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Equation of state and crystal structure of Sb_2S_3 between 0 and 10 GPa

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Abstract High-precision unit-cell volume data of stibnite, collected in the pressure range of 0–10 GPa, was used for fitting a third-order Birch–Murnaghan equation of state. The zero-pressure volume, bulk modulus and its pressure derivative were found to be $487.73(6) \text{ \AA}^3$, $26.91(14) \text{ GPa}$ and $7.9(1)$, respectively. A series of X-ray intensity data was collected in the same pressure range using a CCD-equipped Bruker diffractometer. The high-pressure structures were all refined to $R1(|F_0| > 4\sigma)$ values of approximately 0.03. Crystal-chemical parameters as polyhedron volume, centroid and eccentricity were calculated for the seven coordinated cation positions using the software IVTON. The cation eccentricity appears to be a very useful tool for quantification of the lone electron pair activity. U_2S_3 , Dy_2S_3 and Nd_2Te_3 are all isostructural with stibnite, but the cations in these materials have no lone electron pair. Their eccentricity is much smaller than that of Sb, and close to zero. This confirms that the stibnite structure type alone does not force eccentricity upon the cations involved and it is the lone electron pairs of Sb that generate the eccentricity of cation positions in the structures of stibnite. At increasing pressure the eccentricity of Sb is decreasing. It is therefore reasonable to conclude that the lone electron pair activity is decreasing with increasing pressure.

Keywords Stibnite · High pressure · Lone electron pair · Equation of state

1 Introduction

Antimony is a group-five element, which in the studied compound, stibnite (Sb_2S_3), is in a trivalent state and has a lone electron pair with pronounced steric requirements. There are two distinct Sb positions in the structure of stibnite, each coordinated to seven S (Hofmann 1933; Scavnicar 1960). Each Sb atom is bonded to three S atoms with short bonds (2.45–2.68 Å). These short-bonded Sb and S build strongly bonded rods which are the primary building element of the structure. In the *Pnma* setting the rods are parallel to the [010] direction. The space between the rods accommodates the lone electron pairs of Sb. There are only weak interactions between the rods (Fig. 1, 4). In this study we are interested in the effect of pressure on the structure of stibnite and the effect of pressure on the lone-pair activity of Sb.

2 Experimental

A natural stibnite from Romania was used for this study. Microprobe analysis gave the chemical composition Sb_2S_3 without any trace elements.

For the pressure–volume equation of state a series of high-precision unit-cell parameters was collected in the pressure range of 0–10 GPa. A single crystal in an ETH-type diamond-anvil cell (Miletich et al. 2000), a Huber diffractometer with non-monochromatized Mo-radiation and the SINGLE99 software were used for data collection. The stibnite crystal was loaded into a 210- μm diameter hole drilled into a stainless steel gasket preindented to a thickness of 80 μm . A 1:4 ethanol:methanol mixture was used as hydrostatic pressure medium. Unit-cell parameters of quartz were used for pressure calibration (Angel et al. 1996).

For structure analyses a series of X-ray intensity data was collected in the same pressure range using a CCD-equipped Bruker AXS 4-circle diffractometer, and a DXR-6 Diacell diamond-anvil cell (DAC). The data were collected at 298 K using graphite-monochromatized $\text{MoK}\alpha$ radiation. One zero-pressure dataset with crystal loaded in DAC and six high-pressure datasets were collected. For this experiment a 220- μm hole was drilled into a steel gasket preindented to a thickness of 80 μm . The same type of pressure medium and pressure calibration was used as for the above-described experiment. The intensity data was integrated with

