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THE CRYSTAL STRUCTURES OF WULFENITE AND SCHEELITE.

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1. Introduction.

Wulfenite, $PbMoO_4$, and scheelite, $CaWO_4$, are substances showing both chemical and crystallographic similarities. Both crystallize in the tetragonal system, and the two crystals possess nearly equal axial ratios. Wulfenite is placed by Groth[1] and by Tutton[2] in the pyramidal or hemimorphic-hemihedral class, the class of lowest possible tetragonal symmetry, characterized by the possession of a tetragonal axis only. Scheelite is placed by Groth and by Tutton in the bipyramidal or pyramidal-hemihedral class, which, in addition to a tetragonal axis, possesses a symmetry plane perpendicular to that axis. According to Dana's "Mineralogy"[3] the etch figures of wulfenite do not, however, show hemimorphism, *i. e.*, lack of the equatorial symmetry plane.

At all events wulfenite and scheelite possess considerably less symmetry than other tetragonal crystals of similar composition, such as rutile, anatase, cassiterite, zircon, and xenotime, which have been studied by Vegard[4] and by Williams.[5] Thus a knowledge of the structure of these substances would, in addition to giving information on the general problem of interatomic forces, show what dissymmetry in the atomic arrangement, if any, corresponds to the dissymmetry of the crystalline substances. Whereas this research has not led to a complete solution of the structure, enough information has been obtained to make a discussion profitable, and to indicate some of the difficulties of the application of the Bragg method, in its present stage of development, to other than fairly simple crystals.

2. Apparatus and Procedure.

The apparatus is essentially the same as that used by Burdick and Ellis[6] in the study of chalcopyrite in this laboratory. One modification used in the later part of the investigation deserves mention. Instead of reading the electroscope directly by means of a microscope provided with an optical micrometer, as was done in some of the measurements on wulfenite, the position of the shadow of the electroscope-leaf projected on a screen was read. This was accomplished by placing behind the

[1] *Chemische Krystallographie.*

[2] *Crystallography and Practical Crystal Measurement.* MacMillan, 1911.

[3] *Mineralogy,* 1900, Appendix I, p. 74.

[4] *Phil. Mag.*, 33, 395 (1917); 32, 65 (1916); 32, 505 (1916).

[5] *Proc. Roy. Soc.* (*London*), 93A, 418–27 (1917).

[6] THIS JOURNAL, 39, 2518 (1917).

electroscope an electric lamp and collimator; in front of the electroscope was placed the microscope in the usual manner, but with the eyepiece fitted with a 45° prism which deflected the beam on to a mirror, and this in turn on to the screen which was contained in a darkened box. The arrangement is shown in Fig. 1. It was thus possible without appreciable loss of sensitiveness, to make observations with both eyes at the distance of normal vision. This eliminated the eye-strain to a considerable extent.

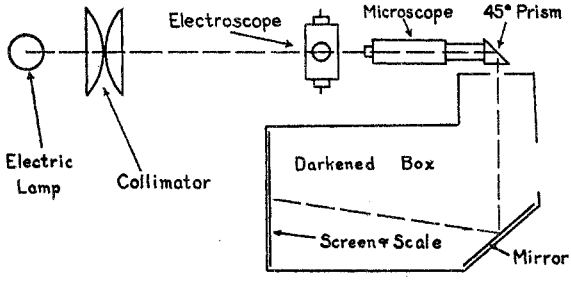

Fig. 1.—Plan of apparatus for projecting image of electroscope leaf.

The wulfenite crystal used was loaned by Prof. W. H. Clapp, of this College. It was of tabular habit with 001 and 102 faces considerably developed. It was 16 mm. wide by 4 mm. thick. The color was bright orange-red.

Two of the scheelite crystals (marked A and B in the table of results) were loaned by the Smithsonian Institution and came from Korea. Both had only the 101 faces developed. A weighed over 50 g. A was grey in color, while B was brown.

