

The Crystal Structure of Valentinite (Orthorhombic Sb_2O_3)¹⁾.

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Abstract.

Natural valentinite from Su Suergiu, Sardinia, and also artificial valentinite made by subliming chemically pure Sb_2O_3 above its inversion point, have been studied by the Weissenberg method. The structure has been completely and uniquely determined.

The three symmetry planes indicated by Weissenberg symmetry study confirm the orthorhombic character of this crystal. These all prove to be glide planes, which permits a unique determination of the space group. An intensive intensity study has been made resulting in a unique determination of the correct antimony equipoint combination and all antimony parameters, and a unique determination of the oxygen equipoint combination and oxygen x and y parameters. The only parameters remaining undetermined by direct intensity deduction are the two which fix the elevations of the two kinds of oxygen atoms. In order to avoid an unduly lengthy

1) The structure was worked out independently by the two authors, who derived identical symmetry information, substantially identical cell dimensions, and also closely the same parameter values. When this duplication of effort was discovered, joint publication was agreed upon. The methods and arguments given in this paper are essentially those used by Buerger.

investigation, these last parameters were tentatively fixed by simple physical considerations. A slight permissible adjustment of these predicted values yielded perfect agreement between observed and calculated intensities.

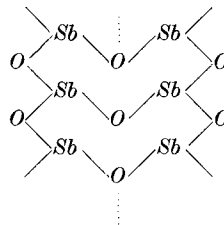
The valentinite structure and some of its characteristics may be described in the following terms:

Diffraction symbol:	$mmmPccn$
Crystal class	$mmm = D_{2h}$
Space group	$Pccn = D_{2h}^{10}$
Unit cell	$a = 4.92 \text{ \AA}$
	$b = 12.46$
	$c = 5.42$
	$Z = 4Sb_2O_3$ per cell

Equipoints and parameters:

	x	y	z	u
$8Sb$ in $8e$ with	.044 ₄	.128 ₃	.179	
$4O_I$ in $4c$ with				.029
$8O_{II}$ in $8e$ with	.147	.058	-.139	

The structure is composed of strings of



extending along one set of two-fold rotation axes. The $Sb-O$ distances within a string are about 2.00 \AA , which is in good agreement with the electron-pair bond distance. The strings pack together across symmetry centers in such a way that the antimonys of one chain come about opposite the oxygens of the neighboring chain and are held apart by $O-O$ contacts of 2.54 \AA separation. This structure of indefinitely long chain molecules accounts well for the perfect prismatic cleavage of the crystal.

Data are presented for the construction of a model illustrating the structure.

Introduction.

Sb_2O_3 is dimorphous. According to sublimation experiments by Roberts and Fenwick¹⁾ the cubic form, senarmonite, is stable below 570°C . while the orthorhombic form, valentinite, is stable above this temperature. Confirmation of this in a general way has been provided

1) Roberts, E. J., and Fenwick, F., The antimony-antimony trioxide electrode and its use as a measure of acidity: *J. Amer. Chem. Soc.* **50** (1928) esp. 2134.

in measurements of the vapor pressures of the two forms by Hincke¹). The crystal structure of the cubic modification has been determined by Bozorth²). No information regarding the structure of the orthorhombic form has hitherto been published.

Material.

A complete investigation was carried out (by Buerger) using natural valentinite from Su Suergiu, Sardinia. Crystals from this source have been crystallographically described by Millosevich³). This valentinite is in the form of small, more or less equidimensional crystals, each consisting of a very short prism of height about equal to width, surmounted by rounded termini. Good goniometric measurements, unfortunately, are impossible on this material due to an extreme tendency to lineage. The cleavage prism angle is in the general region of $42^\circ 18'$, corresponding to an axial ratio .3869 : 1, but this can not be duplicated.

