CRYSTALS OF THE REALGAR TYPE: THE SYMMETRY, UNIT CELL, AND SPACE GROUP OF NITROGEN SULFIDE

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ABSTRACT

An attempt has been made to find other crystalline compounds analogous to the mineral realgar, AsS. The recorded characteristics of NS, and NSe and NTe suggested that these might be realgar-like crystals. Nitrogen sulfide, the only one of this series to have received crystallographic attention, had previously been reported as monoclinic on the basis of a study of surface morphology, and orthorhombic on the basis of an x-ray study, the latter symmetry being made the groundwork for a proposed crystal structure. In the present paper, new and different x-ray results are reported, based upon an equi-inclination Weissenberg study. The correct characteristics are:

Crystal system: monoclinic
Crystal class   : $2/m = C_{2h}$
Simplest cell   :
$a = 8.78$ Å
$b = 7.14$
$c = 8.64_5$
$\beta = 87°39'$
Formula weights NS per cell: 16
Diffraction symbol   : $2/mP2_1/n$
Space group   : $P2_1/n$

The general characteristics of this cell are identical with those of the realgar cell, but the cells of the two compounds differ markedly in dimensional aspects. This difference is attributed to the difference in radii of the N and As atoms, and the two compounds are believed to be isostructural. Jaeger and Zanstra's crystal structure proposed for nitrogen sulfide must be incorrect because it is based upon an erroneous symmetry.

INTRODUCTION

The unit cell and space group of realgar have already been determined.[1] The large monoclinic cell of this mineral contains 16 formula weights of AsS and has the symmetry of $P2_1/n$, C_{2h}^5. This space-group contains only four specialized equipoints, all inversion centers. Its extremely unfavorable geometry provides 21 distinct, permissible ways of accommodating the 16 As and 16 S atoms at the same time. The simplest available structure requires the determination of 15 parameters, five at a time, while the least simple structure requires the determination of 24 parameters, eight at a time. The crystal structure of realgar can, therefore, hardly be determined by straightforward methods. A search was made

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[1] Buerger, M. J., The unit cell and space group of realgar: *Am. Mineral.*, vol. **20**, pp. 36–43, 1935.

accordingly for other compounds likely to have the realgar structural type, in the hope of finding physical, chemical, and diffractive clues to the structural plan.

Realgar stands alone among minerals. It is a member of no recognized mineral group and the analogous antimony and bismuth minerals are unknown. It appears reasonable to expect, however, that other structurally similar compounds exist. The formula of realgar may be generalized to AB, where A is an element of group V B, and B is an element of group VI B of the periodic table. The descriptions of compounds of this class suggest that NS, NSe, and NTe are probably of the realgar type. These are all of non-metallic luster, yellowish to reddish in color, and have low melting points. It is also possible that solid NO is of this type; it is described as a colorless, snow-like solid. Certain other compounds of type AB in question are also known, notably PTe, AsTe, SbTe, BiTe, also BiSe and probably BiS. All of these compounds, however, appear to be of metallic luster and, therefore, not obviously related to realgar. All of them have been prepared by reactions essentially in the molten state, as contrasted with those previously mentioned, which are prepared by precipitation from solution.

The best known of the realgar-like compounds, AB, is nitrogen sulfide, usually assigned the formula N_4S_4 because of its molecular weight in solution.[2,7] This is the only compound of the type other than realgar which has received crystallographic attention.

CRYSTALLOGRAPHIC STATUS OF NITROGEN SULFIDE

Nitrogen sulfide has received four previous crystallographic investigations. Nicklès[3] first made some very rough measurements and decided that the crystals were orthorhombic hemimorphic. A very complete investigation was carried out later by Artini,[4] who showed that the crystals were monoclinic, established an orientation and axial elements, and made a study of the twinning which occurs abundantly according to two laws, viz., with $\{\bar{1}01\}$ and also $\{101\}$ as twinning planes (Artini's orientation). Artini worked with crystals purified by fractional crystallization from CS_2. Shortly afterwards, Smith[5] studied some nitrogen sulfide crystals purified by sublimation *in vacuo*. He confirmed Artini's

[2] Schenck, Rud., Ueber den Schwefelstickstoff: *Ann. der Chemie*, vol. **290**, pp. 171–185, esp. p. 177, 1896.