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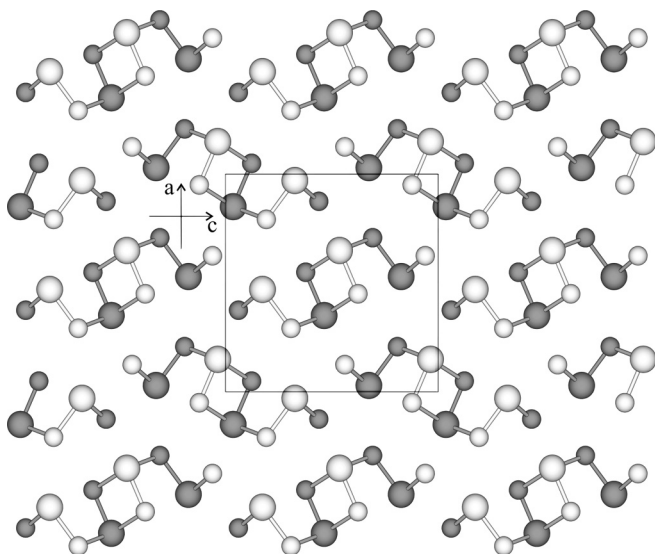


Fig. 1 Structure of stibnite in the $Pnma$ setting. Grey circles represent atoms on the $y = 0.25$ mirror plane, white circles represent atoms on the $y = 0.75$ mirror plane. Large circles are Sb atoms and small circles are S atoms

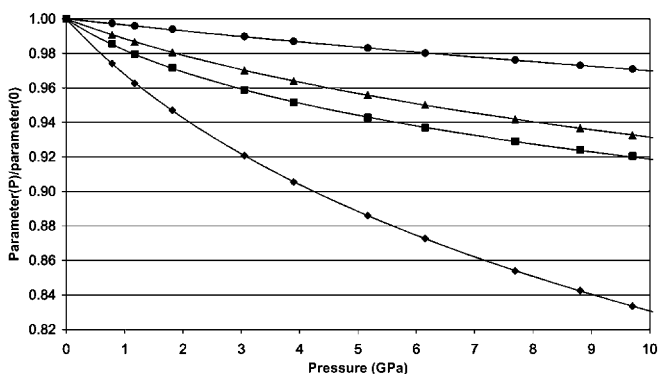


Fig. 2 Evolution of unit-cell parameters of stibnite with increasing pressure. Values are given relative to their zero-pressure value. Squares indicate a , circles b and triangles c value; rhombs stand for unit-cell volume

SAINT+, and XPREP (Bruker 2000) was used for numerical face-indexed absorption correction. The data were subsequently corrected for absorption due to the DAC components. All the structures were refined with anisotropic displacement parameters for Sb and isotropic for S, using SHELXL-97 (Sheldrick 1997). The structures were all refined in the $Pnma$ space group to R values of approximately 0.03 (Table 1). F_0/F_c tables are deposited.

3 Results and discussion

3.1 Equation of state

Unit-cell parameters of Sb_2S_3 were found to alter smoothly with pressure and no phase transition was detected in the pressure range 0.0001–10 GPa. The zero-pressure bulk modulus, defined as $K_0 = -V_0(\partial P/\partial V)_{P=0}$,

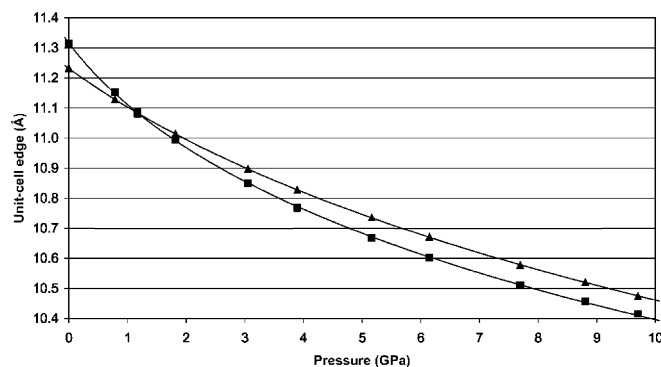


Fig. 3 Observed a and c unit-cell parameters of stibnite. The lines are obtained by fitting a BM3 equation of state to the unit-cell parameters. Squares indicate a , triangles c parameter