Only 3 of the spectra measured (*viz.*, 001 and 102 from wulfenite and 101 from scheelite) were obtained from developed faces. In other cases it was attempted to set the crystal in such a way that reflection would take place without making it necessary for the X-ray beam to pass through any considerable amount of crystal; for, owing to the high absorption coefficients of lead and tungsten, the relative intensities of the successive orders might be considerably affected if the amount of crystal the beam passed through were different for different orders.[1] For instance, the 100 spectrum with scheelite was obtained by setting the crystal with its tetragonal axis vertical, reflection taking place in the region of the horizontal intersection of two 101 faces. In some cases the crystal was ground to have the desired face.

The usual procedure was to find the proper setting of the crystal for a maximum by moving the crystal while keeping the chamber open wide; then to determine the chamber angle with the chamber slit narrowed, usually to one mm. When the crystal and chamber angles for one maximum were thus determined, the entire region between 0 and 60° (chamber angle) or more was examined for other maxima by moving the chamber with its slit at 2 mm. through successive small angles and moving

[1] See W. H. Bragg, *Phil. Mag.*, **27**, 888 (1914).

the crystal half as fast. After the existence of various maxima was shown the precise position of each was more carefully determined. Finally, with the chamber-slit at 2 mm., the intensities of the maxima were measured in rapid succession. The width of the slit next to the crystal was kept usually at 2 mm., but for some weak spectra it was opened to 4 mm.

3. Treatment of the Observations.

Owing to the fact that the effective reflecting plane is not always at the center of the graduated circle (especially when the face in question is not developed on the crystal), the zero position of the ionization chamber is not at 0° but at some small angle φ_0. For any two orders of reflection, say the ath and the mth, the value of φ_0, which must be chosen in order to bring the observed chamber angles φ_a and φ_m into accord with the equation $n\lambda = 2d \sin \varphi_n/2$ is given by the equation

$$\tan \varphi_0/2 = \frac{m \sin \varphi_a/2 - a \sin \varphi_m/2}{m \cos \varphi_a/2 - a \cos \varphi_m/2}.$$

As a result of experimental error and of the fact that the effective reflecting plane of an imperfect crystal does not remain constant as the crystal is rotated, the values of φ_0 calculated from different pairs of maxima are not always equal, and they sometimes show progressive variation. Consequently, instead of calculating φ_0 from an arbitrarily

TABLE I.—REFLECTION DATA FOR WULFENITE.

Plane.	Order, n.	Half of observed chamber angle.	Zero point, $\frac{1}{2}\varphi_0$.	Corrected angle of reflection, $\frac{1}{2}\varphi_n$.	Sin $\frac{1}{2}\varphi_n$.	$1/n \sin \frac{1}{2}\varphi_n$.	Relative intensity
101	I	5° 3′	—12′	5° 15′	0.0915	0.0915	100
	II	10° 20′		10° 32′	0.1828	0.0914	66
	III	15° 47′		15° 59′	0.2754	0.0918	30
	IV	21° 15′		21° 27′	0.3657	0.0914	13
	V	26° 53′		27° 5′	0.4553	0.0911	5
100	I	8° 45′	0′	8° 45′	0.1521	0.1521	100
	II	17° 49′		17° 49′	0.3060	0.1530	26
	III	27° 0′		27° 0′	0.4540	0.1513	4
110	I	6° 5′	—5′	6° 10′	0.1074	0.1074	91
	II	12° 22′		12° 27′	0.2156	0.1078	100
	III	18° 45′		18° 50′	0.3228	0.1076	50
001	I	5° 27′	—8′	5° 35′	0.0973	0.0973	100
	II	11° 7′		11° 15′	0.1951	0.0976	60
	III	16° 48′		16° 56′	0.2913	0.0971	46
	IV	22° 45′		22° 53′	0.3889	0.0972	11
111	III	9° 58′	—28′	10° 26′	0.1811	0.0604	16
	IV	13° 30′		13° 58′	0.2414	0.0604	100
102	I[a]	14° 0′	—20′	14° 20′	0.2476	0.2476	100
	II	29° 20′		29° 40′	0.4950	0.2475	7

[a] A doubtful reflection of intensity 5 was obtained when half the observed chamber angle was 6° 45′.

chosen pair of reflections, say the first and second orders, a value of φ_0 has been sought for the series of spectra from each plane so as to give the least possible variation to the quantity $1/n \sin \varphi_n/2$ where φ_n is the corrected chamber angle.