A complete investigation was also carried out (by Buerger) on valentinite grown by sublimation from pure Sb_2O_3 in an atmosphere of nitrogen. This material was kindly prepared by Mr. M. C. Bloom of the Mineralogical Laboratory, Massachusetts Institute of Technology. The crystals of sublimed valentinite used are very flat prismatic in habit, consisting essentially of unit prism and blunt pyramid terminus. The prism, which is highly striated, has a interfacial angle of approximately $43^\circ 17'$, corresponding to an axial ratio $a : b = .3967 : 1$, but very considerable variations from these values were observed.

An independent analysis (by Hendricks) was carried out on natural valentinite from an unknown Sardinian locality and on crystals obtained from a vug in pure Sb_2O_3 that had been melted in an atmosphere of nitrogen. The natural valentinite, which was kindly supplied by Dr. W. F. Foshag, was a portion of specimen No. R 1742 from the collection of the National Museum. Crystals were pyramidal in habit showing predominant development of (110) with many other forms. All of the natural crystals were multiple. The artificial crystals were similar in habit to those described above.

1) Hincke, W. B., The vapor pressure of antimony trioxide, J. Amer. Chem. Soc. **52** (1930) 3869.

2) Bozorth, Richard M., The crystal structures of the cubic forms of arsenious and antimonous oxides, J. Amer. Chem. Soc. **45** (1923) 1624.

3) Millosevich, Federico, Appunti di Mineralogia Sarda — 2° Valentinite della miniera de antimonio di Su Suergiu (Gerrei), Atti Accad. Lincei **9** (5) (1900) 340.

Space Pattern Characteristics.

Method. The entire investigation was carried out using the equi-inclination^{1,2)} Weissenberg method. Crystal fragments of the order of half a millimeter in diameter were completely bathed in unfiltered beams of copper radiation for the purpose of determining the cell characteristics. Molybdenum radiation was also employed for the purpose of recording high order reflections necessary in the determination of parameters.

The general methods of interpreting equi-inclination photographs have been discussed elsewhere^{1,2)}. These have been applied as indicated beyond.

Table I.

Possible Ways of Accommodating 8 *Sb* and 12 *O* in *Pccn* (D_{2h}^{10}).

8 <i>Sb</i> in	12 <i>O</i> in
(1) $4_a + 4_b$	(1) $4_a + 4_b + 4_c$
(2) $4_a + 4_c$	(2) $4_a + 4_b + 4_d$
(3) $4_a + 4_d$	(3) $4_a + 4_c + 4_c$
(4) $4_b + 4_c$	(4) $4_a + 4_c + 4_d$
(5) $4_b + 4_d$	(5) $4_a + 4_d + 4_d$
(6) $4_c + 4_c$	(6) $4_b + 4_c + 4_c$
(7) $4_c + 4_d$	(7) $4_b + 4_c + 4_d$
(8) $4_d + 4_d$	(8) $4_b + 4_d + 4_d$
(9) 8_e	(9) $8_e + 4_a$
	(10) $8_e + 4_b$
	(11) $8_e + 4_c$
	(12) $8_e + 4_d$

Photographs. Zero level photographs were taken for rotations about the three crystallographic axes of both natural and pure, sublimed material. First layer photographs were taken about the *a* axis of a natural crystal (Hendricks); first, second, third and fourth layer photographs were taken for *b* axis rotations of the natural Su Suergiu material (Buerger). First, second and third layer photographs were also taken for the *c* axis rotation of the sublimed material (Buerger).

Centrosymmetrical point-group. The photographs of all levels investigated for each of the three crystallographic axial rotations of both natural and sublimed valentinite agree in assigning the symmetry C_{2i} to the reciprocal lattice levels represented by the photographs.

1) Buerger, M. J., The Weissenberg reciprocal lattice projection and the technique of interpreting Weissenberg photographs, *Z. Kristallogr. (A)* **88** (1934) 356.

2) Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs, *Z. Kristallogr. (A)* **91** (1935) 255.

