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The Crystal Structure of Barytes, Celestine and Anglesite.

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1. Barytes, $BaSO_4$, Celestine, $SrSO_4$, and Anglesite, $PbSO_4$, crystallise in the di-digonal equatorial class of the orthorhombic system, and are members of a very interesting isomorphous series,* which includes, among other substances, the selenates and chromates of strontium and barium, the perchlorates and permanganates of potassium, rubidium and ammonium, and potassium fluoborate, KBF_4. Although these compounds belong to several chemically very dissimilar classes, they are all of the type XRO_4, where X is a kation and RO_4 an anion, and there can be little doubt that, when they crystallise, the size and shape of the RO_4 ion, which is probably very much the same whatever the nature of R, determines the arrangement of the atoms.

This paper describes an attempt to analyse the structures of three crystals of this series. The structures of such crystals must be determined by a process of trial and error. Atomic arrangements must be assumed, and then tested by comparing the intensities of the X-ray spectra predicted from them with those actually observed. The crystals are orthorhombic, and therefore, so far as symmetry is concerned, the atoms have considerable freedom of position. The process of selecting the right structure will be simplified if we can get any idea as to the nature of the SO_4 group. The most reasonable assumption we can make is that the centres of the oxygen atoms lie at the corners of a regular tetrahedron with the sulphur atoms at its centre. The work of Bradley† on the structure of $LiKSO_4$ shows that this assumption is well founded: the ion in this crystal certainly has a trigonal axis and cannot depart greatly from the regular tetrahedral form, with the distance S to O about 1·5 Å. If we suppose the ion has the same shape and size in other sulphates, we have to deal only with the orientation of the group, considered as a whole, and with the position of its centre. A number of types of arrangement quite consistent with the symmetry of the crystals are thus excluded, and the choice of arrangements to be tested by comparing the observed and

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* T. V. Barker, 'Zeitschr. f. Krist.,' vol. 45, Pt. I (1908); Rinne, 'Centralblatt f. Min.' p. 161 (1924).

† A. J. Bradley, 'Phil. Mag.,' vol. 49, p. 1225 (1925).

calculated intensities is much narrowed down. This method has been followed in the present work, and it has been found possible to assign structures to the three crystals investigated which are practically identical, and which account completely for the observed intensities of the X-ray spectra given by them.

Barytes, celestine and anglesite occur naturally as large well-developed crystals which are very suitable for work with the X-ray spectrometer, since it is possible to compare easily the intensities of the spectra from the different faces. Moreover, the variations in the intensities of a given set of spectra, when one metal is substituted for another in a structure which otherwise probably remains almost unchanged, are of great value in determining the atomic arrangement. The authors have already published a preliminary note on the structure of barytes,* in which the positions of the barium atoms were determined with some degree of accuracy. Considerable doubt remained, however, as to the positions of the SO_4 groups. In the present paper, a more complete study of all three crystals is described, which, while leaving unchanged the positions assigned to the metal and sulphur atoms, has modified considerably those suggested provisionally for the oxygen atoms.

2. The structure of all three crystals appears to be essentially similar. The determination of that of $BaSO_4$ alone will be described in detail, although data obtained from the other crystals will be employed from time to time.

The axial ratios of $BaSO_4$ are given by von Groth as

$$a : b : c = 0 \cdot 8152 : 1 : 1 \cdot 3136.$$

The specific gravity is 4·49. Referred to these axial ratios, the forms which usually develop are {001}, {110}, each very good cleavages, {102}, {011} and {104}. Other faces required for the X-ray examination were ground on the crystals with emery. The measured spacings of the pinakoid planes are (100), 4·43 Å; (010), 2·72 Å; (001), 3·57 Å; but examination of other planes shows that the structure is based on a simple orthorhombic space-lattice whose unit cell has dimensions

$$a = 8 \cdot 85 \text{ Å}, \qquad b = 5 \cdot 43 \text{ Å}, \qquad c = 7 \cdot 13 \text{ Å}.$$

For purposes of calculation it is better, therefore, to use the true axial ratio

$$1 \cdot 6304 : 1 : 1 \cdot 3136,$$

and this has been employed throughout the paper. Referred to this ratio, von Groth's (h, k, l) becomes $(2\,h, k, l)$.

From the specific gravity and molecular weight of the crystal we find the unit parallelepiped *abc* contains *four* molecules of $BaSO_4$.

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* 'Manchester Memoirs,' vol. 69, No. 5, p. 1 (1924–25).

3. The first step in determining the structure is to find to which of the 28 space groups possible to its crystal class the barytes arrangement belongs. The possible groups are V_h^1 to V_h^{28} in the notation of Schoenflies.

Referred to the spacings of the unit cell given above, the spacings of the important planes are as follows:—

(100) halved
(010) halved
(001) halved
(110) halved
(210) normal
(111) normal
(101) normal
(201) normal
(102) normal
(011) normal

Using tables such as those given by Wyckoff* or Niggli,† of the co-ordinates of typical points for the different space-groups, we are able to eliminate all space-groups but V_h^{16}. In order to be quite certain that the correct space-lattice was used as the basis of the above determination, it would have been desirable to examine more planes of the type (h, k, l). During the course of this work, however, papers have appeared by Rinne, Hentschel and Schiebold,‡ and Wyckoff and Merwin,§ on the determination of the space-group of barytes. In both cases the structure is assigned to V_h^{16}, in agreement with the present work, and we may take the space-group of this crystal as definitely known and proceed to the question of fixing the positions of the atoms.

The symmetry planes parallel to (010) are reflexion planes; those parallel to (001) and (100) are glide planes, with glides $a/2$ and $b/2 + c/2$ respectively. The projection of a unit cell on the plane (010) is shown in fig. 1. The plane of the paper is a reflexion plane; other reflexion planes lie $b/2$ above and below it. The dotted lines show the traces of the glide planes (100) and (001). Digonal screw axes (010), perpendicular to the plane of the paper, pass through the centre, corners and mid points of the edges of the cell shown. Centres of symmetry lie on these axes, midway between the reflexion symmetry planes. For the full symmetry elements of the group reference may be made to one of the sources quoted.

4. From symmetry considerations alone we can get a certain amount of information about the distribution of the atoms in the structure. Suppose an atom, A in fig. 1, to lie on one of the symmetry planes (010). By the action of the symmetry elements of the group this atom is multiplied to four at the

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* Wyckoff, 'Theory of Space Groups.'

† Niggli, 'Geometrische Cristallographie des Discontinuums.'

‡ 'Zeitschr. f. Krist.,' p. 164 (1925).

§ 'Zeitschr. f. Krist.,' p. 453 (1925).

positions A, B, C and D, all lying within the unit cell. A and B lie on one reflexion plane, C and D on another, $b/2$ above or below. Had the atom A been at a point not on a symmetry plane, it would have been multiplied by the operations of the group to eight, unless it had also been at one of the centres of symmetry. There are eight such centres in the unit of structure, but they are of two kinds, and an atom placed at any one of them is multiplied by the operations of the group into four. Now there are only four Ba and four S atoms in the unit of structure, so that we have the following possible types of arrangement for them.

