

The Crystal Structure of MgZn_2

Thesis by

James B. Friauf

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Abstract

Crystals of the intermetallic compound, $MgZn_2$, were prepared and the crystal structure was determined from x-ray data furnished by Laue and rotation photographs. The crystal was found to have hexagonal axes with $a_0 = 5.15A$ and $c_0 = 8.48A$. The unit cell contains four molecules. The effect of absorption in the crystal in determining the wave-length giving a maximum intensity of reflection in Laue photographs was used to confirm the dimensions of the unit cell. The atoms have the positions:

$$\begin{aligned} \text{Zn: } & u, \bar{u}, \frac{1}{4}; 2\bar{u}, \bar{u}, \frac{1}{4}; u, 2u, \frac{1}{4}; \bar{u}, u, \frac{3}{4}; 2u, u, \frac{3}{4}; \bar{u}, 2\bar{u}, \frac{3}{4}; \\ & 0, 0, 0; 0, 0, \frac{1}{2} \end{aligned}$$

$$\text{Mg: } \frac{1}{3}, \frac{2}{3}, v; \frac{1}{3}, \frac{2}{3}, \frac{1}{2} - v; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + v; \frac{2}{3}, \frac{1}{3}, \bar{v}$$

where $u = .830$ and $v = .062$. The least distance between two magnesium atoms is $3.16A$, between two zinc atoms, $2.52A$, and between a magnesium and a zinc atom, $3.02A$.

The constitution diagram for the binary system, magnesium-zinc^{1,2} has a pronounced maximum corresponding

1) Grube, Z. anorg. Chem., 49, 80 (1906).

2) Bruni and Sandonnini, Z. anorg. Chem., 78, 276 (1912).

to the formation of an intermetallic compound, $MgZn_2$, which forms eutectics with both constituents. Since both magnesium and zinc crystallize in the hexagonal close packed arrangement, a determination of the crystal structure of their compound was thought to be of interest.

Crystals of the compound were formed by melting together the calculated amounts of magnesium and zinc under a molten mixture of sodium and potassium chlorides to prevent oxidation. The melt was then allowed to cool slowly in the electric furnace, about four hours being taken to cool from ten degrees above to ten degrees below the melting point of the compound, $595^{\circ}C$. In this way a mass of crystals was obtained from which individual crystals were separated for the production of Laue and spectral photographs.

Two rotation photographs taken with the x-rays from a molybdenum water cooled tube on an x-ray spectrograph

of the kind described by Wyckoff³, furnished data for

3) The Structure of Crystals (New York, 1924), p. 164.

the determination of the size and shape of the unit cell. As no information on the crystal class or axial ratio of crystals of this compound was found in the literature, a consideration of the secondary spectra as well as of the principal spectrum was necessary in order to obtain the quadratic form which gives the spacings of the planes. These spacings can be computed from the positions of the reflections on the plate and furnish information of the same nature as that available from a powder photograph, the difference being that in a rotation photograph taken with the crystal turning about a definite axis, the reflections occur in spots instead of in complete circles as they would in a powder photograph taken on a plate. Furthermore, due to the limited rotation of the crystal (30° in this case) certain planes will never reach a position to reflect, while in a powder photograph reflections are to be expected from all planes having a suitable spacing.

Table I gives the data from a rotation photograph. The observed spacings are the means of those calculated from the reflections produced by the K_α doublet and the

K_{β} line of molybdenum for all the planes of the same form showing on the plate. These spacings were compared with the charts given by Hull and Davey,⁴ and

4) Phys. Rev., 17, 549 (1921).

were found to agree with the spacings for a hexagonal unit cell having $a_0 = 5.15\text{\AA}$ and $c_0 = 8.48\text{\AA}$. Since the crystal was rotated about one of the a_0 axes for this photograph, the assignment of indices obtained from the chart was checked by comparing the computed and observed values for the x and y co-ordinates of the spots. The fact that certain reflections could not occur due to the limited rotation of the crystal could also be used in some cases to distinguish between planes having nearly the same spacings. On another photograph taken with the crystal rotating about the c_0 axis, only the principal spectrum was measured. This gave $a_0 = 5.15\text{\AA}$ which is in agreement with the value just given. The third column of the table gives the values for the spacings computed from the dimensions of the unit cell.

This unit cell agrees with the data from Laue photographs taken with the white radiation from a tungsten target. When the wave-lengths of the x-rays

producing the spots on symmetrical and unsymmetrical Laue photographs were calculated on the basis of this unit cell, no values were found less than the short wave-length limit, about .24A, of the x-rays used. The curves showing the intensity of reflection from different planes of the same form reflecting at different wave-lengths in unsymmetrical Laue photographs, start from the short wave-length limit, rise to a maximum between .36A and .40A, and then decrease for longer wave-lengths. The presence of a maximum intensity so far below the wave-length of the silver absorption edge is due to absorption in the crystal. The photographic intensity, I, of the white radiation from a tungsten target operated at 50 kv can be approximately represented⁵ between the short wave-length limit, λ_0 .