Space group. By comparison with the reciprocal translations given by the n -layer photographs discussed above and with the layer line spacing of the rotation photograph of corresponding axial rotation, the reciprocal translations on the three axial zero-layer photographs appear to be doubled as follows:

crystal rotation axis	doubled translation on zero-level of reciprocal lattice
a	t_c
b	t_c
c	$t_a + t_b$

This indicates three glide planes: ccn . The diffraction symbol is therefore $mmmPccn$. The presence of the three mutually orthogonal glide planes definitely establishes the holohedral orthorhombic symmetry, $mmm = D_{2h}$, of valentinite and definitely establishes the space group as $Pccn = D_{2h}^{10}$.

Unit cell. The dimensions of the unit cell were determined by direct film measurements from the b -axis layer spacing and from the Z -spacing of the pattern along symmetry lines for the b -axis n -layers. These measurements were subsequently refined by direct steel scale measurements of x of high-order reflections on the three zero-layer photographs with the aid of the relation:

$$d = \frac{n}{2 \sin\left(\frac{x}{2} \cdot \frac{360}{2\pi r_f}\right)}$$

The dimensions of cells of the natural Su Suergiu material and of the chemically pure sublimed Sb_2O_3 are substantially the same:

	absolute	ratio	Axial Ratios obtained from Surface Morphological study	
			Millosevich's Su Suergiu ¹⁾	Goldschmidt's average ²⁾
a	4.92 Å	.395	.39122	.3936
b	12.46	1.	1.	1.
c	5.42	.435	—	4339

Lattice dimensions obtained from layer photographs and high order reflections from the pinacoids on equatorial zone Weissenberg photographs (by Hendricks) on the natural material are $a = 4.91$ Å,

1) Millosevich, Federico, Appunti di Mineralogia Sarda — 2° Valentinite della miniera de antimonio di Su Suergiu (Gerrei), Atti Accad. Lincei **9** (5) (1900) 340.

2) Goldschmidt, Victor, Atlas der Kristallformen **9** (1923) 45.

$b = 12.47 \text{ \AA}$, $c = 5.41 \text{ \AA}$. Values for the artificial crystals agreed closely with these. Angles measured on Weissenberg photographs and calculated values according to these lattice dimensions are:

Angle	Measured	Calculated
110:1 $\bar{1}$ 0	42° 48'	43° 00'
011:0 $\bar{1}$ 1	46° 48'	46° 50'

The axial ratio chosen from surface morphological study is thus based upon the correct structural cell.

Using Spencer's value¹⁾ of 5.76 for the density of natural valentinite, these cell dimensions require 4.006 formula weights of Sb_2O_3 per unit cell of the Su Suergiu material.

Possible Structures.

Space group D_{2h}^{10} has the following equipoints:

rank	location	designation
Four-fold positions	symmetry centers	4_a
	symmetry centers	4_b
	two-fold axes	4_c
	two-fold axes	4_d
Eight-fold position	general	8_e

Four formula weights of Sb_2O_3 , or 8 Sb and 12 O , must be accommodated by these equipoints. The possible ways in which this accommodation can be effected are listed in table I. Not all combinations of these positions, however, are possible. Because of the absence of degrees of freedom in 4_a and 4_b , only one of each of these may appear in the entire combination.

Reflection Intensities.

The amplitude of the waves scattered by the atoms occupying the general 8-fold equipoint is given by the expressions of table II for the various cases of h , k , and l , the indices of the reflection. The reflection vanishes for conditions not included in the table.

For comparison of observed with calculated intensities, the former were visually estimated from Weissenberg equatorial films taken chiefly with $Mo-K_\alpha$ and $Mo-K_\beta$ radiation. Comparisons between the stronger reflection intensities were derived from underexposed films and comparisons between the weaker reflections were derived from films made

¹⁾ Spencer, L. J., Notes on some Bolivian minerals (jamesonite, andorite, cassiterite, tourmaline, &c.), Mineral. Mag. 14 (1907) 331.

with extremely long exposures. The intensities of the spectra for these conditions have been calculated by means of the relation

$$\sqrt{I} = \sqrt{\frac{1 + \cos^2 2\theta}{2 \sin 2\theta}} A$$

where I = the intensity
 A = the appropriate structure amplitude
 θ = the Bragg glancing angle

Location of Antimony Atoms.

