

The identity of zinckenite and keeleyite.

(With Plate X.)

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ZINCKENITE was first described in 1826 by G. Rose, who determined it to be an orthorhombic mineral. The crystals were thought to be seldom single, but to occur in nearly hexagonal forms as a result of twinning in some fashion similar to that found in aragonite. The presence of longitudinal striations on the lateral faces was taken as further evidence that the crystals were twinned. The composition was given by H. Rose as PbSb_2S_4 or $\text{PbS.Sb}_2\text{S}_3$. The original specimens which were described came from the antimony mine of Wolfsberg in the Harz.

In 1922 S. G. Gordon described a new lead sulfantimonite from Oruro, Bolivia, which he named keeleyite. This mineral he presumed to be orthorhombic, although no measurable crystals were found, and the formula was given as $\text{Pb}_2\text{Sb}_6\text{S}_{11}$ or $2\text{PbS.3Sb}_2\text{S}_3$. On the basis of this analysis the mineral was assigned to the 'acidic division'. Some question was raised at the time by reviewers as to the validity of the mineral as a distinct species, and the reliability of the formula involved was also doubted.

The first analysis, made by Whitfield, had been corrected on the basis that the contaminating sulphide was chiefly chalcopyrite, although it was later found that in reality this was stannite. Accordingly, Shannon and Short in 1927 conducted a new investigation in an endeavour to ascertain the true status of keeleyite in the light of the above change of contaminant. They conducted various mineragraphic and microscopic examinations which led them to the conclusion that this mineral was in reality sufficiently different in reaction from zinckenite to be considered a separate species. They made a new analysis, in order to correct the assumption with respect to the contaminating sulphide, and deduced the formula $\text{PbS.Sb}_2\text{S}_3$. This is, of course, the same formula as that given by Dana for zinckenite, but Shannon and Short

say that the only other explanation of the difference between keeleyite and zinckenite is that the formula commonly ascribed to zinckenite is wrong and that this mineral actually has the formula $2\text{PbS}\cdot 3\text{Sb}_2\text{S}_3$ or $3\text{PbS}\cdot 4\text{Sb}_2\text{S}_3$.

E. T. Wherry, who had earlier objected to the acceptance of keeleyite as a distinct species on the grounds that it was merely a variety of zinckenite, disagreed with the conclusions of Shannon and Short. He pointed out that the mineral was originally described 'on the basis of an erroneous recalculation of a commercial analysis on an impure specimen', with the result that the formula, to say the least, was unconvincing. He was not in agreement with Shannon and Short's thesis that the mineral was entitled to species rank merely on the basis that they had found present in keeleyite 3.26 % of metals other than lead, as well as certain mineragraphic differences, when compared with another sulphosalt about which no data was given except to say that the specimen was labelled zinckenite. He felt that the sole claim for keeleyite, therefore, rested on the presence of a little more than 1 % of zinc and a few mineragraphic differences as compared to a specimen which may, or may not, have represented zinckenite, or conformed to the ratio $\text{PbS}\cdot\text{Sb}_2\text{S}_3$. He maintained, on the contrary, that they had succeeded only in demonstrating that keeleyite has the zinckenite formula, although there is sufficient replacement of the lead to account for the small differences observed in properties, and hence is merely an impure variety of zinckenite.

The object of the present work was to attempt to shed further light on this question through examination of the minerals by means of single-crystal X-ray diffraction photographs. It was fortunate that, among other material available for examination in the British Museum collections, there were found two specimens, one of each variety, which might be said to be the original material in each case. The first specimen (B.M. 88830), zinckenite, Wolfsberg, Harz, was purchased from H. Heuland, 17 November 1829, and a note on the accompanying label conveys the information that it was presented to Heuland by G. Rose, and therefore undoubtedly represents material identical with that which Rose employed. The second specimen (B.M. 1924,145), labelled keeleyite (type) and stannite, San José Mine, Oruro, Bolivia, is a portion of the original specimen.

Single-crystal photographs were taken of several crystals from each of these specimens, both by rotation and oscillation methods (pl. X, figs. 1-3). It was found that rotation photographs of a crystal from the

keeleyite specimen were in perfect agreement with corresponding rotation photographs of a crystal from the Heuland specimen. From this we conclude that the unit cells of the two specimens are the same, and therefore that keeleyite is identical with zinckenite. A specimen labelled keeleyite from Baia Mare (= Nagybánya), Romania (B.M. 1937,44), was also examined and proved to be the same material.