 5) Wyckoff, The Structure of Crystals (New York, 1924), p. 142.

and the wave-length of the silver absorption edge, .485A, by the equation

$$I = B (\lambda - \lambda_0)$$

where B is a constant. This must be modified, however, if the crystal is strongly absorbing as is the case with MgZn₂. For a first approximation it can be assumed that

all the rays producing spots on a Laue photograph are absorbed for a distance equal to the thickness of the crystal. The absorption coefficient of the crystal can be computed from data given by Richtmeyer and Warburton⁶ for the atomic scattering and fluorescent

 6) Phys. Rev., 22, 539 (1923).

absorption coefficients. Since the absorption due to scattering is small and nearly independent of the wave-length,⁶ it will have no other effect than to decrease the value of the constant, B, but the fluorescent absorption, which is proportional to the cube of the wave-length, will cause greater weakening of the longer wave-lengths and the maximum intensity is accordingly shifted to the short wave-length side of the silver absorption edge. The density of the crystal, 5.16, its thickness, about .3mm, and the computed absorption coefficient give

$$I' = B' (\lambda - \lambda_0) e^{-2.2\lambda^3}$$

where I' is the photographic intensity of the white radiation after passing through the crystal, and B' is the constant, B, multiplied by the factor which represents the common decrease in intensity of all wave-lengths due to scattering. The curve given by

this equation has a maximum at .36A and agrees in form with the curves showing the intensity of reflection as a function of the wave-length, thus furnishing additional evidence for the correctness of the unit cell chosen.

The density of $MgZn_2$ was determined by weighing in a specific gravity bottle after breaking the sample into small pieces in order to avoid, as far as possible, the inclusion of blowholes. Two determinations gave 5.164 and 5.155. Using the value 5.16 for the density, the computed number of molecules in the unit cell was found to be 3.93, the deficiency from the integral number, 4, doubtless being due to the fact that the density determined by the use of a specific gravity bottle is likely to be less than the density determined by x-ray measurements unless porosity of the sample can be completely eliminated.

Smaller unit cells, containing 1, 2, or 3 molecules were found to be inconsistent with the data available.

A Laue photograph taken with the incident beam of x-rays parallel to the principal axis of the crystal had a six-fold symmetry axis intersected by six planes of symmetry. The space-group giving the arrangement of atoms in the crystal must consequently be isomorphous with one of the point-groups D_3^h , C_6^v , D_6 , or D_6^h . Reference to a tabulation of the results of the theory of

space-groups⁷ shows the possible ways of arranging four

7) Wyckoff, The Analytical Expression of the Results of
the Theory of Space Groups (Washington, 1922).

magnesium and eight zinc atoms in the unit cell. If it is assumed that the magnesium atoms are equivalent and that the zinc atoms are likewise equivalent, the possible arrangements are those which can be obtained from the space-groups D_{6h}^2 and D_{6h}^3 since these are the only space-groups considered having a group of eight equivalent positions. All these arrangements give zero for the amplitude factor of the first order reflection from 04.1. The data given in Table II for an unsymmetrical Laue photograph show, however, that 04.1 gives a strong first order reflection. These arrangements are consequently inadmissible and the assumption of equivalence of chemically like atoms must be relinquished. With the freedom of choice thus allowed there are numerous ways of arranging the atoms. The zinc atoms may be in two groups of four equivalent positions, two groups of six and two equivalent positions, or in some other combination giving the required number of atoms. The number of possible combinations for the magnesium atoms is somewhat less. The choice of the correct atomic

arrangement is simplified by the observation that many of the groups of six equivalent positions lie in a plane parallel to the base of the unit cell. If, however, six zinc atoms which constitute more than half the reflecting power of all the atoms contained in the unit cell, are arranged in such a plane, the absence of odd order reflections from 00.1 and the observation that the fourth order reflection from 00.1 is stronger than the second order cannot be satisfactorily explained. Groups of six equivalent positions having such an arrangement are consequently excluded from further consideration.

No ways of arranging four magnesium and eight zinc atoms in the unit cell can be obtained from the space-groups D_6^2 , D_6^3 , D_6^4 , or D_6^5 since none of these space-groups contains the requisite number of equivalent positions. All the arrangements that can be derived from the space-groups D_{3h}^2 , C_{6v}^2 , C_{6v}^3 , D_{6h}^2 , and D_{6h}^3 can be readily eliminated since for each of these space-groups, each group of eight or less equivalent positions (and hence any combination of them) gives zero for the amplitude factor of the first order reflection from 04.1. Such arrangements are consequently inconsistent with the data. With the restriction that has been made as to the character of the groups of six equivalent positions to be considered, all the arrangements that can be derived from the

space-groups C_{6v}^1 , D_6^1 , and D_{6h}^1 give the same amplitude factors for 34.3 and 16.3, and since the data show that the more complicated plane, 16.3, gives a stronger reflection, such arrangements are inadmissible. A number of three or four parameter structures which cannot be so readily eliminated may be obtained from the space-groups D_{3h}^1 and D_{3h}^3 , but none of these seems to offer the slightest possibility of accounting for the observed intensity relations.