The small amount of stray reflection in the neighborhood of the maxima has been subtracted in determining the relative intensities.

4. The Observed Values.

The experimental results are given in Tables I and II, of which the headings are self-explanatory.

TABLE II.—REFLECTION DATA FOR SCHEELITE.

Plane.	Order, n.	Half of observed chamber angle.	Zero point, $\varphi_0/2$.	Corrected angle of reflection, $1/2\ \varphi_n$.	Sin $1/2\ \varphi_n$.	$1/n \sin 1/2\ \varphi_n$.	Relative intensity.
101	I	5° 20′	—7′	5° 27′	0.0950	0.0950	100
A	II	10° 52′		10° 59′	0.1905	0.0953	59
	III	16° 30′		16° 37′	0.2860	0.0953	18
	IV	22° 15′		22° 22′	0.3805	0.0951	8
100	I	8° 45′	—30′	9° 15′	0.1607	0.1607	100
A	II	18° 22′		18° 52′	0.3234	0.1617	28
	III	28° 23′		28° 53′	0.4830	0.1610	8
110	I	6° 40′	—15′	6° 25′	0.1118	0.1118	67
B	II	13° 14′		12° 59′	0.2247	0.1123	100
	III	19° 52′		19° 37′	0.3357	0.1119	49
	IV	26° 48′		26° 33′	0.4457	0.1114	25
	V	34° 17′		34° 2′	0.5597	0.1119	8
001	I	6° 8′	—10′	5° 58′	0.1040	0.1040	75
A	II	12° 11′		12° 1′	0.2082	0.1041	100
	III	18° 22′		18° 12′	0.3124	0.1041	82
	IV	24° 38′		24° 28′	0.4142	0.1037	19
111	I	3° 19′	—10′	3° 29′	0.0608	0.0608	weak
A	III	10° 33′		10° 43′	0.1860	0.0620	26
	IV	14° 12′		14° 22′	0.2481	0.0620	100
	V	17° 49′		17° 59′	0.3087	0.0617	4
	VIII	29° 22′		29° 32′	0.4929	0.0616	11

5. Interpretation of the Crystal Structure.

The various planes of atoms parallel to a possible crystal face constitute an array that may be formed by the indefinite repetition of a pattern made by a small number of planes. The thickness of the thinnest possible pattern of this character will be called here the interplanar distance. An example is shown in Fig. 3. It will be noticed that interplanar distance as here defined is not the distance between two adjacent planes, nor even the smallest distance between two similarly constituted planes. Since the entire atomic array may be considered to be made up of atoms on several equal interpenetrating lattices, the distance calculated from the formula $n\lambda = 2d \sin \varphi_n/2$ cannot be larger than that between two ad-

jacent planes of one lattice;[1] it is equal to it, or is a small submultiple of it. On the other hand, the crystallographic ratios must be obtainable from the ratios of the corresponding *lattice* distances by multiplication by small integers; hence the crystallographic ratios are obtainable also from the interplanar distances, as above defined, by multiplication by small integers.

If $c : a$ is the crystallographic ratio of a tetragonal crystal, then $n\,c : m\,a = d_{001} : d_{100}$, where n and m are small integers. From the fundamental equation for reflection it follows that $d_{001} : d_{100} = \sin (\varphi/2)_{100} : \sin (\varphi/2)_{001}$. For wulfenite this becomes $0.1521/0.0973 = 1.563$. From crystallographic data $c : a = 1.577$. For scheelite we have $0.1611/0.1040 = 1.549$, while crystallographic data give 1.536. Evidently in each case n and m may be taken as unity.

We may now investigate the type of lattice underlying the atomic arrangement. It will be convenient to find various simple arrangements that make the ratio of d_{001} to d_{100} equal to the crystallographic ratio and to choose from these the arrangement that gives the observed ratios of the other interplanar distances.