[3] Nicklès, M. J., Sur la forme cristalline du sulfure d'azote: *Ann. Chim. Phys.*, ser. 3, vol. **32**, pp. 420–421, 1851.

[4] Artini, E., Über die Kristallform des Schwefelstickstoffes, N_4S_4: *Rendic. R. Istit. Lombardo di Sc. e Lett. Mailand*, (2) vol. **37**, pp. 864–869, 1904; *Zeit. Krist.*, (A) vol. **42**, pp. 68–69, 1905.

[5] Smith, G. F. Herbert, On the crystalline form of nitrogen sulphide: *Mineral. Mag.*, vol. **16**, pp. 97–99, 1911.

results, retained his orientation and elements, but obtained slightly different values.

Recently, Jaeger and Zanstra,[6] apparently aware only of Nicklès' early paper, again measured some crystals, this time recrystallized from benzene. They concluded that the crystals were *orthorhombic* and established an axial ratio not to be compared with those of Artini or Smith. Jaeger and Zanstra followed their optical goniometric study with a crystal structure study which included a powder photograph and also 30° (60°?) oscillation photographs for each of the three crystallographic axes selected. These data lead them to assign the crystals to space group V_h^1 (*Pmmm*) upon which they based a complete crystal structure composed of loosely packed N_4S_4 molecules.

In the present paper it will be shown that Jaeger and Zanstra's fundamental groundwork was incorrect and that, therefore, the crystal structure upon which it was based is incorrect.

MATERIAL

The writer is greatly indebted to Mr. Mortimer C. Bloom for the careful preparation of suitable nitrogen sulfide crystals. These were prepared following the procedure of Van Valkenburgh and Bailar.[7] They were recrystallized repeatedly from CS_2 until suitable material was obtained. The final material was crystallized by extremely slow evaporation. In this way the abundant formation of twins was avoided. Earlier crops were largely twinned material of the habit illustrated by Jaeger and Zanstra.[6]

METHOD

The writer has shown[8,9] that the symmetry, crystal system, space lattice type, simplest unit cell, and space group can all be determined by the inspection of several x-ray films taken with the equi-inclination Weissenberg method. An especially designed apparatus is used for this purpose.[10] This inspective method has been used throughout the present investigation. Unscreened copper x-radiation was furnished by a sharply focussed Hadding tube passing about 10 ma. at 40 kv. half wave rectification.

[6] Jaeger, F. M., and Zanstra, J. E., The crystal structure [sic] of nitrogen-tetrasulphide and tetra-hydro-nitrogentetrasulphide: *Proc. Acad. Sci. Amsterdam*, vol. **34**, pp. 782–807, 1931.

[7] Van Valkenburgh, H. B., and Bailar, John C. Jr., Nitrogen tetrasulfide and nitrogen tetraselenide: *Jour. Am. Chem. Soc.*, vol. **47**, pp. 2134–2137, 1925.

[8] Buerger, M. J., The Weissenberg reciprocal lattice projection and the technique of interpreting Weissenberg photographs: *Zeit. Krist.*, (A) vol. **88**, pp. 356–380, 1934.

[9] Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs: *Zeit. Krist.*, (A) vol. **91**, pp. 255–289, 1935.

[10] Buerger, M. J., An apparatus for conveniently taking equi-inclination Weissenberg photographs: *Zeit. Krist.*, (A) vol. **94**, pp. 87–99, 1936.