The only structures remaining to be considered are those arising from the space-groups D_{3h}^4 , C_{6v}^4 , D_6^6 , and D_{6h}^4 . Of the structures which can be obtained from the space-groups D_6^6 and D_{6h}^4 , the only one not conflicting with the data is that in which the atoms have the following positions:

$$\text{Zn: } u, \bar{u}, \frac{1}{4}; 2\bar{u}, \bar{u}, \frac{1}{4}; u, 2u, \frac{1}{4}; \bar{u}, u, \frac{3}{4}; 2u, u, \frac{3}{4}; \bar{u}, 2\bar{u}, \frac{3}{4}; \\ 0, 0, 0; 0, 0, \frac{1}{2}$$

$$\text{Mg: } 1/3, 2/3, v; 1/3, 2/3, \frac{1}{2}-v; 2/3, 1/3, \frac{1}{2}+v; 2/3, 1/3, \bar{v}.$$

This arrangement is obtained by placing the magnesium atoms in one group of four equivalent positions and the zinc atoms in two groups of six and two equivalent positions. A consideration of the type of structure involved shows that it is sufficient to consider only values of the parameters satisfying the conditions $0 \leq u \leq .5$ and $-.25 \leq v \leq .25$. If it is assumed that there

is a reasonable distance between the two magnesium atoms in the same vertical line, v will be restricted to the middle half of this range.

The amplitude factor, S , is computed from

$$S = \sqrt{A^2 + B^2}$$

where A and B have their usual significance of sine and cosine summations,⁸ and is zero for first order reflections

8) Wyckoff, The Structure of Crystals (New York, 1924),
p. 107.

from planes of the forms $hh.2p+1$ irrespective of the values of u and v . No first order reflections from any such planes were found on any of the Laue photographs although planes of the forms 22.1, 33.1, 44.3, 55.3, and 44.5 were in a position to give first order reflections at a favorable wave-length. Another characteristic feature of this structure is that the magnesium atoms contribute nothing to the amplitude factors for first order reflections from planes of the forms $03h.2p+1$. The intensities of such reflections are consequently useful in determining the positions of the zinc atoms. Of the observed planes of this kind, 03.1 was found to give a weak first order reflection while no reflections were found from 06.5 and 09.5 although planes of both

these forms were in a position to reflect at favorable wave-lengths and reflections were observed from more complicated planes. The value of the parameter, u , must consequently be such as to give only a small value to the amplitude factors for these planes. By plotting these amplitude factors as a function of the parameter it is readily seen that the only values of u which will reduce them all to zero are 0, $1/6$, $1/3$, and $1/2$. While u cannot be equal to one of these values because of the weak reflection from 03.1, it can hardly be much different from them because of the rapidity with which the amplitude factors change. Consideration of the amplitude factors for other planes shows that the only values of u giving general agreement with the requirements of the Laue data are those in the neighborhood of $u = 1/6$.

With this restriction on the value of u , some information concerning v can be obtained from a consideration of the intensity relations for the planes 26.3, 26.5, and 26.7. The amplitude factors for the first order reflections from these planes are:

$$26.3 \quad S = 2Zn(\sin 28\pi u - \sin 8\pi u - \sin 20\pi u) + 4Mg \sin 60^\circ \sin 6\pi v$$

$$26.5 \quad S = 2Zn(\sin 28\pi u - \sin 8\pi u - \sin 20\pi u) - 4Mg \sin 60^\circ \sin 10\pi v$$

$$26.7 \quad S = 2Zn(\sin 28\pi u - \sin 8\pi u - \sin 20\pi u) + 4Mg \sin 60^\circ \sin 14\pi v.$$

The first part, due to the zinc atoms, is the same for all three planes, positive for values of u near $1/6$,

and changes only slightly for small changes in the value of u . As the data show that 26.5 is stronger than 26.3 it must have a larger amplitude factor since it is a more complicated plane. Also, since 26.7 is a more complicated plane than 26.3 and gives an equally strong reflection, it must have a greater amplitude factor than 26.3. These conditions are satisfied by giving v a small negative value. A consideration of the intensity relations for the planes 08.3, 08.5, and 08.7 leads to the same conclusion.

With the values of u and v restricted in this way it was found by trial that satisfactory agreement with the data was obtained for $u = .170$ and $v = -.062$. The extent of the agreement is shown in Table II which gives the data from an unsymmetrical Laue photograph. The table shows the spacing of the plane producing the reflection in A. U., the intensity as estimated visually by comparison with a plate which had been given a series of graduated exposures, the product of the order of reflection by the wave-length producing the reflection, and the amplitude factor computed for the values of the parameters given on the assumption that the reflecting powers of the zinc and magnesium atoms are proportional to their atomic numbers. In comparing the intensities of two planes, if the plane with the smaller spacing

gives the greater intensity under comparable conditions of wave-length, it must have a greater amplitude factor. As previously stated, the maximum intensity falls between .36A and .40A and the intensities in the table have been given in this region when possible.