There are only two distinct lattices having tetragonal symmetry. One is formed by placing points at the vertices of a rectangular parallelepiped with a square base; the other is formed by placing points at the vertices and at the center of the faces of a rectangular parallelepiped with a square base. Various relative interplanar distances, however, may be obtained by arranging these lattices differently with respect to the crystallographic axes, or by allowing two or more identical lattices to interpenetrate at rational fractions of some lattice interplanar distance. Six cases will be considered.

Case I. The lattice is formed by placing points at the vertices of rectangular parallelepipeds with square bases, the crystallographic axes coinciding in direction with the edges of the parallelepipeds.

Case II. The same as Case I, except that the two equal crystallographic axes are at 45° with the edges of the square base of the parallelepiped.

Case III. The lattice is formed by placing points at the vertices and centers of the faces of rectangular parallelepipeds with square bases, the crystallographic axes coinciding in direction with the edges of the parallelepiped.

[1] It will be observed that the term "lattice" or "space-lattice" is here used in the strict sense given it by crystallographers and also given by W. H. and W. L. Bragg in their book, "X-Rays and Crystal Structure." The following definition is from Harold Hilton, "Mathematical Crystallography." "A series of parallel planes such that the distance between any two consecutive planes is constant and equal to a will be called a set of planes of interval a. The sum total of the points of intersection of any three sets of planes is called a 'regular space-lattice,' or more simply a 'lattice'." It seems desirable to avoid the loose terminology of many X-ray investigators.

Case IV. The same as Case III, except that the two equal crystallographic axes are at 45° with the edges of the square base of the parallelepiped.

Case V. Two lattices each arranged as in Case III interpenetrating in such a way that a point of the second lattice is situated on a diagonal of the first, one-quarter of the distance between two points of the first.

Case VI. The same as Case V, except that the two equal crystallographic axes are at 45° with the edges of the square base of the parallelepiped.

The ratios of the various interplanar distances may now be calculated starting in each case with $d_{001} : d_{100} = c : a$ or simply c. For the planes studied there is some distinction between any two of the above cases. It is found that agreement with the observed ratios is obtained in Case V and in no other. For Case V the ratios $d_{001} : d_{100} : d_{110} : d_{101} : d_{111} : d_{102}$ may be calculated with aid of the expressions

$$c : 1 : \sqrt{2} : \frac{2}{\sqrt{1 + 1/c^2}} : \frac{4}{\sqrt{2 + 1/c^2}} : \frac{1}{\sqrt{1 + 4/c^2}}.$$

The ratios so calculated from crystallographic data are to be compared with the ratios of the reciprocals of the sines of the glancing angles.

In the case of wulfenite we have for $d_{001} : d_{100} : d_{110} : d_{101} : d_{111} : d_{102}$, from crystallographic data: 1.577 : 1 : 1.414 : 1.689 : 2.581 : 0.619; from X-ray reflection data: 1.563 : 1 : 1.414 : 1.666 : 2.522 : 0.615.

In the case of scheelite we have for $d_{001} : d_{100} : d_{110} : d_{101} : d_{111}$; from crystallographic data: 1.536 : 1 : 1.414 : 1.676 : 2.569; from X-ray reflection data: 1.549 : 1 : 1.440 : 1.692 : 2.598.

Before proceeding further we will investigate whether this arrangement is in agreement with the observed densities of the crystals. To do this it is necessary to note the number of atoms associated with some arbitrary unit volume of the structure. Consider for each of the 6 cases a parallelepiped whose dimensions are the interplanar distances d_{100}, d_{100}, d_{001}. The number of $PbMoO_4$ or of $CaWO_4$ groups associated with it is in: Case I, one; Case II, one-half; Case III, one-half; Case IV, one-quarter; Case V, one-eighth; Case VI, one-quarter. The value of d_{001} which must be taken in order to give this number x atom groups in a volume equal to $(d_{100})^2 \times (d_{001})$ cc. is given by the expression: $d_{001} = \sqrt[3]{xMc^2/\rho N}$, where M is the formula weight, c is the crystallographic ratio, ρ is the density, and N is Avogadro's number. For wulfenite ρ was found to be 6.82, and for scheelite 6.06. This gives, placing x equal to one-eighth, d_{001} for wulfenite equal to 3.02×10^{-8} cm., and for scheelite equal to 2.85×10^{-8} cm. Values of d_{100} may also be obtained from the X-ray data by placing, for the palladium target, $\lambda = 0.584 \times 10^{-8}$ cm., in the expression $n\lambda = 2d \sin {}^1/_2 \varphi_n$. This gives for wulfenite 3.00×10^{-8}, and for scheelite 2.81×10^{-8} cm.