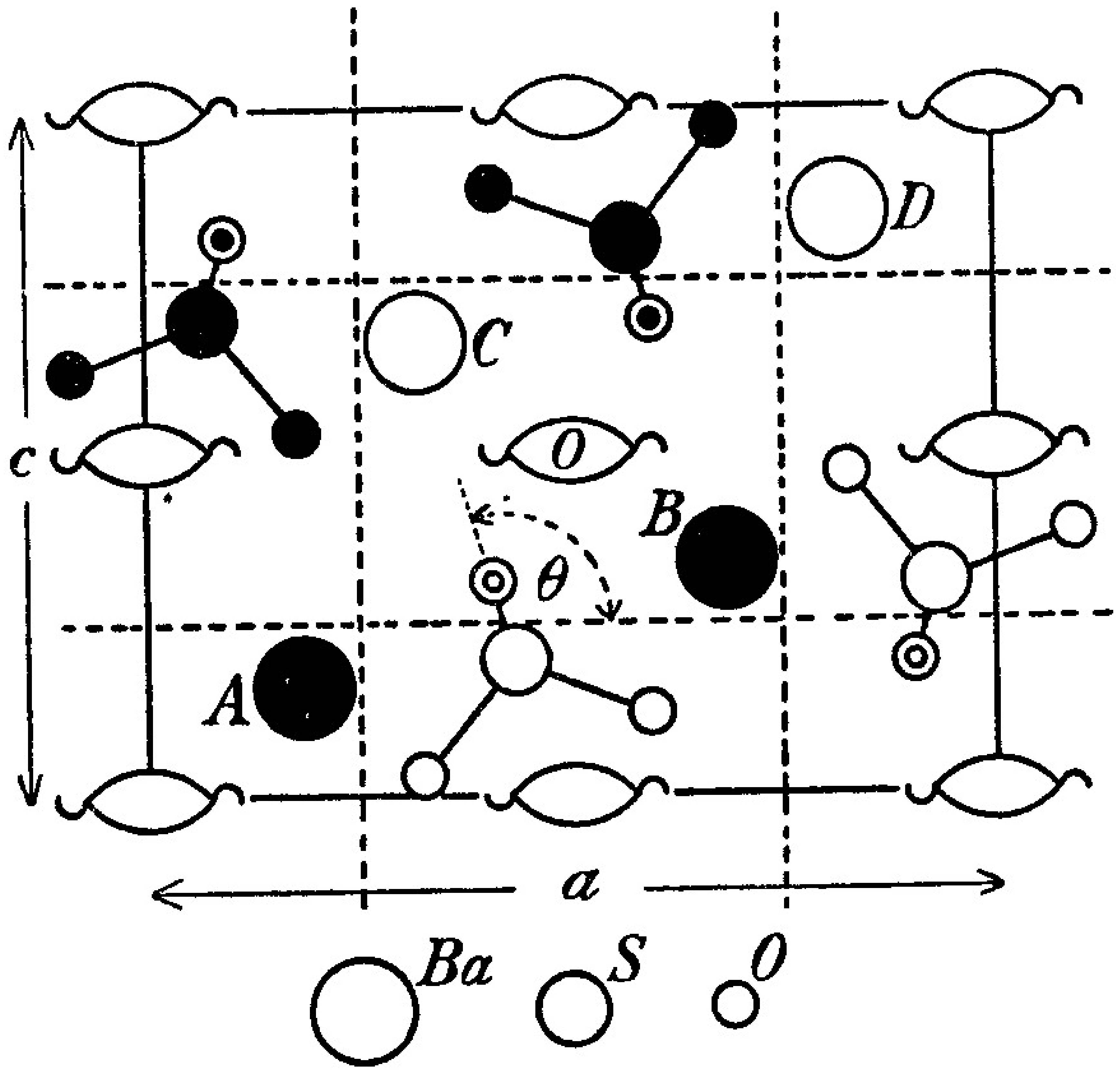

FIG. 1.

(*a*) The Ba atoms lie at the symmetry centres of one kind, the S atoms at those of the other.

(*b*) The Ba atoms lie at symmetry centres, the S atoms on the (010) reflexion planes.

(*c*) The S atoms lie at symmetry centres, and the Ba atoms on the symmetry planes.

(*d*) Both Ba and S lie on the (010) symmetry planes as in fig. 1.

An inspection of the intensities of the spectra eliminates the arrangements (*a*), (*b*) and (*c*) at once. In arrangement (*a*) Ba and S will always be in phase for the spectra from the pinakoid faces. All these faces should give very similar spectra, all of which should be fairly strong. Actually the three sets of spectra are entirely different, and some are very weak. In arrangements (*b*) and (*c*) the planes parallel to (010), containing Ba, lie half-way between those containing S, which would cause much weaker (020) and (060) spectra than are actually observed, as will be explained in a later section. We are therefore left with arrangement (*d*) in which both Ba and S lie on the (010) reflexion planes. Two parameters, x and z, fix one of the barium atoms, and another pair, x' and z', the sulphur. Once x, z, x', z' are known, symmetry fixes all the Ba and S atoms, but, so far as symmetry considerations alone are concerned, the parameters may have any value.

There are 16 oxygen atoms in each unit, and this permits several different types of arrangement.

(*e*) Let none of the atoms lie on symmetry planes. Any one atom is fixed by three parameters u, v, w, and by the operations of symmetry this multiplies into eight atoms. There may, therefore, be a second independent atom, fixed by u', v', w', and the total number of oxygen parameters is six.

(*f*) Let half the atoms lie on the reflexion planes and half off them. The eight off the plane are fixed by parameters (u, v, w), the two sets of four on them by u', w' and u'', w''—giving a total of seven oxygen parameters.

(*g*) Let all the oxygen atoms lie on the reflexion planes. So far as symmetry is concerned there are now four sets of four atoms, each fixed by two parameters, and the total is eight. For the sake of completeness, we must add the following possible arrangements of oxygen atoms, although they are physically very improbable ones.

(*h*) Eight of the sixteen oxygens in the unit may lie at symmetry centres and eight at points not on the symmetry planes, giving three parameters.

(*k*) Eight at the symmetry centres, and two sets of four on the symmetry planes: four parameters.

(*l*) Four at symmetry centres, eight more off the symmetry planes, and four on them: five parameters.

(*m*) Four at symmetry centres, and three sets of four on the symmetry planes: six parameters.

Thus, taking the barium and sulphur into consideration as well, a complete determination of the structure from first principles would require, in the least favourable case, 12 independent parameters to be fixed.

These parameters can only be fixed by considering the intensities of the spectra from the different planes, and, at the present time, our knowledge of the conditions governing the intensity of X-ray reflexion from different atoms and groups is insufficient for an attack on this problem, in its most general form, to be capable of yielding useful results. But, as we have seen, we are able to make certain assumptions as to the form of the SO_4 group, which simplify matters considerably. It is highly probable that the SO_4 group consists of four oxygen ions strongly attracted to a central sulphur ion with a charge of + 6.* Such a group, if isolated, would assume a form in which the centres of the oxygen ions lay at the corners of a regular tetrahedron with the sulphur ion at its centre. In a crystal, we might expect the groups to be deformed to a certain extent by the unequal attractions in different directions of the surrounding groups, but the attraction of the oxygen ions to the highly charged sulphur would be much greater than the deforming forces, so that, as a working hypothesis, we are probably justified in treating the SO_4 group as a regular tetrahedral arrangement of oxygen ions around a central sulphur ion.

Bradley† has recently determined the structure of $LiKSO_4$. This crystal possesses a trigonal axis, and symmetry considerations show that the SO_4 group must also possess such an axis. This is consistent with a tetrahedral SO_4 ion and, in fact, Bradley finds that a regular tetrahedron with a distance S to O of 1·5 Å fits the observed spectra well. The *Reststrahlen*‡ from $LiKSO_4$ indicate that the SO_4 group has trigonal symmetry, while those from celestine indicate that here the symmetry of SO_4 is no higher than that of the point group V. The *Reststrahlen* are governed by forces brought into play when small displacements of the ions take place; we may expect these forces to be unsymmetrical, even though the group does not depart from the regular tetrahedral arrangement to any appreciable extent. Finally, the very small double refraction of all sulphates may be taken as a further indication of such an arrangement.