Zinckenite was originally described by Rose as being orthorhombic, and other writers have attributed the hexagonal form of the crystals as due to twinning. However, Laue photographs reveal that it is really a hexagonal mineral. No evidence was found in any of the photographs to support any theory of twinning which might produce pseudo-hexagonal crystals. The cell sides were measured on crystals from specimen B.M. 1906,213, Wolfsberg, Harz, by means of a series of oscillation photographs. These were found to be a 44.06, c 8.60 Å. Both the Laue and the oscillation photographs show that there are no vertical planes of symmetry, and only the even orders of the (0001) diffractions occur. Hence the space-group is either $C_6^2 = C6_3$ or $C_{6h}^2 = C6_3/m$. The odd layer-lines on oscillation photographs about the a - and c -axes are very weak so that there is a well-marked pseudo-cell of dimensions a 22.03, c 4.30 Å. with the same space-group. Moreover most of the spots on the weak layer-lines show a spread which suggests in a lesser degree the disorder effect recently reported by L. W. Strock (1936) for silver iodide. W. Hofmann (1935) has measured the spacing in the direction of elongation of a few sulpharsenites, sulphantimonites, and sulphobismuthites of copper, silver, and lead. He reports a pseudo-period of 4.33 Å. for zinckenite, in close agreement with our value of 2×4.30 Å. Our measurements, however, do not agree with those of Ferrari and Curti (1934), who gave a 6.37, b 3.81, c 14.53 Å. Their values a/b and c/b are related to Dana's axial ratios by the multiples 3:1:6. There is no obvious explanation of the discrepancy. Short exposure photographs might lead to an erroneous choice of axes.

Formerly the isomorphism of zinckenite with sartorite, chalcostibite, and emplectite has been considered to rest upon their similarity of chemical formulae and crystallography. Palache and Peacock (1933) in a recent study of emplectite show that zinckenite can be set up so that its few crystal forms can be related to those of the isomorphous, orthorhombic pair, emplectite and chalcostibite. This agreement, however, they regard only as provisional and say that zinckenite is the most imperfectly known member of the group. It should be added that still less is known about galenobismutite.

Dana (1892), from Rose's early measurements on zinckenite, indexed the two prism and dome forms as (102) and (061), deducing the axial ratios $a:b:c = 0.5575:1:0.6353$. This setting, in which the elongation of the mineral is chosen for the b -axis, was adopted by Dana because he was convinced that sartorite and zinckenite are isomorphous. Luedecke (1896), however, reverted to Rose's orientation in which the elongation is parallel to the c -axis, and Dana's forms (102) and (061) become (110) and (104) with the axial ratios $a:b:c = 0.5698:1:0.5978$.

Groth and Mieleitner (1921) adopted Luedecke's orientation, changing the indices of Luedecke's (104) to (101), giving axial ratios $a:b:c = 0.5693:1:0.1495$. They therefore separated zinckenite from emplectite and chalcostibite, but did not exclude the possibility that the mineral might be monoclinic and isomorphous with sartorite, for which latter they adopted Trechmann's symmetry and setting. V. Goldschmidt (1923) interchanged the a - and b -axes of Dana's setting and the form (061) becomes (301), yielding axial ratios $a:b:c = 0.8976:1:1.140$. L. J. Spencer (1897) published further measurements on zinckenite from Wolfsberg in the Harz and used Dana's setting, adding c (001) to the forms already observed by Rose and Luedecke. X-ray photographs show that the crystals he studied are zinckenite, but his forms (001) and (102) should be interchanged.

The axial ratio of zinckenite using the X-ray measurements is $c = 8.60/44.06 = 0.195$. Dana's (102) and (061) and Spencer's (102) then become $m(10\bar{1}0)$, (2243), and $a(11\bar{2}0)$ respectively. The interfacial angles $(22\bar{4}3):(2\bar{2}43)$ and $(10\bar{1}0):(2243)$ calculated from the X-ray measurements are $29^\circ 10'$ and $77^\circ 24'$ respectively, compared with Rose's measured values $29^\circ 24'$ and $77^\circ 11'$ to $77^\circ 26'$. Rose's measured values for the prism angle varied from $55\frac{1}{2}^\circ$ to $61\frac{1}{2}^\circ$. They should, of course, all be equal to 60° . L. J. Spencer has commented on the difficulty of measuring the prism zone of zinckenite, which he found gave a continuous band of images. He did, however, obtain values for $m(10\bar{1}0) \wedge a(11\bar{2}0)$ of 29° – 31° . Our measurements of the small prism of zinckenite from Wolfsberg used for the X-ray photographs showed, amidst a mass of reflections from vicinal faces in the prism zone, two good images yielding an interfacial angle of $30^\circ 8'$. One of these, $a(11\bar{2}0)$, is parallel to a poor cleavage on the crystal. The vicinal faces include two further faces of the form $(10\bar{1}0)$ which yield values $59^\circ 14'$ and $64^\circ 4'$ respectively. One other face of the form $a(11\bar{2}0)$ is present inclined at $60^\circ 52'$. A face corresponding to $(31\bar{4}0)$ was also observed, but in accordance with the lack of symmetry already revealed by X-ray

photographs (1340) is absent. The final proof of the true symmetry of zinckenite rests on the X-ray measurements. The habit of growth of the mineral, rather like the radiating fibrous nodules of pyrite from the chalk of the south of England, is not conducive to well-developed prism forms and many of the specimens in the British Museum carry evidence of furrowing and etching from solution after crystallization.