This two parameter structure is the simplest which will give agreement with the data available. The only other possible structures are a three parameter structure derived from D_{3h}^4 and a five parameter structure derived from C_{6v}^4 . Neither of these can be eliminated since suitable values for the parameters reduces each to the two parameter structure which has been found to give agreement with the data. A consideration of these two more general structures indicates, however, that neither will give satisfactory agreement with the data except for values of the parameters which reduce them to forms closely approaching that of the two parameter structure, and it is consequently concluded that this structure or a more general structure so similar as to be indistinguishable from it, represents the crystal structure of $MgZn_2$ when u and v have the values given.

This structure can be described in an alternative way without the use of a negative parameter by setting $u = .830$ and $v = .062$. Figure 1 shows the arrangement of atoms in the unit cell. The least distance between

two magnesium atoms is 3.16A, between two zinc atoms, 2.52A, and between a magnesium and a zinc atom, 3.02A. The values computed from the atomic radii determined from the crystal structures of magnesium and zinc are respectively 3.22A, 2.67A, and 2.95A.

In conclusion, the writer wishes to express his thanks to Dr. R. G. Dickinson for reading the manuscript and suggesting some modifications.

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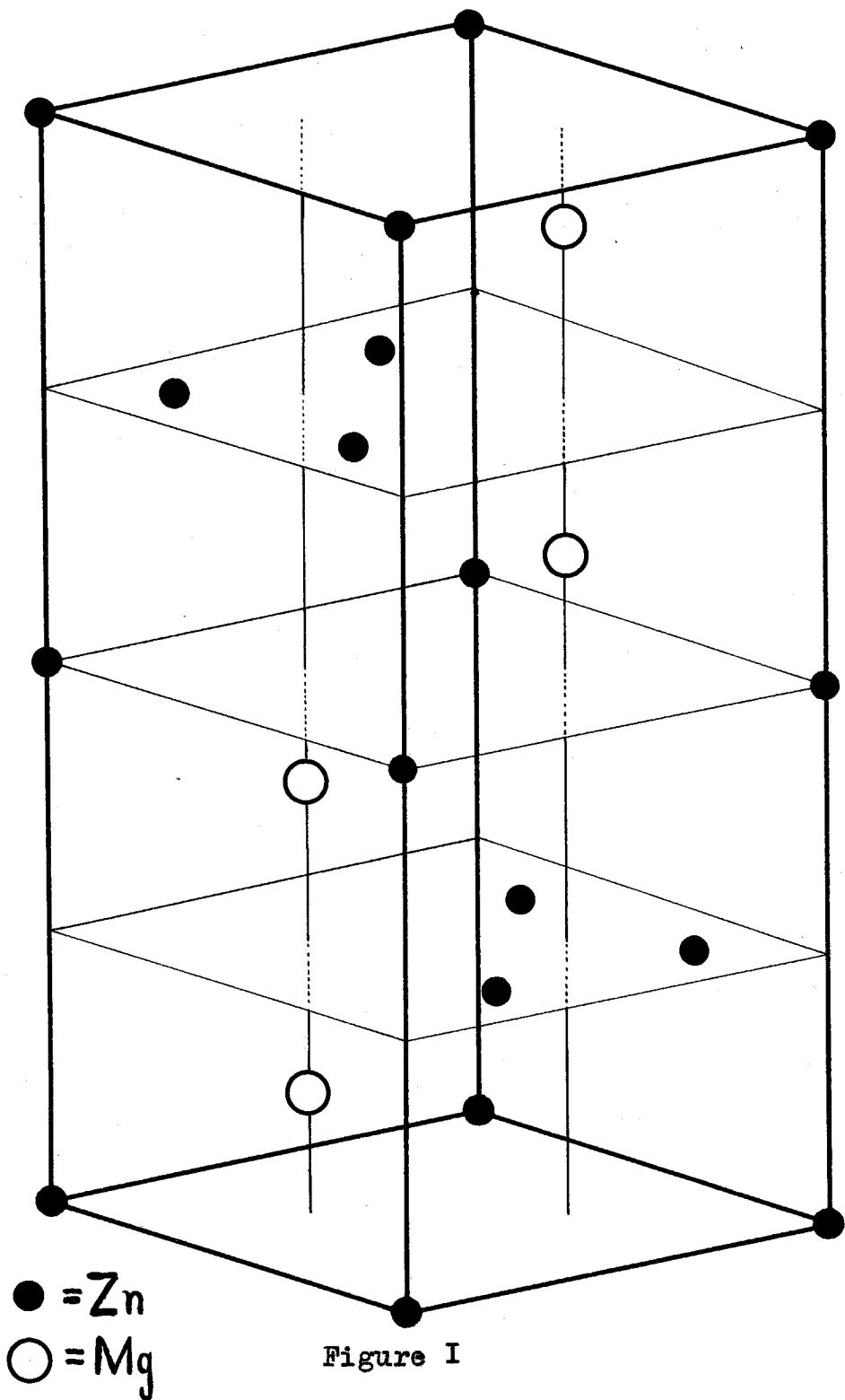
Table I