5. Assuming the tetrahedral arrangement of the SO_4 group, and remembering that the S ion must lie on a reflexion plane of symmetry, we see that such a plane must also be a plane of symmetry of the group. Two of the oxygen ions will lie in the reflexion plane and two at equal distances on either side of it, and, once the sulphur ion is fixed, two more parameters suffice to fix the group, the distance ρ between the sulphur and oxygen centres and an angular co-ordinate θ (fig. 1) expressing the orientation of the group in the reflexion plane. The total number of parameters to be determined thus reduces to six.

6. To determine these parameters it is necessary to take into account the

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* Kossel's assumption has been made here, but it should be pointed out that, had it been assumed that the sulphur and oxygen atoms were bound together by some form of electron sharing, no essential difference either in the argument or in the positions assigned to the atoms would have resulted.

† *Loc. cit.*

‡ C. J. Brester, 'Kristallsymmetrie u. Reststrahlen,' p. 125, Utrecht Dissertations.

intensities of the various spectra. The intensities are measured in the ordinary way by rotating the crystal with uniform angular velocity ω through the range of angles over which it reflects, and measuring E, the total ionization received by the chamber during the rotation. If I is the ionization received by the chamber in the same time, if the direct beam is allowed to enter it, the quantity $E\omega/I$, which is called the "integrated reflexion" and is denoted by R, is a measure of the reflecting power of the face. In every case the crystal face used was large enough for the whole incident beam to fall on it, and all intensities were expressed in terms of a standard, the (400)* reflexion from rock-salt, so that the intensities from one face may be compared with those from another. The angle at which a given spectrum occurs depends only on the spacing of the series of planes from which reflexion takes place, the intensity of the reflexion on the distribution of the diffracting material in each repetition. Suppose in each repetition all the atomic centres are concentrated on a single plane. For any given spectrum, for which the glancing angle is θ, the contributions from the different atoms will all be in phase, and the intensity of the spectrum is the maximum which could occur at that angle, and may be called the normal intensity R_n. If the atoms, considered as diffracting units, are spherically symmetrical, R_n for a given crystal will be a function of θ, the glancing angle of reflexion, and we may write

$$R_n = kf(\theta), \qquad (1)$$

where $f(\theta)$ decreases rapidly as θ increases. If the atomic planes are not normal, which is the case for every set of planes in $BaSO_4$, the intensity will be less than normal. If R is the intensity for a given spectrum, the ratio R/R_n is known as the "intensity ratio" for that reflexion. The intensity ratio depends on the arrangement of the planes in the repeat of the pattern, and hence on the structure of the crystal. For a given structure, with certain assumptions, the intensity ratios for the different planes can be calculated. Suppose the correctness of an assumed structure is to be tested. Let all the spectra be arranged in order of increasing glancing angle, and let each observed intensity R be divided by the calculated intensity ratio, thus giving R_n. If the structure assumed is the true one, the value of R_n so calculated will die away rapidly and steadily with increasing θ without any violent oscillations in value.† The theoretical difficulty in this process lies in the calculation of the intensity ratio.

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* The index (400) is referred to the full spacing of the NaCl lattice; the spectrum is the second order which actually occurs.

† W. L. Bragg, 'Proc. Roy. Soc.,' A, vol. 105, p. 16 (1924).

7. It is usual to treat each atom as a diffracting point, to calculate the resultant amplitude diffracted in any given direction, and to assume that the resultant intensity is the square of the amplitude. Assuming for the moment that this process is valid, a difficulty arises in assigning the appropriate scattering power to a given atom. It has been usual to take the scattering power as proportional to the atomic number—or rather, to the number of electrons in the atom or ion. This would only be correct if all the electrons lay at distances from the atomic centre small compared with the wave-length of the X-rays employed. This is not the case, and we must write for the scattering power of an atom a quantity F, where

$$F = Z\phi(\theta), \qquad (2)$$

Z being the total number of electrons in the atom or ion, and $\phi(\theta)$ a function of the glancing angle depending on the distribution of electrons in the atom, which is the unity when $\theta = 0$ and decreases in general as θ increases. This function will be different for each atom, and thus the ratio of the scattering power of two different atoms will itself be a function of θ, which introduces considerable complications for crystals containing several different kinds of atom. For example, we may be sure that the diffracting power of an oxygen ion falls off much more rapidly than that of a barium ion, owing to the fact that the high nuclear charge of the latter will cause a much greater concentration of electrons near the centre of the atom, and we should expect that for high values of θ, the intensities are very little influenced by the oxygen ions and almost entirely due to barium and sulphur; there remains, however, the difficulty of getting numerical values of F for the different atoms.

Mr. D. R. Hartree* has been able to obtain an estimate of the dimensions of the electronic orbits in a number of ions from the consideration of spectral terms. He had already compared the values of F for Na and Cl calculated from his orbits with those obtained experimentally from measurements on rock-salt,† and had found a general agreement, although the measured F fell off more rapidly with θ than the calculated. He kindly undertook to calculate F curves for a variety of ions and his results have recently been published,‡ but we are much indebted to him for supplying us with the necessary figures previous to publication. The values of F used in this work are all based on Hartree's curves, although a few modifications have been introduced which

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* 'Proc. Camb. Phil. Soc.,' vol. 21, p. 625 (1923).

† W. L. Bragg, James and Bosanquet, 'Phil. Mag.,' vol. 41, p. 309 ; vol. 42, p. 1 (1921) ; vol. 43, p. 433 (1922).

‡ 'Phil. Mag.,' vol. 50, p. 289 (1925).

will be described later. Some of the assumptions on which the calculations of F are based may, perhaps, not be very certain, but there can be little doubt that Hartree's curves represent the general type of diffraction curve of an atom fairly well, and that we shall get nearer to the truth by employing even approximate values than by making no allowance for the effect at all.

8. Suppose now there are n atoms in the unit of structure, and let F_1, F_2.... F_n be the diffracting powers of the atoms for the angle corresponding to the mth order spectrum. Let x_n, y_n, z_n, be the co-ordinates of the nth atom referred to a centre of symmetry as origin, and expressed as fractions of the lengths a, b, c, of the sides of the unit cell. We shall denote by S the ratio of the amplitude contributed by these atoms to the mth order spectrum from the plane (h, k, l) to that which would have been contributed had the planes been normal. On the ordinary diffraction theory we have

$$S = \frac{\Sigma F_n \cos 2\pi m (hx_n + ky_n + lz_n)}{\Sigma F_n}. \tag{3}$$

In what follows we shall calculate S from this formula and assume that the intensity ratio R/R_n is equal to S^2. Doubt has been thrown by Ewald* on the validity of this procedure, but reasons which appear to justify it will be given in a later section.† In carrying out the calculations we have assumed Hartree's curves for Ba, and Sr, while that for Pb has been estimated from his figures for thallium. The metal has been supposed ionised in each case. We have also assumed the oxygen and sulphur to be ionised and to be O^{-2} and S^{+6} respectively. But we have not applied Hartree's curves directly to these ions. It appears practically impossible to get agreement between observed and calculated spectra for the higher orders, unless O^{-2} is made to die away more rapidly with θ than Hartree assumes. Bradley found the same thing in the case of $LiKSO_4$, and it may possibly be due to the heat motion of the molecules, which would perhaps be more important for the lighter ions. In addition to this, we have tried to make some allowance for the fact that the O ions must be strongly polarized by the S^{+6} ion. This might as a first approximation be regarded as equivalent to increasing the number of electrons surrounding the sulphur. We have taken 16 as the number for $\theta = 0$ and based the F curve on Hartree's curve for S^{+6}. The difference between the curve so obtained and that for S^{-2} becomes inappreciable for the higher orders. For $\theta = 0$ oxygen must now be taken as 8·5. This procedure appears to be, and is, somewhat arbitrary. It

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* Ewald, 'Phys. Zeitsch.,' vol. 26, pp. 29-32 (1925).