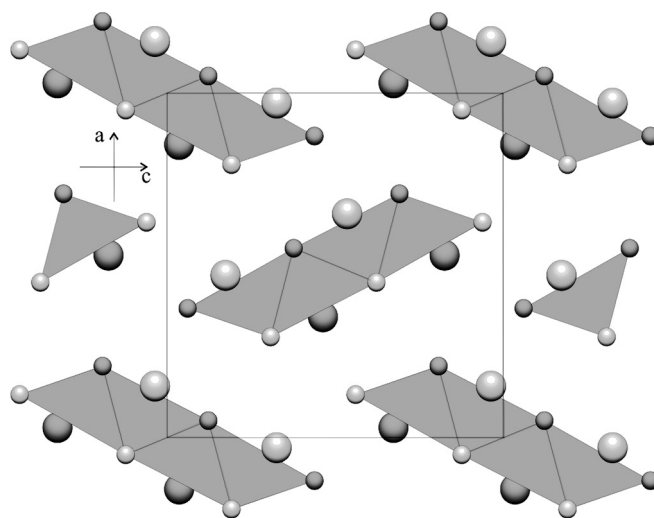


Fig. 4 Grey polyhedra represent the rod volume (V_{rod}) and the rest of the unit-cell volume is defined as the lone electron pair volume (V_{lone}). Grey circles represent atoms on the $y = 0.25$ mirror plane; white circles represent atoms on the $y = 0.75$ mirror plane; large circles are Sb atoms and small circles are S atoms

and its pressure derivative were determined from fitting an isothermal third-order Birch–Murnaghan (BM3) equation of state (Birch 1947) to the unit-cell volume data using EosFit52 (Angel 2001). By substituting the cube of the unit-cell edges for the volume in the equation, a BM3 EOS were fitted to the unit-cell edges (Table 2). The zero-pressure “bulk modulus” obtained from fitting is equal to minus one-third of the inverse of the zero-pressure linear compressibility β_0 of the unit-cell axis (Angel 2001). The zero-pressure compressibility is defined as $\beta_0 = l_0^{-1}(\partial l/\partial P)_{P=0}$ where l_0 is the length of the unit-cell edge at zero pressure.

Stibnite is a very compressible material with a bulk modulus of 26.91(14) GPa. Because the strong bonded rods are oriented along the b unit-cell edge, stibnite is not very compressible in this direction. The lone electron pairs are pointing approximately along the [100] direction (Fig. 1). That is the reason why the

Table 1 Experimental data for Sb₂S₃

Pressure (GPa)	0.0001	1.115	1.591	2.118	3.235	7.406	7.832
Crystal data							
<i>a</i> (Å)	11.299(4)	11.098(3)	11.044(3)	10.959(3)	10.836(2)	10.529(2)	10.508(3)
<i>b</i> (Å)	3.8313(6)	3.8232(5)	3.8124(5)	3.8060(6)	3.7919(5)	3.7458(4)	3.7409(5)
<i>c</i> (Å)	11.227(4)	11.091(2)	11.043(2)	10.983(2)	10.884(2)	10.604(1)	10.579(2)
<i>V</i> _{uc} (Å ³)	486.04	470.59	464.96	458.13	447.20	418.22	415.85
ρ (g cm ⁻³)	4.642	4.794	4.853	4.925	5.045	5.395	5.426
μ (mm ⁻¹)	12.21	12.61	12.76	12.95	13.27	14.19	14.27
Data collection							
No. of measured reflections	1486	1548	1515	1460	1432	1382	1368
No. of unique reflections	244	171	169	162	158	154	151
No. of observed reflections ^a	182	123	126	122	125	114	117
R _{int}	0.0961	0.0796	0.0776	0.0803	0.0847	0.0787	0.0762
2 θ _{max} (°)	46.46	46.48	46.46	46.36	46.37	46.44	46.51
Range of <i>h</i> , <i>k</i> , <i>l</i>	-9 ≤ <i>h</i> ≤ 9 -4 ≤ <i>k</i> ≤ 4 -11 ≤ <i>l</i> ≤ 11	-5 ≤ <i>h</i> ≤ 5 -4 ≤ <i>k</i> ≤ 4 -12 ≤ <i>l</i> ≤ 12	-5 ≤ <i>h</i> ≤ 5 -4 ≤ <i>k</i> ≤ 4 -12 ≤ <i>l</i> ≤ 12	-5 ≤ <i>h</i> ≤ 5 -4 ≤ <i>k</i> ≤ 4 -12 ≤ <i>l</i> ≤ 12	-5 ≤ <i>h</i> ≤ 5 -4 ≤ <i>k</i> ≤ 4 -12 ≤ <i>l</i> ≤ 11	-5 ≤ <i>h</i> ≤ 5 -4 ≤ <i>k</i> ≤ 4 -11 ≤ <i>l</i> ≤ 11	-5 ≤ <i>h</i> ≤ 5 -4 ≤ <i>k</i> ≤ 4 -11 ≤ <i>l</i> ≤ 11
Refinement							
R1 ($ F_o > 4\sigma$)	0.0336	0.0310	0.0353	0.0314	0.0336	0.0336	0.0293
wR2	0.0825	0.0562	0.0749	0.0638	0.0635	0.0959	0.0571
Goof	0.975	1.146	1.183	1.172	1.067	1.190	1.183
No. of parameters	23	23	23	23	23	23	23

