and chlorite, and the implications of this behavior with respect to problems in the earth sciences, will be considered in two subsequent papers.

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