† *See also* W. L. Bragg, 'Phil. Mag.,' vol. 50, p. 306 (1925).

merely represents an attempt to allow for some of the effects which must occur in complex groups of this kind.

Table I.

Sin θ	0	0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50	0·55	0·60	0·65	0·70
Ba	54·0	52·6	49·1	44·8	40·7	37·4	34·8	32·5	29·9	27·4	24·6	23·1	21·9	21·1	20·4
Sr	36·0	35·2	33·2	30·6	27·8	25·5	23·8	22·6	21·8	20·6	19·3	17·7	16·0	14·4	13·1
Pb	80	78·5	76·1	72·6	68·5	63·4	58·8	54·4	50·3	46·8	43·7	40·9	38·8	37·0	34·7
S	16	15·2	13·1	10·6	9·3	8·8	8·5	8·1	7·5	6·9	6·3	5·7	5·1	4·6	4·1
O	8·5	8·0	7·2	5·7	4·1	2·5	1·0	—	—	—	—	—	—	—	—

In Table I are given the values of F used, for different values of sin θ, for the Kα radiation of molybdenum, which was employed in these experiments.

9. Column 4 in Tables II, III, and IV give the observed values of the intensity R, for a number of spectra from $BaSO_4$, $SrSO_4$ and $PbSO_4$ respectively. The spectra are arranged in order of increasing glancing angle, and are expressed in absolute measure. The measurements are made in terms of (400) rock-salt, for which the absolute intensity R may be taken as 10^{-4} to a close enough degree of approximation for this work.* The intensities for $PbSO_4$ and $SrSO_4$ are weaker on the whole than those for $BaSO_4$, owing to the fact that each of these substances has a higher absorption coefficient for Mo radiation than $BaSO_4$. The high absorption of $SrSO_4$ is due to the fact that the wave-length of Mo Kα, 0·7096 Å, is just shorter than the critical absorption wave-length of Sr, 0·767 Å, so that the radiation is abnormally absorbed, and is therefore unsuitable for investigating crystals containing strontium. If allowance is made for the different absorptions, it will be seen that the general run of intensities is very similar for all three crystals. Some of the principal spectra from $BaSO_4$ are plotted in fig. 2; the ordinates give values of R, the abscissæ sin θ. It will be seen that the spectra from (010) are on the whole stronger than those from the other faces, and that they decrease steadily in intensity with increasing order. This is to be expected, for we have seen that symmetry requires Ba, S, and two O ions to lie on the (010) planes, which are symmetry planes. These planes are, in fact, nearly normal, with a spacing half that of the *b* spacing of the unit cell, so that all the odd orders are absent and only (020), (040), (060) and so on occur. Assuming the SO_4 group to have the regular tetrahedral arrangement, and taking the radius sulphur to oxygen as 1·5 Å, it is easy to calculate the amplitude factors for these spectra, and so to calculate the normal intensities. The calculated normal curve is shown in

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* $E\omega/I$ for Mo $K\alpha$ (200)/NaCl $= 4\cdot8 \times 10^{-4}$ and (200) : (400) $= 5 : 1$, approximately.

fig. 2 (curve A), and is of great value, for from it we can now estimate the ratio S for each spectrum to which the ratio calculated from any assumed arrangement of atoms must correspond if the structure is correct.

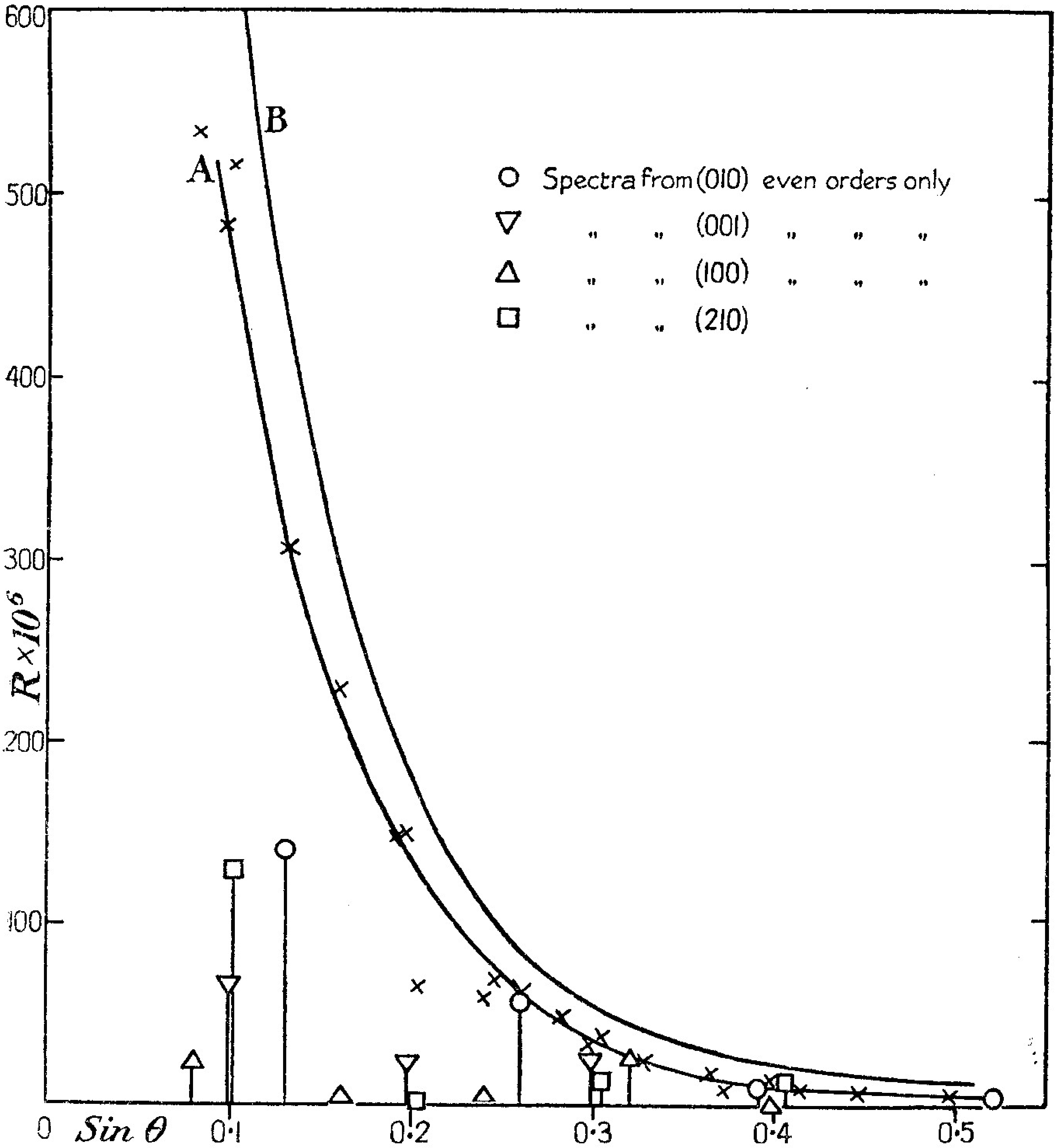

Fig. 2.—The crosses represent the values of R/S^2 calculated from the structure.

In the case of $BaSO_4$ and $PbSO_4$ the intensities of the higher orders of spectra will be almost entirely governed by the positions of the metal ions, and even the lower orders very largely influenced by them. The first step is then to obtain the approximate positions of these ions. The Ba and S can only move in the (010) planes; each have, therefore, an x and z parameter to be determined. The (100) and (210) spectra are affected by the x parameter only, and (011) and (001) by the z only, and an examination of these four spectra suffices to fix approximately the position of Ba and S.