^a Criterion for observed reflections is $|F_o| > 4\sigma$

Table 2 BM3 equation of state parameters

BM3	Zero-pressure value	K ₀ [GPa]	K'
<i>V</i>	487.73(6) Å ³	26.91(14)	7.9(1)
<i>a</i>	11.316(2) Å	14.5(3)	8.5(3)
<i>b</i>	3.8382(4) Å	91.6(17)	3.8(4)
<i>c</i>	11.232(1) Å	26.2(2)	5.4(1)

compressibility of stibnite is largest along the *a* unit-cell edge (Fig. 2).

The slightly longer zero-pressure length of the *a* unit-cell edge, and its higher compressibility compared to the *c* unit-cell edge, result in a crossing of their values at 1.12 GPa (Fig. 3).

3.2 Structure data and interpretation

The atom positions of the refined stibnite structures are given in Table 3, and the atomic displacement para-

eters are given in Table 4. Sb atoms were refined with anisotropic displacement parameters. A table with the full ADPs is deposited.

To determine the effect of pressure on the lone electron pair it will be of great interest to compare the high-pressure structures of stibnite with related sulfides. Bismuthinite (Bi₂S₃) is isostructural with stibnite but with a less active lone electron pair. Not yet published structure data (L. F. Lundegaard, personal communication) have been used for bismuthinite. Dy₂S₃ (Meetsma et al. 1991) and U₂S₃ (Zachariassen 1949) are also isostructural with stibnite but with no lone electron pair. All the calculations which are described below have been made for these three structures as well for all the high-pressure stibnite structures.

Dy₂S₃, Bi₂S₃ and U₂S₃ structures are zero-pressure structures, but in the following figures their calculated values have been plotted in a column to the left of the zero-pressure axis to avoid overlap. The convention used is that black points refer to high-pressure stibnite data and white points are zero-pressure values for Dy₂S₃,

Table 3 Atom positions. The y coordinate is 0.2500(0) for all atom positions in the table

Pressure (GPa)		0.0001	1.115	1.591	2.118	3.235	7.406	7.832
Sb1	x	0.0290(2)	0.0250(4)	0.0242(4)	0.0223(4)	0.0193(4)	0.0119(6)	0.0120(5)
	z	0.6738(1)	0.6740(1)	0.6741(1)	0.6740(1)	0.6740(1)	0.6735(2)	0.6734(1)
Sb2	x	0.3503(2)	0.3468(5)	0.3467(6)	0.3458(6)	0.3430(5)	0.3389(7)	0.3376(5)
	z	0.4641(2)	0.4638(1)	0.4636(1)	0.4636(1)	0.4634(1)	0.4632(2)	0.4631(1)
S1	x	0.0493(6)	0.0529(16)	0.0515(18)	0.0506(17)	0.0526(15)	0.0510(20)	0.0524(15)
	z	0.1226(5)	0.1236(4)	0.1246(5)	0.1254(5)	0.1258(4)	0.1270(6)	0.1271(5)
S2	x	0.3745(6)	0.3767(19)	0.3775(21)	0.3736(19)	0.3736(17)	0.3709(24)	0.3715(18)
	z	0.0612(5)	0.0615(4)	0.0612(5)	0.0607(5)	0.0605(4)	0.0606(7)	0.0601(5)
S3	x	0.2077(6)	0.2098(19)	0.2123(19)	0.2113(18)	0.2152(18)	0.2208(24)	0.2185(18)
	z	0.8071(5)	0.8068(5)	0.8066(5)	0.8056(5)	0.8037(4)	0.7994(7)	0.7992(5)