The data include equi-inclination photographs of 0, 1, 2, and 3 levels for rotations about what has been called the *b* axis, from which data the simplest cell was selected. Similar photographs were also made for the 0, 1, and 2 levels for rotations about the *a* axis of this new cell, and also of the 0 level for a rotation about the *c* axis of this cell. Simple rotation photographs were also incidentally prepared for rotations about each of these axes for the purpose of checking the several axial orientations and identity periods.
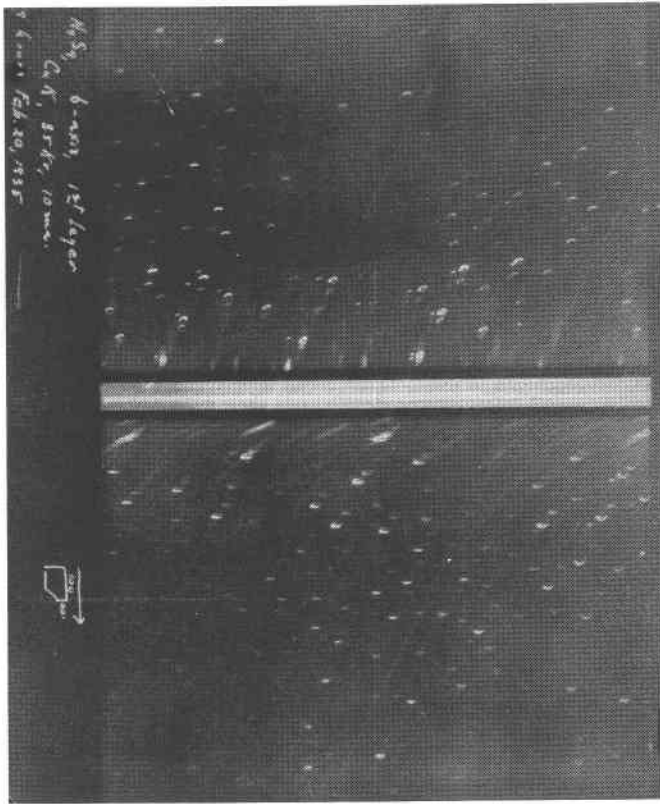

Fig. 1. Equi-inclination Weissenberg photograph from nitrogen sulfide, 1st layer, *b* axis rotation, unscreened copper radiation. The spot intensity distribution is clearly C_2, but the position pseudo-symmetry is close to C_{2l}, with the pseudo-symmetry lines in the positions of the fine slanting lines drawn on the photograph (axes of the simplest reciprocal cell).

SYMMETRY

Although the crystals had an orthorhombic appearance, which was especially enhanced by twinning, those recovered from the final recrys-

tallization had a rather pronounced monoclinic development. Equi-inclination photographs were therefor first prepared for rotations about the suspected 2-fold axis. All such photographs display equi-inclination projections of the plane symmetry[9] C_2, although there is a strong resemblance to C_{2l} for position symmetry alone. These features are plainly visible in Fig. 1. Equi-inclination photographs for rotations about each of the cell axes selected all showed the symmetry C_{2l} for 0 layers and C_l
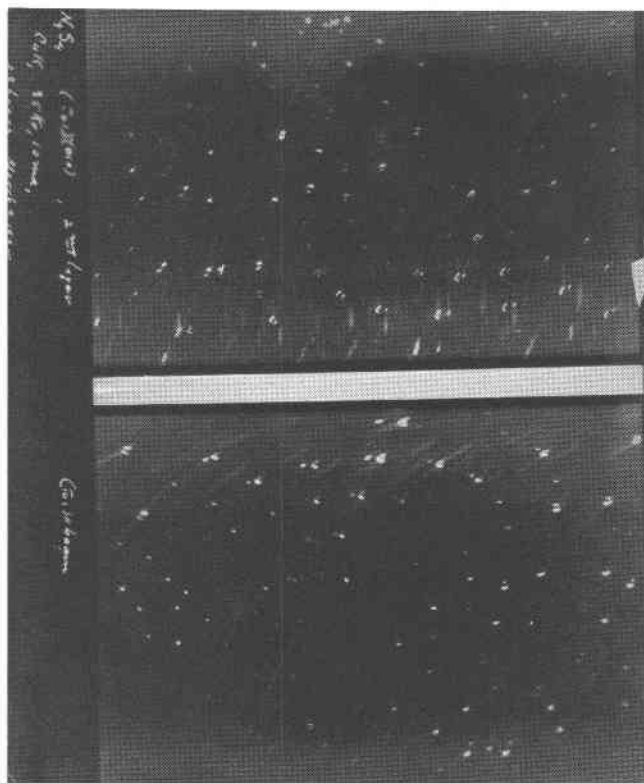