Table II.—$BaSO_4$.

Spectrum.	Glancing Angle θ.	Sin θ.	$\frac{E\omega}{I} \times 10^6$ $= R \times 10^6$.	S.	S^2.	$\frac{R}{S^2} \times 10^6$.	Calculated Values of R_n.
	° ′						
101	3 40	0·0639	—	0·04	0·0016	—	—
200	4 35	0·0799	23·5	0·21	0·044	533	850
011	4 43	0·0822	31·0	0·219	0·048	642	840
201	5 24	0·0941	12·0	0·135	0·018	653	755
002	5 42	0·0993	67·4	0·375	0·141	477	720
210	5 50	0·1016	130	0·502	0·252	517	695
202	7 20	0·1276	—	0·000	0·000	—	—
020	7 29	0·1302	140	0·678	0·458	306	435
400	9 13	0·1602	6·2	0·163	0·027	232	290
022	9 27	0·1642	6·3	0·134	0·018	350	275
402	10 51	0·1882	—	0·066	0·004	—	—
303	11 3	0·1917	47·3	0·578	0·334	142	195
004	11 26	0·1982	24·4	0·396	0·156	155	182
420	11 45	0·2036	2·7	0·064	0·004	65	170
600	13 54	0·2402	4·6	0·276	0·076	60	106
033	14 16	0·2464	0·42	0·076	0·0058	70	100
404	14 48	0·2554	—	0·033	0·001	—	—
040	15 6	0·2605	52·5	0·974	0·940	56	85
603	16 24	0·2823	0·5	0·100	0·011	47	66
006	17 18	0·2974	24·8	0·875	0·762	32·5	55
630	17 47	0·3054	13·0	0·578	0·335	38	50
505	18 38	0·3195	—	0·30	0·090	—	41
800	18 42	0·3206	26·1	0·975	0·950	27·5	40·8
044	19 10	0·3283	6·7	0·523	0·273	24·5	38
804	22 7	0·3765	4·2	0·453	0·205	20·5	26·7
606	22 33	0·3835	3·0	0·570	0·325	9·2	25·4
060	23 1	0·3910	11·2	1·0	1·0	11·2	24·1
008	23 23	0·3969	2·2	0·367	0·134	15·2	23·0
10, 00	23 27	0·3979	2·0	0·326	0·106	19	22·8
840	24 2	0·4073	13·4	1·0	1·0	13·4	21·2
055	24 14	0·4104	4·8	0·724	0·522	9·2	20·8
10, 05	26 34	0·4472	3·1	0·717	0·507	6·1	16·4
066	29 31	0·4927	3·2	0·880	0·772	4·2	12·0
00, 10	29 44	0·4960	1·7	0·560	0·309	5·5	11·7
10, 50	30 36	0·5090	4·0	0·835	0·698	5·8	10·7
080	31 25	0·5213	3·7	1·0	1·0	3·7	9·9
0, 10, 0	45 39	0·6514	1·4	1·0	1·0	1·4	5·3

Table III.—$SrSO_4$.

Spectrum.	θ.		Sin θ.	$R \times 10^6$.	S.	S^2.	$\frac{R}{S^2} \times 10^6$.	Calculated values of $R_n \times 10^6$.
	°	′						
101	3	50	0·0669	—	0·024	0·0006	—	—
011	4	49	0·0842	4·52	0·091	0·0083	595	460
200	4	52	0·0849	2·03	0·080	0·0064	320	455
201	5	43	0·0995	trace	0·064	0·004	—	—
002	5	57	0·1037	22·6	0·330	0·109	208	350
210	6	11	0·1077	43·2	0·478	0·228	194	330
020	7	36	0·1323	54·5	0·636	0·404	135	220
202	7	41	0·1339	—	0·057	0·003	—	—
022	9	42	0·1683	1·44	0·136	0·018	77·6	134
400	9	46	0·1697	trace	0·217	0·046	—	—
402	11	29	0·1990	—	0·115	0·010	—	—
303	11	35	0·2008	19·6	0·594	0·352	55·6	89
004	11	58	0·2074	7·7	0·339	0·114	67·2	83
420	12	26	0·2154	—	0·101	0·010	—	—
033	14	37	0·2525	—	0·052	0·003	—	—
600	14	45	0·2546	trace	0·232	0·054	—	—
040	15	21	0·2646	23·4	0·892	0·782	30·0	39
404	15	32	0·2678	—	0·045	0·002	—	—
603	17	22	0·2985	—	0·065	0·004	—	—
006	18	7	0·3111	7·8	0·798	0·635	12·3	23
630	18	51	0·3231	5·1	0·480	0·232	22	18·7
505	19	33	0·3347	—	0·320	0·102	—	—
044	19	40	0·3366	1·5	0·409	0·167	8·8	16·7
800	19	51	0·3395	7·8	0·925	0·855	9·1	16·1
060	23	23	0·3969	3·47	1·00	1·00	3·47	11·2
804	23	27	0·3980	—	0·186	0·035	—	—
606	23	41	0·4016	trace	0·535	0·286	—	—
008	24	31	0·4148	1·6	0·420	0·176	9·1	10
055	24	53	0·4208	1·2	0·664	0·440	2·75	9·8
10, 00	25	7	0·4243	trace	0·091	0·008	—	—
840	25	31	0·4306	4·7	0·930	0·860	5·5	9·1
10, 05	29	50	0·4976	0·24	0·646	0·418	0·5	6·3
080	31	57	0·5292	1·64	1·00	1·00	1·64	5·1
10, 50	32	35	0·5385	1·27	0·962	0·925	1·37	4·8

In terms of the normal intensities, the spectra from (100) are as follows :—Odd orders all absent, showing that the *a* spacing is halved. Of the even orders (200) is small, (400) small, (800) nearly normal, (10, 00) fairly large. Those from (210),* which is not halved, are (210) large, (420) very small, (630) small, (840) normal. The large (800) and small (400) suggest at once that the

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* Note that (210) is the crystallographers' (110), an important cleavage plane of the crystal.

Table IV.—$PbSO_4$.

Spectrum.	θ.	Sin θ.	R × 10^6.	S.	S^2.	$\frac{R}{S^2}$ × 10^6.	Calculated Values of R_u × 10^6.
101	3 47	0·0660	—	0·062	0·004	—	—
200	4 49	0·0839	19·8	0·331	0·109	182	455
201	5 39	0·0983	7·9	0·260	0·067	120	350
002	5 52	0·1022	24·2	0·437	0·191	127	335
210	6 8	0·1069	30·1	0·518	0·268	112	313
020	7 35	0·1318	61·0	0·780	0·608	101	225
202	7 35	0·1320	—	0·131	0·017	—	—
400	9 37	0·1679	trace	0·030	0·009	—	—
303	11 25	0·1979	20·3	0·726	0·526	38·6	109
004	11 47	0·2044	5·7	0·307	0·094	60	103
420	12 21	0·2138	—	0·034	0·001	—	—
600	14 35	0·2518	3·1	0·386	0·149	20·8	62
040	15 17	0·2636	18·3	0·988	0·975	18·5	57
404	15 18	0·2639	—	0·0095	0·0009	—	—
006	17 51	0·3066	8·6	0·902	0·814	10·6	35
630	18 42	0·3207	4·3	0·774	0·597	7·2	19·2
800	19 37	0·3358	8·5	1·00	1·00	8·5	17·2
060	23 17	0·3954	2·7	1·00	1·00	2·7	16·0
606	23 19	0·3958	0·87	0·50	0·25	3·5	15·9
008	24 8	0·4088	1·9	0·824	0·675	2·8	14·7
840	25 19	0·4276	2·31	0·988	0·975	2·4	12·9
00, 10	30 44	0·5110	trace	0·13	0·017	—	8·2
080	31 49	0·5272	0·44	1·00	1·00	0·44	7·3
10, 50	32 19	0·5345	0·44	0·553	0·305	1·43	7·1
0, 10, 0	41 13	0·6590	trace	1·00	1·00	—	4·1