The following table shows the relation between the various settings which have been adopted for zinckenite and the new X-ray setting. The axial ratios calculated from X-ray data are given in square brackets.

Dana (1892)	$a : b : c = 0.5575 : 1 : 0.6353$	[0.555 : 1 : 0.641]
Luedecke (1896)	$a : b : c = 0.5698 : 1 : 0.5978$	[0.577 : 1 : 0.601]
Groth and Mieleitner (1921)	$a : b : c = 0.5693 : 1 : 0.1495$	[0.577 : 1 : 0.150]
Goldschmidt (1923)	$a : b : c = 0.8967 : 1 : 1.140$	[0.901 : 1 : 1.154]
Vaux and Bannister	$a : c = 1 : 0.195$	

A critical examination of the chemical analyses of zinckenite, including keeleyite, reveals that only five out of eleven can be regarded as suitable for the determination of the chemical composition. The remaining six have been rejected on the score of very bad summations and excess of positive or negative valencies. The sulphur content of the unit cell of zinckenite has been calculated direct from the five fairly good chemical analyses and the X-ray and specific gravity measurements.

TABLE I. Atomic contents of the unit cell of zinckenite.

	1.	2.	3.	4.	5.	5a.
Pb	70.7	67.0	76.0	64.9	63.6	64.4
Cu	3.0	—	5.1	4.5	—	—
Ag	—	—	—	2.2	—	—
Fe	—	—	0.5	6.8	0.6	0.6
Sb	167.7	171.0	158.9	162.2	170.5	172.7
S'	324.4	328.4	323.1	328.8	333.8	323.7
Σm... ..	73.7	67.0	81.6	87.6	64.2	65.0

S' Sulphur atoms calculated from chemical analysis, specific gravity, and X-ray data.

Σm = Pb + Cu + Ag + Fe; in no. 4 also some Zn and Sn.

1. Wolfsberg, Harz. H. Rose, 1826.
 2. Ludwig mine, Adlersbach, Kinzigthal, Baden. H. A. Hilger, 1877.
 3. Wolfsberg, Harz. C. Guillemain, 1898.
 4. Oruro, Bolivia. E. V. Shannon and M. N. Short, 1927.
 5. Baia Mare, Romania. I. de Finály and S. Koch, 1929.
- 5a. No. 5 recalculated subtracting sulphur.

Table I shows that the sulphur content varies from 323.1 to 328.4. From space-group considerations we have assumed the probable number to be 324, i.e. an exact multiple of 6. On this basis the number

of antimony, lead, &c. atoms has been calculated, and table I shows that the antimony content is 158.9 to 172.7 atoms per unit cell and for lead, copper, &c. 65 to 87.6 atoms per unit cell. Bearing in mind the hexagonal symmetry of the mineral, we regard these indifferent analyses as showing that the antimony and the lead, copper, &c. contents approximate to 168 and 72 respectively. Only H. Rose's original analysis gives full support to this conclusion, and of the remainder nos. 2 and 5a give figures nearer to the ideal than do nos. 3 and 4. On the whole, the evidence suggests a closer approach to $Pb_{72}Sb_{168}S_{324} = 12(6PbS.7Sb_2S_3)$ than to $Pb_{81}Sb_{168}S_{324} = 81(PbS.Sb_2S_3)$. Zinckenite, therefore, both in its chemical composition and symmetry, is not to be regarded as isomorphous with sartorite, emplectite, and chalcostibite. The unit-cell dimension parallel to the elongation of these minerals and many others, including stibnite, jamesonite, plumosite, baumhauerite, rathite, and dufrenoyite, are of the same order or a simple multiple thereof (see table II). Thus there is probably some structural relationship running throughout the large family of sulphantimonites and sulpharsenites, which, however, even for apparently simple chemical compounds like sartorite and emplectite, does not extend to isomorphism.

TABLE II. Symmetry and formulae of zinckenite and related minerals.