It is thus evident that Case V gives not only the correct ratios of the distances between various planes, but also the proper absolute values of those distances to accord with the density of the crystals. So far, then, it has been demonstrated that the lattice upon which the crystal is built is the face-centered, and that the metal atoms (*e. g.*, the lead atoms) are associated in pairs with each point of the lattice in such a way as to produce the arrangement described under Case V. This arrangement has often incorrectly been termed a "diamond lattice."

The next step will be to locate the molybdenum atoms with respect to the lead atoms, and the tungsten atoms with respect to the calcium atoms. It may be seen that the only kind of tetragonal rotation axis possessed by the diamond arrangement is a tetragonal screw axis. If it is desired to superpose two such arrangements (*e. g.*, the lead atoms and molybdenum atoms) in such a way that the resulting arrangement will have a tetragonal axis, it is evidently necessary to bring into coincidence the tetragonal screw axes of each of the separate arrangements. Similarly the only equatorial symmetry plane possessed by a tetragonal diamond arrangement is a glide reflection plane. If these also are brought into coincidence (scheelite it will be remembered, possesses an equatorial plane), the arrangement shown in Fig. 2 is obtained.

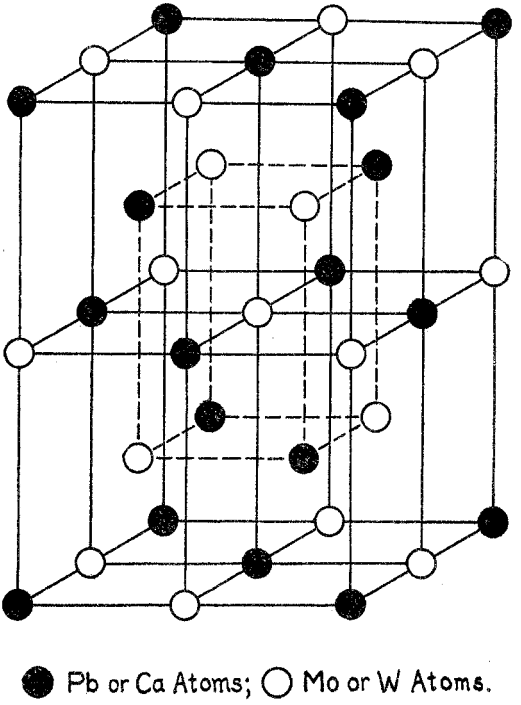

Fig. 2.—Arrangement of metal atoms in wulfenite and scheelite.

By far the most striking abnormality in the relative intensities of successive orders of reflection was found in the case of the 111 plane. With each crystal the fourth order was found to be by far the strongest of all. In the case of scheelite, which gave somewhat stronger 111 reflections than wulfenite, it was also found easily possible to locate the eighth order, whereas the sixth and seventh could not be found. It will now be shown that the chosen arrangement of molybdenum atoms relative to lead atoms and of tungsten atoms relative to calcium atoms accounts for this great

abnormality. The oxygen atoms, certainly in the case of wulfenite, are too small compared with the other atoms to account for it.

The arrangement of the planes of atoms that are parallel to the 111 face is, leaving the oxygens out of consideration, shown in Fig. 3. The distance corresponding to first-order reflection is also indicated on the figure.

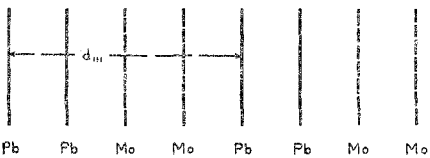

Fig. 3.—Diagrammatic representation of spacing of 111 planes.