(100) planes containing barium are separated by $\frac{1}{8}$ of the whole *a* spacing of 8·85 Å, and this is confirmed by the small second and large fourth order from (210). The fact that both (800) and (840) are practically normal means that the sulphur atoms must be helping the barium atoms in these orders, whereas they are nearly out of phase with them in (400) and (420). To decide which of several possible arrangements of sulphur will fulfil these conditions we notice that (210) is large while (200) is small. A projection of an approximate structure, in which only Ba and S are shown on the (001) plane, is shown in fig. 3 (i), and it will be seen that the arrangement there shown explains the difference in the two sets of spectra. For (100), the planes follow in the sequence Ba, Ba, S, S, Ba, Ba, S, S, each separated by $\frac{1}{8}$ of the complete spacing. Thus, Ba and S reinforce in (800), but act against one another in (200). For (210) the sequence of planes is BaS, BaS, separated by $\frac{1}{4}$ of the spacing, followed by a gap of $\frac{3}{4}$ of the spacing, and so on, so that here Ba and S always

help one another. To confirm the hypothesis that the metal and sulphur ions help one another in the 4th orders, we have taken a few spectra from

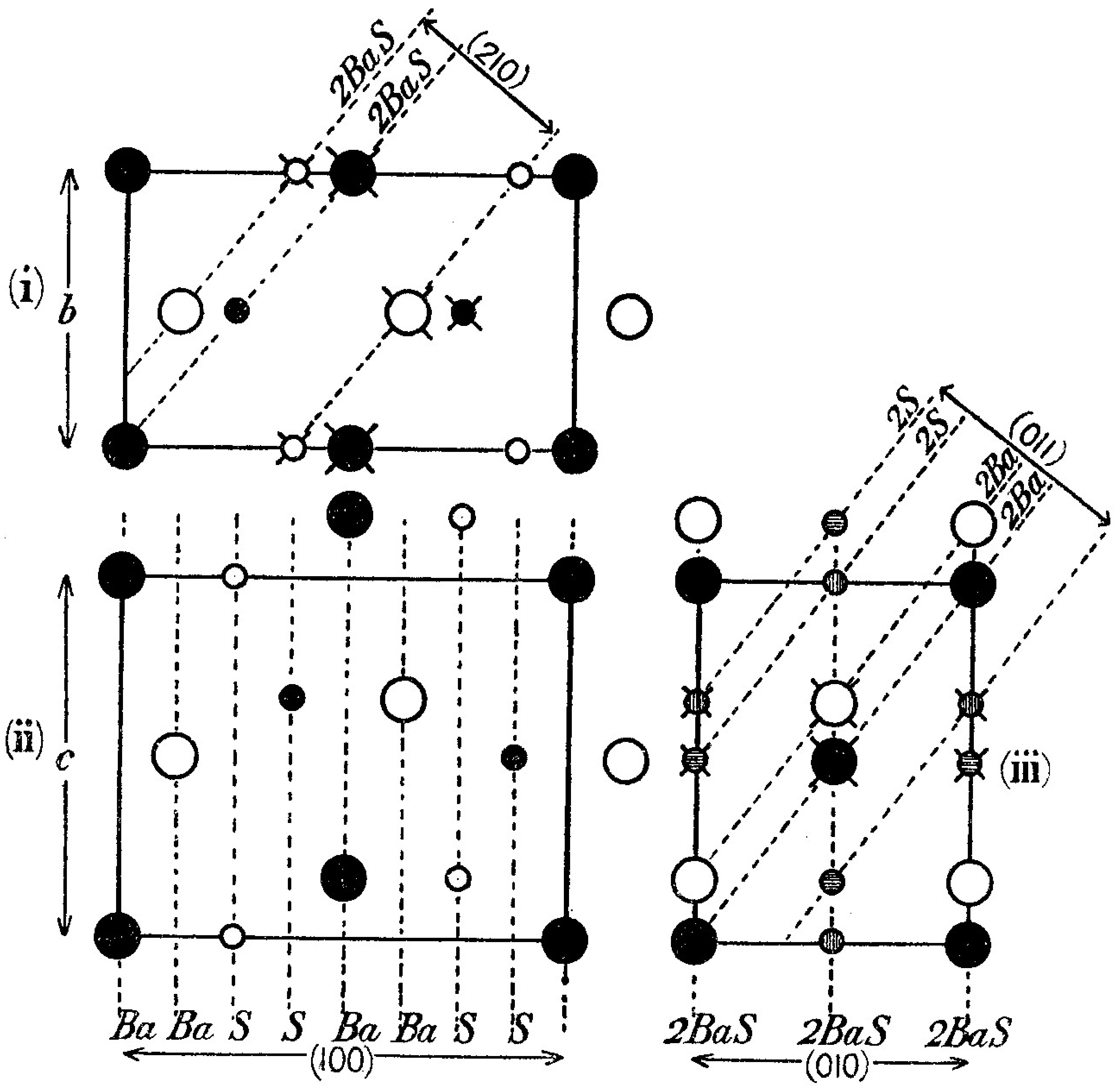

FIG. 3.

Large circles represent Ba atoms, small circles S.

Plain black circles represent atoms in the plane of the paper.

Plain white circles represent atoms in half a unit above or below the black.

Horizontally shaded circles represent atoms $a/4$ below the plane of the paper, vertically shaded, those $3a/4$ below.

Circles with crosses lie $c/6$ above the corresponding plain circles in 3 (i), and $a/8$ above in 3 (iii).

$KMnO_4$, where the heavier Mn replaces the lighter S, and the light K the heavy Ba. Here again we find a large (800) and small (200) and (400), as we should expect from the structure assumed.

To get an approximate idea of the z parameters, we notice that (006) is fairly large, (033) small or absent, (066) large, and (011) comparatively small.

This indicates that the (001) planes containing Ba are separated by about $\frac{1}{6}$ of the complete c spacing, while the small (011) and the larger (001) suggest that the S ions help the Ba ions in the latter, but are out of phase with them in the former. These simple considerations enable us to assign the following provisional co-ordinates to the four Ba and four S ions in the unit of the structure.

Ba.			S.		
$-\frac{5}{16}-x$,	$-\frac{1}{4}$,	$-\frac{1}{3}-z$,	$-\frac{1}{16}-x'$,	$\frac{1}{4}$,	$-\frac{1}{3}-z'$,
$\frac{5}{16}+x$,	$\frac{1}{4}$,	$\frac{1}{3}+z$,	$\frac{1}{16}+x'$,	$-\frac{1}{4}$,	$\frac{1}{3}+z'$,
$-\frac{3}{16}+x$,	$\frac{1}{4}$,	$\frac{1}{6}-z$,	$-\frac{7}{16}+x'$,	$-\frac{1}{4}$,	$\frac{1}{6}-z'$,
$\frac{3}{16}-x$,	$-\frac{1}{4}$,	$-\frac{1}{6}+z$,	$\frac{7}{16}-x'$,	$\frac{1}{4}$,	$-\frac{1}{6}+z'$.

Here the co-ordinates are referred to the centre of symmetry (O in fig. 1) as origin, and are given as fractions of the lengths a, b, c, of the sides of the unit cell. The quantities x, x', z, z' are small adjustments to the approximate co-ordinates assumed, which must be determined by a closer comparison of the spectra. As a matter of fact they all turn out to be quite small. The positions of the atoms in fig. 3 are plotted from the above co-ordinates, neglecting the x's and z's.