Fig. 2. Equi-inclination Weissenberg photograph from nitrogen sulfide, 2nd layer, *a* axis (Artini's [101] axis) rotation, unscreened copper radiation. The resolution of the spots into increasingly separated pairs along the right hand sloping fine line demonstrates the monoclinic nature of the space lattice type.

for *n* layers. This information determines the centrosymmetrical point group to be $2/m$ ($=C_{2h}$). This definitely fixes the crystal system of nitrogen sulfide as monoclinic, although it does not distinguish between the several crystal classes $2/m$, *m*, and 2. The holohedral nature of the crystal is fixed by space group data noted beyond.

Space Lattice Type

The plane lattice stacking sequence[9] along the *b* axis is plainly 2, coincident parallelograms. Along the *a* axis the plane lattice type is rectangular and the stacking sequence is 5, side staggered rectangles. That the rectangles are truly staggered, a dimensional and further proof of the monoclinic nature of nitrogen sulfide, is illustrated in Fig. 2, the 2nd level photograph. In this it can be seen that while one line of dome reflections is a central lattice line (the symmetry line), the other prominent line of dome reflections, in a position approximately 90°ω from the first, is a curved, non-central line. This feature is rendered more striking by the presence of a satellitic twin, whose corresponding dome reflections deviate more and more from those of the main crystal near the center line of the film. These data fix the space lattice type as primitive monoclinic, $2/mP$.

Unit Cell

The *b*-axis rotation, *n* layer films clearly show that the smallest cell results by choosing axes parallel to Artini's[4] [$\bar{1}01$] and [101] directions. The approximate dimensions of this cell are obtained by the use of the Z scale[8] on the *n* layer photographs. The dimensions are refined by measurements of high θ pinacoid reflections from the zero layer photographs. The reciprocal lattice vectors a^*, c^*, and $c^* - a^*$ form a triangle, one of whose angles is the crystallographic element, β. Accurate measurements of the reflections from (100), (001), and ($\bar{1}01$), therefore, yield data for the calculation of β to the same degree of accuracy as that of the other cell constants. The complete set of cell constants for nitrogen sulfide calculated from *x*-ray data are:

	absolute	*ratio*
a	8.74 Å	1.224
b	7.14	1.
c	8.64₅	1.211
β		87°39′

If this cell contains 16 formula weights of NS, corresponding with the case of realgar, the density of the crystals may be calculated as:

$$d = \frac{\text{cell mass}}{\text{cell volume}} = 2.23_7.$$

The specific gravities measured by various investigators and collected by Mellor[11] are as follows:

[11] Mellor, J. W., *A comprehensive treatise on inorganic and theoretical chemistry*, vol. **VIII**, London, p. 625, 1928.

	2.1166	10°C.	A. Michaelis
	2.2	—	S. A. Vosnessensky
	2.22	15°	M. Berthelot and P. Vieille
unsublimed:	2.20	24°	F. P. Burt and F. L. Usher
sublimed:	2.24	24°	

The calculated and observed densities are in excellent agreement, which thoroughly confirms the expectation that the cell contains 16 NS.