Table 4 Atomic displacement parameters

Pressure (GPa)	0.0001	1.115	1.591	2.118	3.235	7.406	7.832	
Sb1	Ueq	0.0180(6)	0.0146(28)	0.0177(30)	0.0151(30)	0.0103(29)	0.0154(33)	0.0159(24)
Sb2	Ueq	0.0218(7)	0.0212(31)	0.0157(34)	0.0121(31)	0.0160(31)	0.0175(35)	0.0167(25)
S1	Uiso	0.0150(14)	0.0102(16)	0.0115(18)	0.0113(16)	0.0100(15)	0.0068(23)	0.0108(16)
S2	Uiso	0.0152(14)	0.0120(15)	0.0140(16)	0.0130(15)	0.0121(13)	0.0140(22)	0.0125(15)
S3	Uiso	0.0154(14)	0.0164(17)	0.0143(17)	0.0134(16)	0.0131(14)	0.0125(22)	0.0129(15)

Bi_2S_3 and U_2S_3 . The effective ionic radius of the trivalent ions Sb^{3+} , Dy^{3+} , Bi^{3+} and U^{3+} is 0.76, 0.91, 1.03 and 1.03 Å, respectively (Shannon 1976).

An asymmetric unit in a unit cell can be divided into nine polyhedral units with vertices in S sites. Four of these polyhedra belong to what we have defined as the rod volume, and five belong to the volume occupied by the lone electron pairs of Sb (Fig. 4).

The rod volume consists of square pyramids and intervening tetrahedra. The two distinct square pyramids are the capping part of the monocapped trigonal prisms at the two Sb positions. Seen along the *b*-axis there is a lying trigonal prism at the Sb1 position and a standing trigonal prism at the Sb2 position.

The sum of the volumes of these nine polyhedra gives the volume of the asymmetric unit of the unit cell. The program IVTON (Balic-Zunic and Vickovic 1996) was used for calculating the polyhedral volumes.

A BM3 equation of state was fitted separately to the calculated rod volumes and lone electron pair volumes at increasing pressures (Fig. 5). The lone electron pair volume is much more compressible compared to the rod volume. The bulk modulus and its pressure derivative of the lone electron pair volume was found to be 20.7 GPa and 7.5, respectively. For the rod volume they were found to be 54.8 GPa and 6.3. Whereas the rod volumes of Dy_2S_3 and U_2S_3 at zero pressure are similar to those of Sb_2S_3 and Bi_2S_3 , there is a pronounced difference in the zero-pressure lone electron pair volume for Sb_2S_3 and Bi_2S_3 compared to the inter-rod volume of Dy_2S_3 and U_2S_3 . This is because the structures of stibnite and

bismuthinite have to accommodate active lone electron pairs.

The ratio $V_{\text{rod}}/V_{\text{lone}}$ is plotted in Fig. 6. The $V_{\text{rod}}/V_{\text{lone}}$ ratio of U_2S_3 and Dy_2S_3 was found to be 0.440 and 0.432, respectively. The zero-pressure value for stibnite is 0.385 and at 9.0 GPa it is 0.424, converging slowly to a value comparable with the ratios found in U_2S_3 and Dy_2S_3 . This indicates that the lone electron pair activity is decreasing with pressure.

Besides polyhedral volumes, the following crystal-chemical parameters as defined by (Balic-Zunic and Makovicky 1996) were evaluated using the program IVTON.

- The centroid of a coordination polyhedron, defined as the point which comes closest to the condition of being equidistant to all the coordinated ligands.
- The fitted sphere of a coordination polyhedron, defined as the sphere with the centroid as the centre and the mean centroid–ligand distance as radius.
- The eccentricity of a coordination polyhedron, defined as the distance between the central atom and the centroid divided by the fitted-sphere radius.
- The sphericity of a coordination polyhedron, defined as $(1 - \sigma/r)$ where *r* is the fitted-sphere radius and σ is the standard deviation of the centroid–ligand distances.