10. The approximate values given above are used to calculate the structure ratio S for the high-order spectra where the effect of the oxygen can be neglected, and from these, the small adjustments x, x', z, z' are determined. Very similar values for the metal and sulphur co-ordinates are found to give good fits in the case of $SrSO_4$ and $PbSO_4$. Assuming now that the positions of Ba and S are known, we turn our attention to the oxygen atoms. So long as we keep to the tetrahedral group, we have to determine only two parameters, the radius of the group, which we have taken as 1·5 Å, and θ, which expresses the orientation of one of the SO_4 groups in the (010) planes. (The angle θ is shown in fig. 1.) We have been able to get correspondence between the observed and calculated spectra with a group of the type assumed. Possibly a closer agreement could have been obtained by introducing distortions into the SO_4 group, but it is doubtful whether they would have had any physical significance. To determine θ the values of S′ were calculated for a series of values of θ from 0° to 360°. Certain ranges of θ were at once ruled out, and much the best fit was given by values in the neighbourhood of $\theta = +100°$. It is not possible to be sure of the best value of θ within a range of from 5° to 10° on either side of the value $\theta = 100°$. The exact value assigned to θ depends on the assump-

tions made as to the form and diffracting power of the SO_4 group. The O atoms contribute a relatively small amount to the total intensity, and we must not base more on the initial assumptions than they can fairly bear. It will be seen later that, physically, there appears to be some reason for preferring a value of θ in the neighbourhood of 100°, although actually the value was determined independently, entirely from intensity measurements.

Probably in crystals like $KClO_4$, or NH_4ClO_4 where the O atoms are relatively much more important as regards their diffracting power, it would be easier to determine their position accurately, but only quite small crystals of these substances have been obtained, and the technical difficulties of making accurate intensity measurements with them are considerable. The values of R/S^2 calculated with this value of θ are shown in column 7, Tables II, III and IV. The values of R/S^2 even now do not fall away quite regularly, but on the whole the agreement for all three substances is good. There is no case where a small structure factor corresponds to a large spectrum, or *vice versa*, and all the spectra which are absent would be predicted as absent, or very small, from their structure factors. Many of the irregular spectra are rather weak, and therefore difficult to measure accurately; several different crystals have been used in each case, which may cause irregularities, due to the different degrees of perfection of the faces, and it must be remembered that we have assumed the atoms to be spherically symmetrical as regards their scattering power. That this will be the case when the ions are combined to form a group such as SO_4 is by no means certain.

11. In calculating the intensity ratio R/R_n we have assumed it equal to S^2. This needs some justification, since, according to Ewald,* it should vary as S for a perfect crystal. This, in fact, appears to be true, or nearly so, for diamond,† calcite‡ and aragonite§ which are all very perfect crystals, with small absorption coefficients. The matter has also been considered theoretically by Darwin‖ and experimentally, in the case of rocksalt, by W. L. Bragg, James and Bosanquet.¶ We may interpret the matter by supposing a largely increased effective absorption coefficient at the reflecting angle, the increase being propor-

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* *Loc. cit.*

† W. H. Bragg, 'Proc. Phys. Soc. Lond.,' vol. 33, p. 304 (Aug., 1921).

‡ W. H. Bragg, 'Phil. Trans. Roy. Soc.,' A, vol. 215, p. 253 (1915).

§ W. L. Bragg, 'Roy. Soc. Proc.,' A, vol. 105, p. 16 (1924).

‖ C. G. Darwin, 'Phil. Mag.,' vol. 43, p. 800 (1922).

¶ 'Phil. Mag.,' vol. 42, p. 1 (1921).

tional to the reflecting power of the faces, and being greater the more perfect the crystal. We may then write

$$R \propto \frac{S^2}{\mu + kR} \tag{11.1}$$

where k may be called the extinction coefficient. If kR is large compared with μ, this leads at once to the law $R \propto S$,* but for crystals such as those under investigation, where μ is large, we might expect on this view that $R \propto S^2$ would be more nearly true. It appears desirable, however, to have some numerical confirmation of this assumption. The integrated reflexion R is given by the following expression :—

$$R = \frac{E\omega}{I} = \frac{N^2\lambda^3}{4\mu} \cdot \frac{e^4}{m^2c^4} \frac{1 + \cos^2 2\theta}{\sin 2\theta} S^2 e^{-B\sin^2\theta} \times (\Sigma F)^2. \tag{11.2}$$

Here N is number of molecules per c.c. in the crystal.

λ is wave-length of the radiation employed.

e, m are the charge and mass of an electron.

c is velocity of light.

μ is linear absorption coefficient for wave-length λ, and should include extinction.

The factor $(\Sigma F)^2$ is the square of the sum of the F factors for the atoms in the molecule, and $e^{-B\sin^2\theta}$ is the Debye factor, which allows for the decrease in intensity due to heat-motion. It will be different for each atom, and probably different for different crystallographic directions, and should not strictly be separated from (ΣF). If the planes are normal, S is unity, and, using the values for F employed already, we can calculate the numerical values of R_n for a series of glancing angles, neglecting for the time the Debye factors, which are not known for these substances. The absorption coefficients for $BaSO_4$, $SrSO_4$, and $PbSO_4$ have not been measured directly, but, from tables of mass absorption coefficients for molybdenum radiation given by Windgårdh† the linear absorption coefficients for the crystal can be calculated. We find in this way for $BaSO_4$ $\mu = 116$, for $SrSO_4$, $\mu = 184$, and for $PbSO_4$ $\mu = 451$. These are, of course, the ordinary absorption coefficients, unaffected by extinction. Using these values, we obtain

$$Re^{-B\sin^2\theta} = \frac{(\Sigma F)^2}{b} \frac{1 + \cos^2 2\theta}{\sin 2\theta}$$

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* W. L. Bragg, 'Phil. Mag.,' vol. 50, p. 306 (1925).

† 'Zeitsch. f. Phys.,' vol. 8, p. 363 (1922).

where

$$b = 1 \cdot 21 \times 10^8 \text{ for } BaSO_4$$
$$b = 1 \cdot 53 \times 10^8 \text{ for } SrSO_4$$
$$b = 4 \cdot 02 \times 10^8 \text{ for } PbSO_4.$$

The last column in tables II, III and IV give the values of R_n for the different spectra, calculated from this formula. In fig. (2), curve B, the calculated normal curve for $BaSO_4$, uncorrected for the Debye factor, is plotted as well as the normal curve A, estimated from the (010) face. The values of R/S^2 all lie on or near this estimated normal curve, but it will be seen that the calculated values are all much higher than the observed ones. Allowance for the Debye factor will reduce this discrepancy to some extent, particularly for the high orders, for the crystals are all soft, and the Debye factor, therefore, probably considerable, but it will not affect the lower orders very much. These, however, will be more likely to be reduced by extinction. The discrepancies are all in the right direction, and the manner of plotting such as to emphasise them, since the intensities depend on F^2. The values of R_n calculated in a similar manner, and based on the idea that $BaSO_4$ is a perfect crystal, which is that considered by Ewald, and which leads to the result that $R \propto S$, are far below those actually observed. $BaSO_4$ must approximate more to the fine mosaic type of crystal, consisting of small more or less perfect fragments set at slightly differing angles, to which alone, as shown by Darwin,* the formula (11.2) can be applied. It appears from these results that in working out these crystals it is better to assume that the intensity ratio varies as S^2. The difference between the observed and calculated normal orders is greatest in the case of lead sulphate. This is interesting, because, for equal perfection of crystal, we should expect the extinction effect to be least in the case of lead, owing to the large value of μ. If, however, any layer is produced by grinding, in which the orientation of the particles is quite different from that of the crystal as a whole, it will tend to reduce the intensities of the spectra much more for crystals with a high absorption coefficient, and the reduction will be most for low glancing angles, and should be a function of the glancing angle. It is possible that at least some of the discrepancy is due to this. There remains, however, the possibility that the inner electrons in an atom as heavy as lead do not contribute the full quota to the diffraction to be expected from the simple classical formula. Accurate intensity measurements from a crystal which contains a heavy atom, and whose structure is known, so that

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* Darwin, *loc. cit.*

there is not the additional uncertainty of structure factor, would be of great interest in this connection.