Elimination of incorrect antimony equipoint combinations. Certain possible combinations of antimony equipoints listed in

Table III.

Regularities in structural amplitude series for even orders of pinacoid reflections.

<i>Sb</i> equipoint combination	(100)	(010)	(001)
$4_a + 4_b$	$F(8, 8, 8, 8----$)	$F(8, 8, 8, 8----$)	$F(8, 8, 8, 8----$)
$4_a + 4_c$	$F(8, 0, 8, 0----$)	$F(8, 0, 8, 0----$)	irregular
$4_a + 4_d$	$F(8, 0, 8, 0----$)	$F(8, 0, 8, 0----$)	irregular
$4_b + 4_c$	$F(8, 0, 8, 0----$)	$F(8, 0, 8, 0----$)	irregular
$4_b + 4_d$	$F(8, 0, 8, 0----$)	$F(8, 0, 8, 0----$)	irregular
$4_c + 4_c$	$F(-8, 8, -8, 8--)$	$F(-8, 8, -8, 8--)$	irregular
$4_c + 4_d$	$F(-8, 8, -8, 8--)$	$F(-8, 8, -8, 8--)$	irregular
$4_d + 4_d$	$F(-8, 8, -8, 8--)$	$F(-8, 8, -8, 8--)$	irregular
$8e$	irregular	irregular	irregular

Note: designation irregular indicates that the series does not necessarily contain regularities, although it may show regularity with certain parameter values.

table I can be easily eliminated by very simple intensity considerations: For the present purpose it is sufficient to compare observed pinacoid reflection intensities with those to be expected with the antimony atoms occupying the several possible equipoint combinations. The expected intensities can be approximated closely enough for the purpose by means of the structure amplitudes of the antimony atoms alone. These are listed in table III. The actual intensities must follow the essential features of the several series listed in this table because of the relatively great scattering power of the antimony atom compared with that of the oxygen atom. The actual location of the oxygen atoms can effect the intensities indicated, at most, by giving rise to weak reflections where the structure amplitudes of table IV indicate an absent reflection, O ,

and by very slightly disturbing the relative intensities involved in regular declines indicated by the designation $F(8)$.

Table III indicates that regular intensity declines for the even order reflections of the 100 and 010 series, either with or without alternate absences, characterize all structures containing antimony occupying the special equipoints. The actual photographs display an intensity