A sphere was fitted to the seven-coordinated polyhedra around the two metal positions in the structure. The polyhedron volumes and the fitted-spheres volumes are illustrated in Fig. 7.

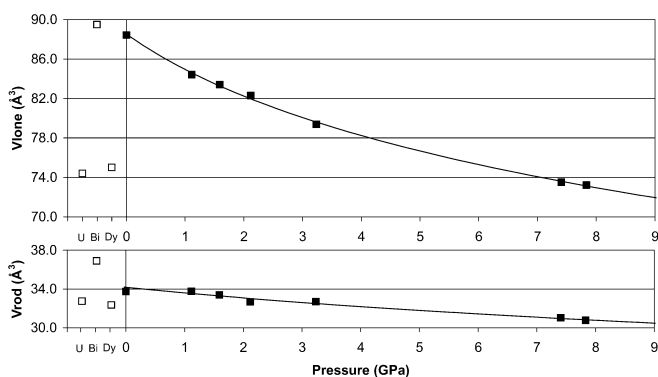


Fig. 5 Calculated lone electron pair volume (V_{lone}) and rod volume (V_{rod}). *Black squares* represent the stibnite pressure data, and the *white squares* represent zero pressure data for Dy_2S_3 , Bi_2S_3 and U_2S_3 ; the *curves* are obtained by fitting a BM3 equation of state to the volumes

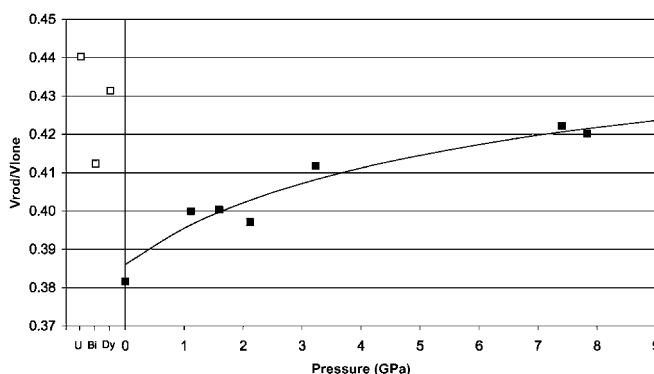


Fig. 6 Observed ratio between the rod volume and the lone electron pair volume. *Black squares* represent the stibnite pressure data, and the *white squares* represent zero pressure data for Dy_2S_3 , Bi_2S_3 and U_2S_3

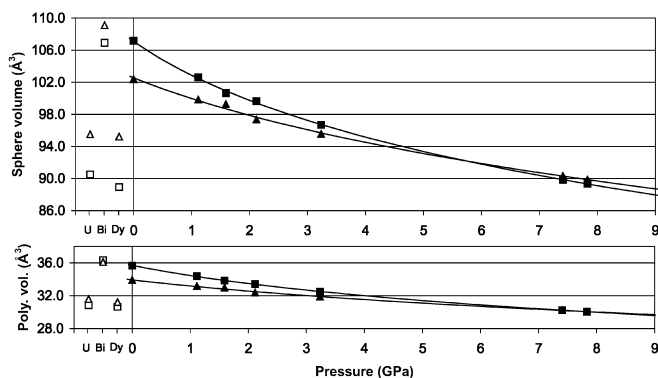


Fig. 7 Polyhedron volume and fitted sphere volume for the two seven-coordinated metal positions. *Squares* indicate Sb1 and *triangles* Sb2. *Black symbols* represent the stibnite pressure data, and the *white symbols* represent zero-pressure data for Dy_2S_3 , Bi_2S_3 and U_2S_3 ; the *curves* are obtained by fitting a BM3 equation of state to the volumes