	System.	a.	b.	c.	Contents of unit cell.
Zinckenite	... Hexagonal	44.06	(76.31)	8.60 Å	$12Pb_6Sb_{14}S_{17}$
Sartorite	... Monoclinic ($\beta = 90^\circ$)	58.38	7.79	83.30	$240PbAs_4S_4$
Chalcostibite	... Orthorhombic	6.008	3.784	14.456	$4CuSb_4S_4$
Emplectite	... Orthorhombic	6.125	3.890	14.512	$4CuBi_4S_4$

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EXPLANATION OF PLATE X.

X-ray photographs of a single crystal of zinckenite (B.M. 1906,213) from Wolfsberg, Harz.

All the photographs were taken with filtered Cu-K_α radiation, $\lambda = 1.539 \text{ \AA}$., in a cylindrical camera of diameter 6.04 cm. A length of 20 cm. on the original film is equivalent to 15 cm. on the reproduced figures.

FIG. 1. Rotation photograph about the axis $[11\bar{2}0]$.

FIG. 2. Rotation photograph of the same crystal about the axis $[0001]$.

FIG. 3. Oscillation photograph through 5° of the same crystal about the axis $[10\bar{1}0]$. Owing to the large unit-cell dimensions perpendicular to the c -axis, series of spots corresponding to planes with the same l value lie on well-marked curves.

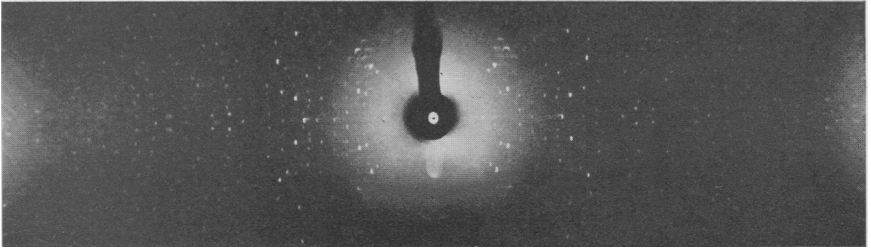


Fig. 1

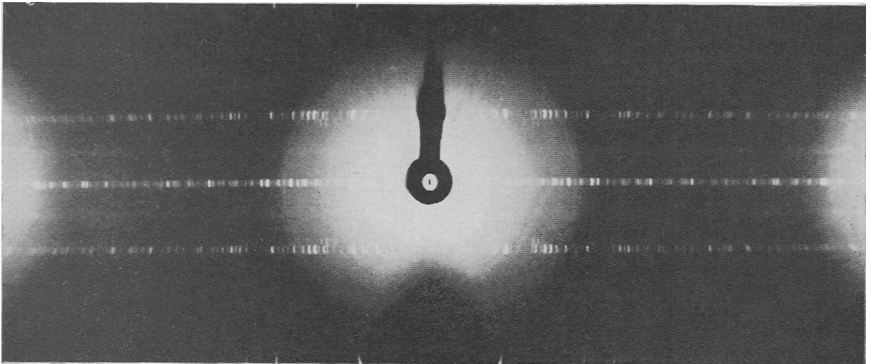


Fig. 2

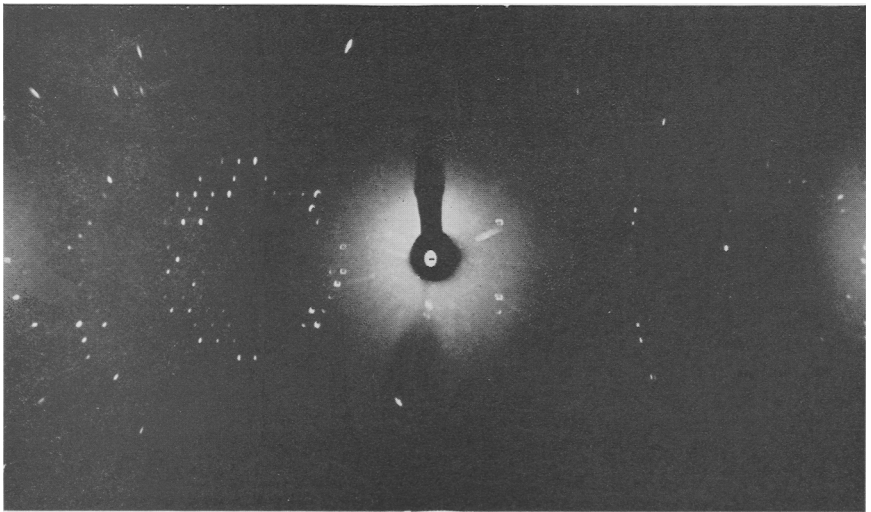


Fig. 3