Plane	Observed Spacing in A. U.	Calculated Spacing
00.1(2)	4.241	4.240
10.3	2.377	2.388
11.2	2.204	2.201
00.1(4)	2.122	2.120
10.1(2)	1.966	1.974
10.4	1.916	1.915
20.3	1.746	1.751
12.1	1.658	1.653
12.3	1.449	1.448
00.1(6)	1.411	1.413
20.5	1.351	1.350
12.4	1.321	1.320
11.6	1.244	1.239
20.6	1.198	1.194
20.7	1.071	1.065
00.1(8)	1.062	1.060

Hexagonal axes, $a_0 = 5.15\text{\AA}$, $c_0 = 8.48\text{\AA}$, $c_0/a_0 = 1.646$

Table II

Plane	Spacing	Intensity	$n\lambda$	Amplitude Factor
12.1	1.65	32	.37	31
03.1	1.46	4	.46	15
13.1	1.22	20	.36	38
04.1	1.10	90	.43	171
02.1(2)	1.08	70	.76	132
23.1	1.01	12	.41	46
23.2	.99	6	.37	30
14.2	.95	60	.36	153
05.3	.85	11	.38	77
33.2	.84	36	.38	152
24.1	.84	28	.31	170
24.3	.81	23	.40	116
12.2(2)	.78	3	.91	29
15.3	.77	11	.43	83
15.4	.75	12	.41	98
03.1(2)	.73	8	.75	83
34.3	.71	4.2	.39	77
25.2	.70	10	.36	155
03.2(2)	.70	50	.77	237
34.4	.69	8	.37	111
16.3	.66	5	.39	98
16.4	.65	3	.36	72
07.3	.62	5	.37	108
35.3	.62	4.8	.38	89
35.4	.61	3	.43	84
26.3	.60	5	.36	114
22.3(2)	.58	6	.80	149
26.5	.58	10	.35	191
07.6	.58	2.5	.41	71
13.3(2)	.57	9	.74	164
35.7	.56	1.4	.44	68
26.7	.55	5	.42	136
08.3	.55	2.5	.30	113
17.6	.54	2.5	.36	83
08.5	.53	5	.35	192
04.3(2)	.51	5	.73	164
18.4	.50	1	.32	108
08.7	.50	2.5	.36	134
46.5	.49	3	.36	190
27.8	.48	1	.38	149
46.7	.47	1	.34	134



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The Crystal Structure of Tetragonal Lead Monoxide

By Roscoe G. Dickinson and James B. Frauf

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THE CRYSTAL STRUCTURE OF TETRAGONAL LEAD MONOXIDE

BY ROSCOE G. DICKINSON AND JAMES B. FRIAUF

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Lead monoxide, PbO , may be prepared in two modifications, a yellow, rhombic form and a red, tetragonal form. Of these the former is the more stable^{1,2} at higher, and the latter more stable at ordinary temperatures. It has been suggested³ that the differences between these forms are due simply to a difference in state of subdivision; but this hypothesis

¹ Geuther, *Ann. Chem.*, **219**, 56 (1883).

² Ruer, *Z. anorg. Chem.*, **50**, 265 (1906).

³ Glasstone, *J. Chem. Soc.*, **119**, 1689, 1914 (1921).

is not regarded⁴ as tenable in the face of a difference in solubility determined both gravimetrically and electrometrically and in the face of crystallographic evidence. Moreover, the two forms have been found⁵ to give quite different X-ray powder diagrams.

Apparently no goniometrical measurements of the red modification have been published, but the fact that it gives optically uni-axial, rectangular plates places it in the tetragonal⁶ system. The present paper describes an X-ray investigation of the structure of the tetragonal modification.

Method of Experimentation

One part¹ of lead hydroxide was melted with five parts of potassium hydroxide and the melt allowed to cool slowly in a covered iron crucible. After treatment with water, some very thin red crystals remained. Examination between crossed Nicols showed these to be basal plates.