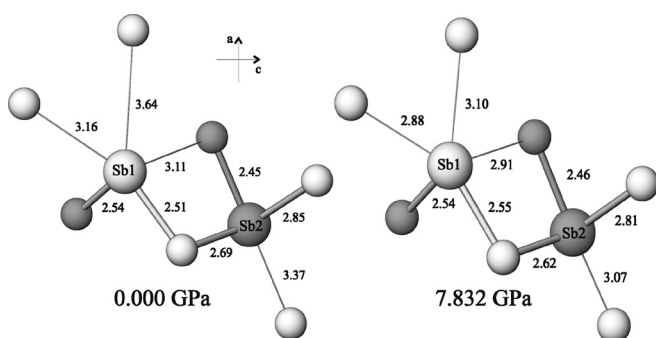


Fig. 8 Important Sb–S distances at 0.0001 GPa and 7.832 GPa. *Grey circles* represent atoms on the $y = 0.25$ mirror plane, *white circles* represent atoms on the $y = 0.75$ mirror plane

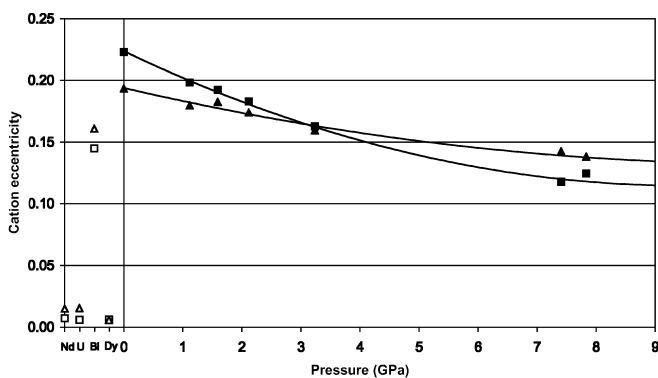


Fig. 9 Cation eccentricities for the two seven-coordinated metal positions. *Squares* indicate Sb1 and *triangles* Sb2. *Black symbols* represent the stibnite pressure data, and the *white symbols* represent zero pressure data for Dy_2S_3 , Bi_2S_3 , U_2S_3 and Nd_2Te_3

At zero pressure, both the sphere and the polyhedron volume of the position 1 are larger than those of the position 2 for stibnite. The opposite is true for U_2S_3 and Dy_2S_3 , and Bi_2S_3 , as regards the volumes of the spheres.

The situation becomes reverse for stibnite at higher pressures (over 6–7 GPa).

The pronounced shortening of the long Sb–S distances on compression is compensated by the constancy or even lengthening of the short Sb–S bonds (Fig. 8). This behaviour of the Sb–S distances is in agreement with the inverse hyperbolic dependence found by (Berlepsch et al. 2001) in the meneghinite homologues, to which Sb_2S_3 belongs.

The position of the Sb atoms inside the two coordination polyhedra becomes more symmetrical with increasing pressure. This also indicates a decrease of the lone electron pair activity with increasing pressure.

The cation eccentricity was calculated for the two seven-coordinated metal positions and the results are shown in Fig. 9. The isostructural Nd_2Te_3 was added to this calculation. Nd^{3+} does not have a lone electron pair.

It is clear from Fig. 9 that both Sb atoms in stibnite have very active lone electron pairs, while Bi atoms in bismuthinite have somewhat less active lone electron pairs. The cations in Dy_2S_3 , U_2S_3 and Nd_2Te_3 have eccentricities of approximately zero because they have no lone electron pairs. This confirms that the Sb_2S_3 structure type alone does not force eccentricity upon the cations involved and it is the lone electron pair of Sb (or Bi) that generates the eccentricity of cation positions in the structures of these sulfides. The cation eccentricity appears to be a very useful tool for quantification of the lone electron pair activity.

It is interesting to note that Sb1 and Sb2 reverse their relative eccentricities with increasing pressure in the same manner as their relative sphere volumes are reversed. In this respect, the high-pressure stibnite resembles more bismuthinite at low pressures where position 2 has both larger sphere volume and eccentricity than the position 1. Sb1 position in stibnite is clearly the “softer” one and the one that experiences the greatest change in coordination on compression. As low-pressure bismuthinite resembles the high-pressure situation in stibnite, it can be expected that its structure can break down at lower pressures than the latter. We are presently investigating the high-pressure behaviour of a bismuthinite single crystal in order to eventually record the upper level of compressibility of the lone electron pair.

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