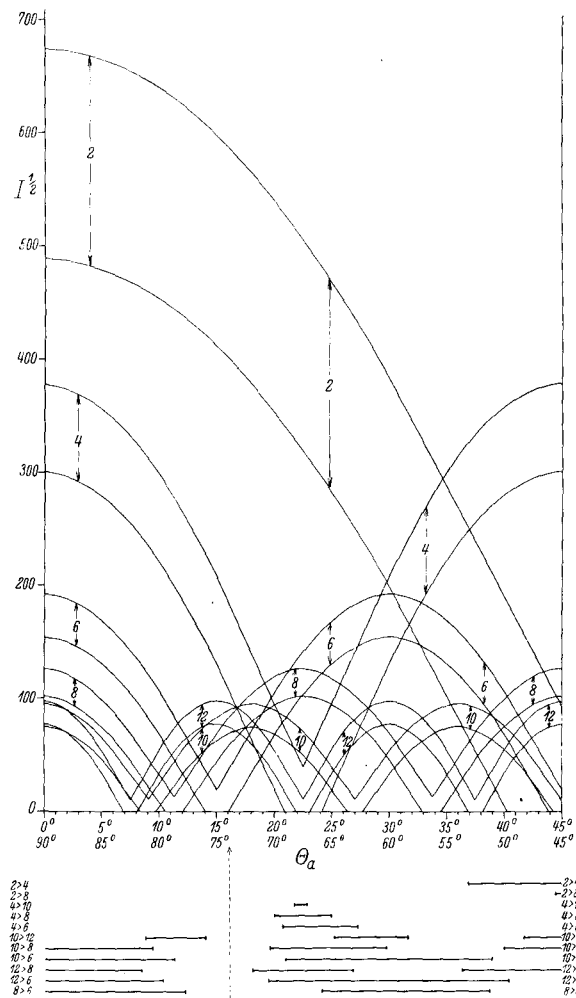


Fig. 1. Variations of intensity of the orders of 100 ($Mo-K_{\alpha}$ radiation) with the antimony parameter, θ_a , and parameter regions eliminated by observed intensity relations. The half-widths of the bands represent the intensity uncertainties due to the initial uncertainty in the positions of the oxygen atoms.

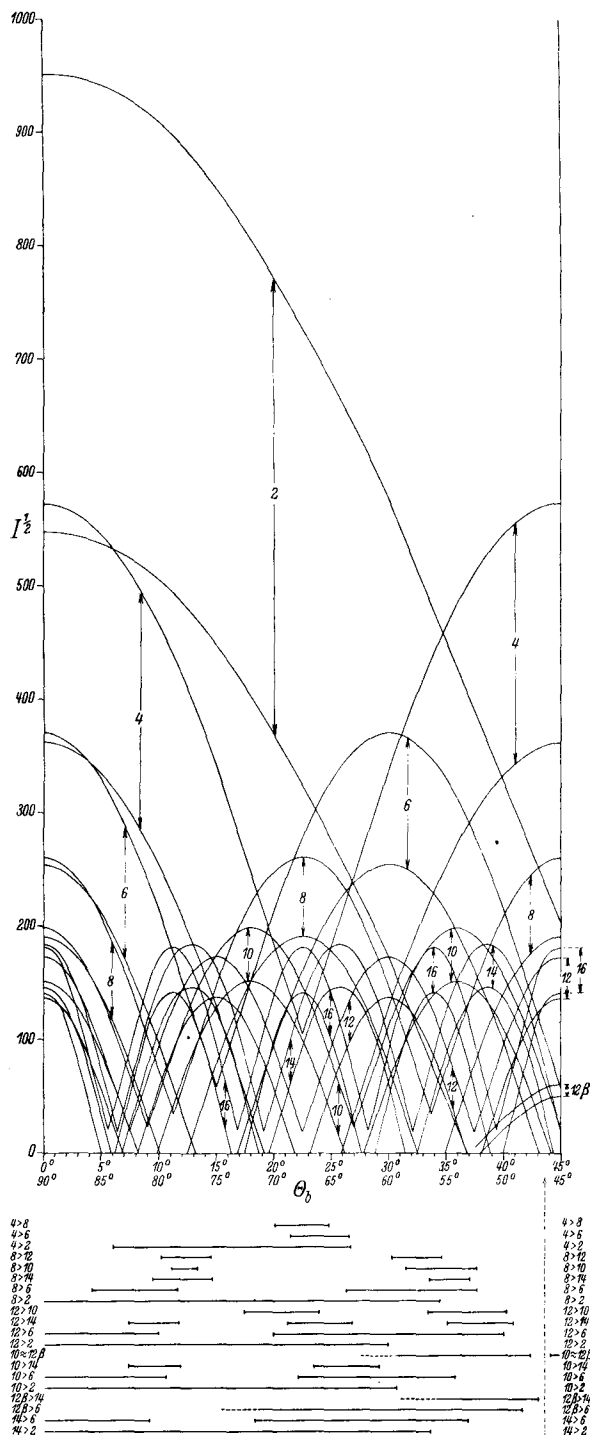


Fig. 2. Variations of intensity of the orders of 010 ($Cu-K_{\alpha+\beta}$ radiation) with the anti-monymy parameter, θ_b , and parameter regions eliminated by observed intensity relations. The half-widths of the bands represent the intensity uncertainties due to the initial uncertainty in the positions of the oxygen atoms.