The angles of reflection of the molybdenum K radiation from the base (001) and from the planes (100) and (110) were measured photographically;⁷

TABLE I
SPECTRAL DATA FROM TETRAGONAL LEAD OXIDE

<i>h k l</i>	Line	Observed angle of reflection	$\frac{d}{n}$	Relative intensities ^a	
(001)	Mo K α	4° 2'	$\frac{1}{1} \times 5.050$	mw	
	γ	7 6	$\frac{1}{2} \times 5.014$	w	
	β	7 14	$\frac{1}{2} \times 5.013$	m	
	α_1	8 7	$\frac{1}{2} \times 5.013$	s	
	α_2	8 11	$\frac{1}{2} \times 5.004$	s	
	α_1	12 14	$\frac{1}{3} \times 5.011$	vw	
	α_2	12 19	$\frac{1}{3} \times 5.008$	vw	
	γ	14 20	$\frac{1}{4} \times 5.006$	vw	
	β	14 36	$\frac{1}{4} \times 5.007$	mw	
	α_1	16 25	$\frac{1}{4} \times 5.009$	ms	
	α_2	16 31	$\frac{1}{4} \times 5.010$	m	
	(100)	γ	8° 57'	$\frac{1}{2} \times 3.983$	w
		β	9 8	$\frac{1}{2} \times 3.976$	ms
		α	10 15	$\frac{1}{2} \times 3.990$	s
(110)	β^b	6° 26'	$\frac{1}{1} \times 2.816$	ms	
	α	7 13	$\frac{1}{1} \times 2.826$	s	
	γ	12 43	$\frac{1}{2} \times 2.815$	w	
	β	12 56	$\frac{1}{2} \times 2.820$	m	
	α	14 34	$\frac{1}{2} \times 2.823$	ms	

^a The abbreviations are: s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak.

^b The line γ slightly overlapped β .

⁴ Applebey and Reid, *J. Chem. Soc.*, **121**, 2129 (1922).

⁵ Kohlschütter and Scherrer, *Helvetica Chim. Acta*, **7**, 337 (1924).

⁶ Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, vol. 1, p. 77.

⁷ The X-ray methods used have already been described; Dickinson, *THIS JOURNAL*, **44**, 276 (1922).

the reflections from the last two planes were obtained by transmission of the beam through a basal plate. The data from these photographs are given in Table I. A number of symmetrical and unsymmetrical Laue photographs were taken through (001). To secure proper coördination of all these photographs in the absence of good face-development, a symmetrical Laue photograph and reflections from (110) and (100) were made with the same crystal.

The Unit of Structure

Application of the equation $n\lambda = 2d \sin \theta$ to the data of Table I shows that $d_{001} = 5.01 \text{ \AA.}$ or a multiple of this value. Prior to a structure determination the indices of (100) and (110) may be interchanged. If this is done, then $d_{100} = 2.82 \text{ \AA.}$ or a multiple of this value. The smallest possible unit of structure thus has the dimensions $2.82 \times 2.82 \times 5.01$; taking the density⁸ as 9.27, the number of PbO in this unit is found to be 1.003. But if Laue photographic spots are assigned indices referred to the axes of this unit, the values of $n\lambda$ calculated for them using the

equation $n\lambda = \frac{2d_{001} \sin \theta_{hkl}}{\sqrt{(h^2 + k^2) c^2 + l^2}}$ where $c = d_{001}/d_{100}$, are often found much

lower than the shortest wave length, 0.23 \AA. , which could have been present in the spectrum (the peak voltage was about 53 kv.). This unit is therefore impossible. Any larger unit differing from this one only by having d_{001} a multiple of 5.01 \AA. is impossible for the same reason. When, however, the directions of the axes are taken in accord with the indices of Table I, d_{100} becomes 3.99 \AA. or a multiple of this value. The number of PbO in a unit $3.99 \times 3.99 \times 5.01$ is two, and the Laue photographic data do not conflict with this unit. There is thus no evidence necessitating the assumption of a larger unit.

The Arrangement of the Atoms

On all the Laue photographs examined no plane having $h + k + l$ odd was found to give more than a weak reflection in the first order. Since the reflecting power of the lead atoms must be far greater than that of the oxygen atoms, the weakness of this type of reflection must arise from interference between the lead atoms themselves, rather than from interference between the lead and oxygen atoms. It can readily be shown that the only arrangement of two lead atoms in a unit such that the contribution of the lead atoms to first order reflections from planes having $h + k + l$ odd is zero is the body-centered arrangement; consequently, the lead atoms must have at least approximately this arrangement.

If the lead atoms have precisely the body-centered arrangement, the

⁸ Ref. 4, p. 2132.

reflections of odd order from (001) must be due to the oxygen atoms alone. But reference to a tabulation⁹ of the coördinates of possible positions¹⁰ in the unit of structure shows that, if the lead atoms are given the non-variant body-centered arrangement, there is no way of placing the oxygen atoms with any tetragonal space-group symmetry in such a way as to give the odd orders from (001). Consequently the lead atoms must have an arrangement which involves one or more parameters and which is capable of approximating the body-centered arrangement when suitable values are given the parameters. There is only one such arrangement: $(0 \frac{1}{2} u) (\frac{1}{2} 0 \bar{u})$, where¹¹ u is near 0.25. The oxygen atoms may then have any of the arrangements: (a), $(0 0 u) (0 0 \bar{u})$; (b), $(0 0 0) (\frac{1}{2} \frac{1}{2} 0)$; (c), $(0 \frac{1}{2} v) (\frac{1}{2} 0 \bar{v})$.