It can readily be seen that for first-order reflection there is considerable interference; in the second order this interference amounts to annihilation; in the third order there is interference to the same extent as in the first; but that in the fourth order all of the planes reënforce each other. The cycle is then repeated, complete reënforcement occurring again in the eighth order. This is a very sensitive test of the arrangement.

As far as we have proceeded, the structure will be seen to be of the same type as the structure assigned to zircon and to xenotime by Vegard. The remaining problem is the location of the oxygen atoms; and here no very satisfactory solution can be claimed. The arrangement of the oxygen atoms in wulfenite or scheelite cannot be the same as the arrangement in either zircon or xenotime; for the observed 001 spectra are not normal as this would require. Nor can it be the same as assigned by Vegard to anatase; for this would require for 110 a normal spectrum.

An examination of the arrangement of the heavy atoms (*e. g.*, those of lead and molybdenum) shows that this arrangement possesses holohedral symmetry. Thus it has a tetragonal screw axis with 4 symmetry planes parallel to it, two of which are reflection planes and two are glide reflection planes; also an equatorial glide reflection plane with 4 diagonal axes parallel to it. It thus becomes evident that the dissymmetry of the crystalline substances is to be accounted for, either by the assumption of dissymmetry of the atoms themselves, or more likely by dissymmetry in the arrangement of the oxygen atoms.

Some of the difficulty of further interpretation is illustrated by the spectra from the 110 planes. The relative intensities of the first 3 orders are for wulfenite, 91 : 100 : 50, and for scheelite, 67 : 100 : 49. For the calculation of the relative intensities that a given arrangement may be expected to produce, three assumptions are in accord with much of the published data: (1) Each atom contributes to the amplitude of the resultant wave an amount that is proportional to its atomic number, the resultant being found in the usual manner of vector composition. (2) The intensity is proportional to the square of the resultant amplitude. And (3), the intensity is proportional to that which would be obtained from a set of equally weighted, equally spaced planes. This normal ratio

of intensities has usually been taken as 100 : 20 : 7 or sometimes 100 : 30 : 12.[1] If for the moment we neglect the requirements of symmetry and place the oxygen atoms in planes half way between those already formed by the other atoms, we have an arrangement which will give as strong a second order as possible relative to the first. Taking as the normal ratios the more favorable values 100 : 30 : 12, the calculated intensities become 100 : 86 : 12 and 81 : 100 : 10, respectively. Even for this best arrangement the second order is not strong enough, and the third order is far too weak. Indeed it is not possible to find any way of introducing the oxygen atoms which will make the third order strong enough on the above assumptions, and any attempt to do so necessarily weakens the second order, which at best is too small. Similar difficulties are encountered with some of the other planes.

There are several possible reasons why the above assumptions prove inadequate. It may be desirable to assume higher values for the relative intensities of the higher orders of a normal spectrum. Vegard has already done this in some cases. Possibly light atoms contribute more to the amplitude than an amount proportional to their atomic numbers. It may further well be that the reflecting power of an atom is dependent on its situation relative to neighboring atoms. On the experimental side a more precise definition of the area of crystal from which reflection takes place would be desirable.

For advice and assistance in carrying on this work the author is indebted to Dr. Arthur A. Noyes and to Dr. James H. Ellis.

6. Summary.

1. X-ray spectra from several planes of both wulfenite ($PbMoO_4$) and scheelite ($CaWO_4$) have been measured and tabulated.

2. It has been shown that the face-centered lattice with the atoms so located as to form a "diamond" arrangement accounts in each case for the relative spacings of different planes, and for the density of the crystals.

3. The arrangement of the heavier atoms relative to each other has been determined by a qualitative consideration of the relative intensities.

4. The difficulties in the location of the oxygen atoms have been discussed.

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[1] The proper set of values to choose is a matter of much uncertainty. We have found it possible to vary the ratio of the intensities of the first two orders from the 100 plane of sodium chloride from 100:30 down to 100:15 by narrowing the slit nearest the crystal by steps from 1 mm. to 0.1 mm.