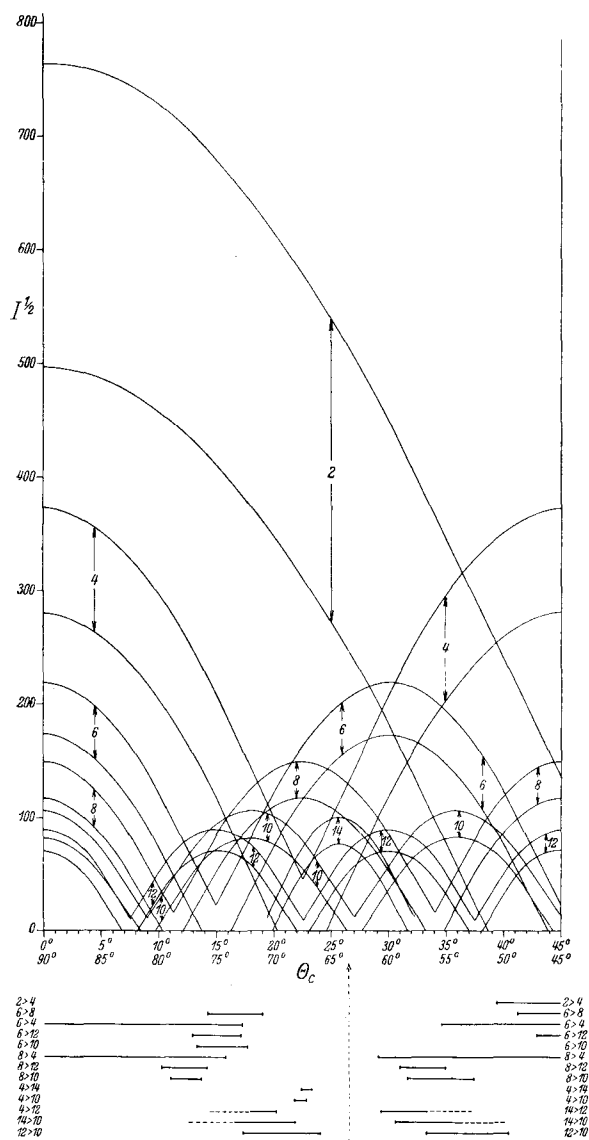


Fig. 3.

Variations of intensity of the orders of 001 ($Mo-K_\alpha$ radiation) with the antimony parameter, θ_c , and parameter regions eliminated by observed intensity relations. The half-widths of the bands represent the intensity uncertainties due to the initial uncertainty in the positions of the oxygen atoms.

series comparable with one of these regularities namely, regular decline with alternate absences, but only for one pinacoid reflection series, 010; other series are distinctly irregular. The antimony atoms can accordingly occupy only the general 8-fold position. The meaning of the regular decline of even order reflections from (010) with alternate absences is obviously that the antimony atoms are arranged in sheets parallel to (010) which are spaced approximately one quarter of the b identity period apart. This would give an antimony y parameter of approximately $\frac{1}{8}$.

Antimony parameters. Antimony has such a large atomic number, 51, compared with oxygen, 8, that the scattering power of the antimony dominates the character of the spectra. It is therefore possible to very approximately locate the parameters of the single set of antimony atoms in the general position irrespective of the position of the oxygen atoms. The determination of these parameters is shown graphically in Figs. 1, 2, and 3. In these diagrams the square roots of the intensities of the observable orders of pinacoid reflections are plotted against θ_a , θ_b and θ_c , the angular parameters along the a , b , and c crystallographic axes. The antimony contributions to the intensities impart the general appearances to the intensity variations with parameter, and the oxygen contributions, being unknown at this stage of the investigation, are given their widest possible values. Instead of the usual cosine curves representing the variation of amplitude with position, therefore, the figures show bands whose centers are these cosine curves, and whose widths cover the intensity uncertainties in both directions due to the preliminary lack of knowledge of the oxygen positions.