In view of the probability that future crystallographic work on nitrogen sulfide will be referred to the orientation established here, all earlier crystallographic elements have been recalculated to this orientation and are collected in Table 1. It will be observed that the new x-ray results check all of Artini's values to within 0.1% to 0.2%. Both sets of values were determined on material recrystallized from solution. The deviations of the new results from Smith's values are rather large, but this is to be expected in view of the fact that Smith worked with sublimed crystals.

TABLE 1

CRYSTALLOGRAPHIC DATA FOR NITROGEN SULFIDE, REFERRED TO SIMPLEST CELL AXES

	Artini[4]	Smith[5]	Jaeger and Zanstra[6]		Buerger
	optical	optical	optical	x-ray	x ray
ratio $\begin{cases} a \\ b \\ c \\ \beta \end{cases}$	1.2261 1. 1.2118 87°30′	1.2319 1. 1.2237 87°29′ observed 87°22′ calculated	1.234 1. 1.188	1.230 1. 1.175	1.224 1. 1.211 87°39′
absolute $\begin{cases} a \\ b \\ c \end{cases}$				8.87Å 7.21 8.47	8.74Å 7.14 8.64$_5$

The transformations involved in the change to the new orientation are as follows:

Artini and Smith		Buerger
b	$\rightarrow$	b
$\dfrac{a}{2} - \dfrac{c}{2}$	$\rightarrow$	a
$\dfrac{a}{2} + \dfrac{c}{2}$	$\rightarrow$	c
$[101] \wedge [\bar{1}01]$	$\rightarrow$	β
$h - l$	$\rightarrow$	h
$h + l$	$\rightarrow$	l
k	$\rightarrow$	k

The crystal forms observed by Artini and Smith thus become:

Artini and Smith		Buerger
(100)	$\rightarrow$	(101)
(001)	$\rightarrow$	($\bar{1}$01)
(101)	$\rightarrow$	(001)
(10$\bar{1}$)	$\rightarrow$	(100)
(010)	$\rightarrow$	(010)
(12$\bar{1}$)	$\rightarrow$	(110)
(111)	$\rightarrow$	(012)
(110)	$\rightarrow$	(111)
(011)	$\rightarrow$	($\bar{1}$11)

The transformation from Jaeger and Zanstra's axes is:

Jaeger and Zanstra		Buerger
a	$\rightarrow$	a
b	$\rightarrow$	c
c	$\rightarrow$	b

SPACE GROUP

Comparison of zero layer with n layer equi-inclination photographs for rotations about the b axis shows[9] that both a and c reciprocal translations are doubled in the zero layer. This indicates that a diagonal glide plane exists normal to the b axis. Comparison of the zero layer with the n layer equi-inclination photographs for rotations about the a axis shows[9] that the reciprocal translation along the [010] line is doubled. This indicates that a 2-fold screw axis exists parallel with the b axis. The diffraction symbol[9] is therefore $2/mP2_1/n$. The space group is consequently uniquely determined as $P2_1/n(=C_{2h}^5)$.

The existence of both glide plane and screw axis requires the existence of a symmetry plane and a 2-fold axis in the point group, consequently the symmetry of nitrogen sulfide is holohedral monoclinic, $2/m=C_{2h}$.

EQUIPOINT COMBINATIONS

The discussion of possible equipoint combinations follows that for realgar exactly.[1]

DISCUSSION

The complete cell data for nitrogen sulfide may now be compared with those of realgar:

	nitrogen sulfide	realgar
a	8.78 Å	9.27 Å
b	7.14	13.50
c	$8.64_5'$	6.56
β	87°39'	73°27'
formula weights AB per cell	16	16
space group	$P2_1/n$	$P2_1/n$

The general characteristics of the crystal, namely, the formula type, the space group and orientation, and the number of formula weights per unit cell, are identical in the two crystals. The specific cell dimensions, however, differ widely. A difference of this sort is to be expected due to the differing radii of the nitrogen and arsenic atoms, 0.70 Å and 1.21 Å, respectively; the volumes of the cells are proportional to the sums of the atomic volumes to within about 10%. It is the opinion of the writer that the two crystals are isostructural.