12. The co-ordinates of the four typical *Ba* and four typical S ions have already been given in Section 9. We repeat them here for convenience of reference :—

	Ba.			S.	
$-\frac{5}{16}-x$,	$-\frac{1}{4}$,	$-\frac{1}{3}-z$,	$-\frac{1}{16}-x'$,	$\frac{1}{4}$,	$-\frac{1}{3}-z'$,
$\frac{5}{16}+x$,	$\frac{1}{4}$,	$\frac{1}{3}+z$,	$\frac{1}{16}+x'$,	$-\frac{1}{4}$,	$\frac{1}{3}+z'$,
$-\frac{3}{16}+x$,	$\frac{1}{4}$,	$\frac{1}{6}-z$,	$-\frac{7}{16}+x'$,	$-\frac{1}{4}$,	$\frac{1}{6}-z'$,
$\frac{3}{16}-x$,	$-\frac{1}{4}$,	$-\frac{1}{6}+z$,	$\frac{7}{16}-x'$,	$\frac{1}{4}$,	$-\frac{1}{6}+z'$.

The co-ordinates are referred to a centre of symmetry as origin, and are expressed as fractions of the lengths a, b, c of the side of the unit lattice cell. The atoms whose positions are given are those shown in fig. 1. The quantities x, x', z, z' are small variations from the approximate co-ordinates assumed provisionally, which are those shown in fig. 2. These approximate co-ordinates are the same for all three crystals examined, while the values of x, x', z, z' differ slightly from one to the other.

The centres of the oxygen ions form a regular tetrahedron with the sulphur ion at its centre, the radius S to O being 1·5 Å. The (010) reflexion planes are reflexion symmetry planes of the SO_4 groups whose centres lie in them, and the orientations of the groups in the planes are fixed by an angular co-ordinate θ (see fig. 1). The value $\theta = 100°$ has been used for all three crystals, although it probably differs slightly for each one, and it cannot be fixed with great accuracy, since the intensities of the spectra are not very sensitive to small changes of θ.

The following summary gives the data for the three crystals investigated :—

Barytes : $BaSO_4$. Axial ratio, 1·6304 : 1 : 1·3136.*

$a = 8{\cdot}85$ Å, $b = 5{\cdot}43$ Å, $c = 7{\cdot}13$ Å.

$x = 0{\cdot}0055$, $x = 0{\cdot}0055$, $z' = 0{\cdot}0055$, $z' = -0{\cdot}028$.

In Ångström units

$ax = 0{\cdot}019$ Å, $cz = 0{\cdot}039$ Å, $ax' = 0{\cdot}019$ Å, $cz' = -0{\cdot}20$ Å

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* No attempt has been made to obtain a more accurate value of the axial ratio from the X-ray data. The crystallographers' values, which are well known for these crystals, have been assumed throughout, but the calculated and observed positions of the spectra agree very closely in all cases.

Celestine :

$a = 8$

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or $ax =$

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reasonably suppose that t
the distance of approach to some ext
centre a sphere of 1·35 Å radius, the spheres
sidered as defining the boundary of the SO_4 group, w
divalent ions in the structure will not be able to penetrate.
limitation to the meaning of the term, we may take as the radius of
ion 1·4 Å, and might therefore be doubtful of the correctness of any structure in which the centres of a Ba ion lay within less than about 2·7 Å of an oxygen ion.

In fig. 4 the structure of $BaSO_4$ is shown diagrammatically, viewed in a direction perpendicular to the (010) face. The circles represent to scale the radii of the ionic domains. The black circles represent barium, the white oxygen, which are combined to form the tetrahedral SO_4 groups. The three Ba ions at the top and the three at the bottom of the diagram lie in one plane, say that of the paper, the remaining three a distance $b/2$ below. The middle row of SO_4 groups have their centres in the plane of the paper, the other $b/2$ below. Consider now the five Ba ions on the left and lower portion of the diagram, together with the two more which lie $b/2$ above the plane of the paper and directly over the middle pair of ions. Into the space between these seven ions the SO_4 group S shown in the diagram fits quite neatly. The two lower O ions touch the two lower barium and the upper barium touches each of the two upper O ions, which lie above and below the plane of the n any particular barium ion, and calculate the neighbouring oxygen ions, we find that in this structure ithin a sphere of a little more than 3 Å radius described about a ion. The distances are as follows: Two at 2·89 Å, two at 2·78 Å, two at 2·82 Å, two at 3·31 Å, two at 3·08 Å, one at 2·80 Å, and one at 2·71 Å. Moreover, in the structure assumed, none of the ionic domains of O ions belonging to different SO_4 groups intersect one another. Thus the structure appears to be one in which each positive metallic ion is surrounded as closely and as uniformly as possible by negative oxygen ions, perfect freedom of adjustment of the ions being hampered, because they are attached together in fours in the sulphate groups. The position of a typical barium ion may be understood by considering the middle ion in fig. 4. Five of the SO_4 groups concerned are shown, accounting for eight of the 12 oxygen ions. The remaining groups are those which lie a whole spacing below the right-hand pair in the middle row.

The similarity of structure and axial ratio in crystals isomorphous with barytes would thus be accounted for, for the structure on this view is determined by the tetrahedral arrangement of O ions in the group RO_4. If the middle ion R is larger we might expect the whole structure to be expanded with but little alteration of the axial ratio. Change in the size of the metallic ion would no doubt affect the closeness with which the oxygens could pack, and hence the orientation of the groups and the axial ratios, but we should not expect the effect to be very large. A certain number of observations have been made on $KMnO_4$ and $KClO_4$, and these entirely confirm the view that the structures are essentially similar to those of the three sulphates. The main spacings of the five crystals are given below in Table V for comparison.

Table V.—Spacings in Å units.

Crystal.	*a.*	*b.*	*c.*
$BaSO_4$	8·85	5·43	7·13
$SrSO_4$	8·36	5·36	6·84
$PbSO_4$	8·45	5·38	6·93
$KClO_4$	8·84	5·68	7·22
$KMnO_4$	9·08	5·70	7·40

Summary.

1. The structures of the isomorphous sulphates of barium, strontium and lead have been investigated, and all are found to be very similar. The structure is based on a simple orthorhombic lattice having four molecules to the unit cell, and the space group is V_h^{16}. The positions of the atoms in the structure have been determined by a study of intensities.

In calculating the structure factors, the figures for the diffracting power of ions at different angles, calculated by Hartree, have been employed with slight modifications. A comparison of the absolute intensity of reflexion actually observed with that calculated on the classical theory has been made. It is found that the observed intensity is in all cases lower than, although of the same order of magnitude as, the calculated.

A possible reason for the structure which is common to a number of crystals is discussed.

In conclusion we wish to express our thanks to Prof. W. L. Bragg, F.R.S., for his constant interest in this work. We are also greatly indebted to Mr. T. V. Barker, of the Crystallography Department at Oxford, for supplying us with specimens of a number of crystals belonging to the isomorphous series under investigation; and to Mr. J. M. Wordie, of St. John's College, Cambridge, who gave us several very fine natural crystals of celestine. The Coolidge bulb used in this work was the gift of the General Electric Company of Schenectady, and part of the apparatus was purchased with the aid of a grant from Messrs. Brunner, Mond, Ltd., to whom our best thanks are due.

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