Arrangement (a) is rendered improbable by the absence of the first-order reflection from (100) on the spectral photographs.

The values of the structure factor, S , for first-order reflections from arrangements (b) and (c) are given by

Arrangement (b)	$h + k$ even.	$S = 2(-1)^h \text{Pb} \cos 2\pi l u + 2 \text{O}.$
	$h + k$ odd.	$S = 2\text{Pb} \sin 2\pi l u.$
Arrangement (c)	$h + k$ even.	$S = 2\text{Pb} \cos 2\pi l u + 2 \text{O} \cos 2\pi l v.$
	$h + k$ odd.	$S = 2\text{Pb} \sin 2\pi l u + 2 \text{O} \sin 2\pi l v.$

Planes of the forms $\{241\}$, $d = 0.878$, and $\{041\}$, $d = 0.980$, were found to reflect more strongly than those of the forms $\{331\}$, $d = 0.924$, and $\{131\}$, $d = 1.223$. As all of these are planes having $h + k$ even and the same value of l , arrangement (c) gives them all the same structure-factor and is hence ruled out. The structure-factor for these planes for arrangement (a) is shown in Fig. 1 for values of u near 0.25. The above intensity relations evidently necessitate taking u slightly below 0.25. However, the value of u cannot be as low as 0.23 for $\{075\}$, $d = 0.496$, reflected considerably more strongly than $\{546\}$, $d = 0.500$. The value of u must, therefore, be close to 0.24. It will be noted that this conclusion is not dependent on any quantitative assumption as to the relative reflecting powers of atoms of lead and of oxygen.

In Table II are given representative data from one Laue photograph; in the last column of this table are given values of the structure-factor calculated for arrangement (a) placing u equal to 0.24 and placing the reflecting powers proportional to the atomic numbers. We have found no data in conflict with this arrangement.

⁹ Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Washington, *Carnegie Inst. Pub.*, **318**, pp. 73-102.

¹⁰ The assumption is made here that all of the lead atoms are in equivalent positions and likewise all of the oxygen atoms.

¹¹ The value $u = 0.75$ also satisfies the conditions but leads to the same possible structures.

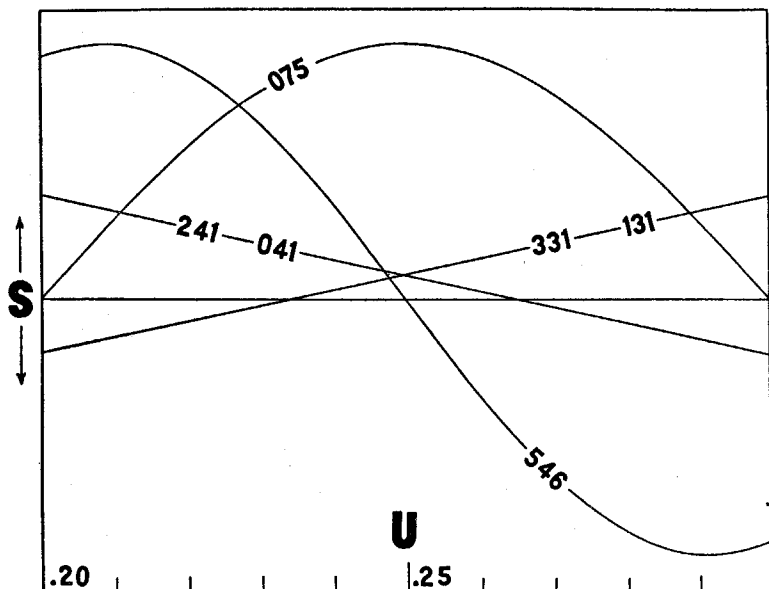


Fig. 1.—Values of the structure factor S plotted against u ; the oxygen atoms have arrangement (a).

TABLE II

LAUE PHOTOGRAPHIC DATA; INCIDENT BEAM 18° FROM PERPENDICULAR TO (001)