Because of the great length of the b axis, 12.46 Å, it is possible to record 34 orders of reflection from (010) with $Mo-K_\alpha$ radiation. It is therefore possible to refine the y parameter of antimony to a very accurate value, irrespective of the positions of the oxygen atoms. This is carried out graphically in figure 4.

Since the space group provides for halved spacings of all the pinacoid sheets, only even orders of pinacoid reflections appear. This absence of odd order reflections gives rise to two solutions for each parameter value. With the eliminations shown in figures 1, 2, 3, and 4, these approximate solutions are:

$$\theta_a = 16^\circ \text{ and } 74^\circ, \quad \theta_b = 43.8^\circ \text{ and } 46.2^\circ, \quad \theta_c = 26\frac{1}{2}^\circ \text{ and } 63\frac{1}{2}^\circ.$$

The incorrect value of each of these pairs may be eliminated by a consideration of more general spectra involving odd values of h , k , and l , respectively.

The structure factor for $hk0$ reflections for odd values of h is $-8 \sin h\theta_a \sin k\theta_b$. When h is 5, this is a maximum at 18° and zero at 72° . Since the spectral series $5k0$ forms one of the strongest festoons on the Weissenberg c axis equator photograph, it may be safely concluded that the correct value of θ_a is approximately 16° , not 74° .

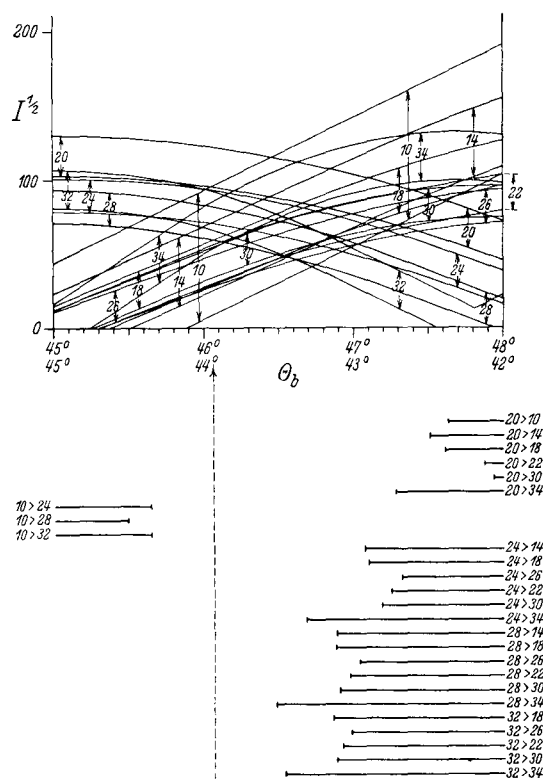


Fig. 4. Variations of intensity of the higher orders of 010 ($Mo-K_\alpha$ radiation) with the antimony parameter, θ_b , and parameter regions eliminated by observed intensity relations. The half-widths of the bands represent the intensity uncertainties due to the initial uncertainty in the positions of the oxygen atoms.

To eliminate the incorrect value of θ_b , the structure factor may be applied to $h \cdot 29.0$ and $h \cdot 34.0$. For these we have:

$$\begin{aligned} \text{at } 43.8^\circ & \begin{cases} \sin(29 \times 43.8^\circ) = \sin 1270^\circ = \sin(-190^\circ): \text{almost zero.} \\ \sin(34 \times 43.8^\circ) = \sin 1358^\circ = \sin(-82^\circ): \text{almost a maximum.} \end{cases} \\ \text{at } 46.2^\circ & \begin{cases} \sin(29 \times 46.2^\circ) = \sin 1340^\circ = \sin(-90^\circ): \text{almost a maximum.} \\ \sin(34 \times 46.2^\circ) = \sin 1432^\circ = \sin(-8^\circ): \text{almost zero.} \end{cases} \end{aligned}$$