Plane	Inter-planar distance	Wave length	Estimated intensity	S for $u=0.24$	Plane	Inter-planar distance	Wave length	Estimated intensity	S for $u=0.24$
$\bar{1}31$	1.222	0.34	faint	6	$\bar{1}54$	0.664	0.40	0.7	143
312	1.128	.33	8	179	$\bar{3}52$.660	.29	1.0	179
$\bar{4}10$	0.968	.40	0	0	$\bar{3}52$.660	.36	1.1	179
$\bar{3}31$.925	.41	0	6	$\bar{1}61$.651	.33	1.1	164
$\bar{2}41$.878	.37	0.1	26	$\bar{6}21$.625	.38	0	26
413	.838	.36	3	161	525	.596	.37	0.4	156
431	.788	.38	2.5	164	$\bar{6}31$.591	.30	.5	164
243	.787	.30	0.1	15	445	.577	.33	.05	67
$\bar{5}10$.782	.34	2.5	148	$\bar{0}71$.567	.32	.5	164
$\bar{1}50$.782	.36	2.7	148	355	.565	.33	.05	35
$\bar{5}10$.782	.45	1.2	148	$\bar{7}11$.561	.37	.00	6
$\bar{2}50$.742	.39	0	0	605	.555	.34	.05	67
053	.720	.34	1.6	161	165	.550	.36	.2	156
$\bar{1}53$.709	.39	0.1	47	172	.550	.38	.3	179
$\bar{3}50$.684	.39	1.2	148	536	.530	.37	.1	169
$\bar{5}31$.678	.34	0	6	273	.522	.41	.1	161
$\bar{5}23$.678	.30	1.0	161	635	.512	.36	.1	156
434	.674	.32	0.1	41	546	.500	.31	faint	60
504	.674	.38	.1	41	075	.497	.30	0.1	156
514	.664	.33	1.0	143					

Discussion of the Structure

The structure obtained for lead oxide is shown in Fig. 2. This structure is derivable from any of the space-groups: V_d^3 , C_{4h}^3 , D_4^2 , D_{4h}^7 . In it the

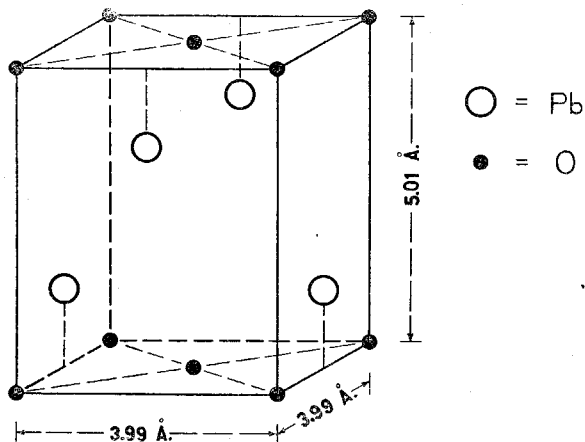


Fig. 2.—Arrangement of the atoms in tetragonal PbO.

shortest distance between lead and oxygen atoms is 2.33 Å. The arrangement of layers of atoms parallel to (001) is shown in Fig. 3. The distance

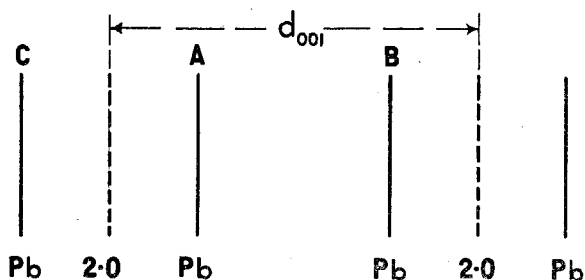


Fig. 3.—Arrangement of atom-planes parallel to (001) in tetragonal PbO.

between the nearest lead atoms in layers A and B is 3.84 Å., while the distance between the nearest lead atoms of layers A and C is 3.71 Å.; the lead atoms are thus closer together when there is a layer of oxygen atoms between them than when there is not.

Summary

The crystal structure of red lead monoxide, PbO, has been determined, using X-ray spectral photographs and Laue photographs. It is found that there are 2 PbO in a tetragonal unit of structure having $d_{100} = 3.99$

and $d_{001} = 5.01 \text{ \AA}$. The oxygen atoms are at $(000) (\frac{1}{2} \frac{1}{2} 0)$, and the lead atoms at $(0 \frac{1}{2} u) (\frac{1}{2} 0 \bar{u})$ with $u = 0.24$.

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THE DESIGN OF A CAM FOR AN X-RAY SPECTROGRAPH

BY

JAMES B. FRIAUF

THE DESIGN OF A CAM FOR AN X-RAY SPECTROGRAPH

JAMES B. FRIAUF

In photographing x-ray spectra by the rotating crystal method it is frequently desirable that the crystal be given such an oscillatory motion that it rotates through a given angle with constant angular velocity, then reverses its direction of rotation and returns with the same constant speed. The same type of motion may be useful in other cases and can be obtained from a suitably designed cam rotating with constant angular velocity. This article contains an account of an analytical method which enables the computation of the proper profile for the cam. This could also be done by graphical construction which was the method used for the spectrograph designed by Dickinson and described by Wyckoff.¹ In these spectrographs the distances designated by R_1 and R_2 in this article have been made equal.

In Fig. 1, O represents the axis, perpendicular to the plane of the paper, about which the cam rotates with constant angular velocity in the direction indicated by the arrow. A represents the axis of rotation of the crystal holder, likewise perpendicular to the plane of the paper, and ACB the curved lever which rests upon the cam at B and serves to rotate the crystal holder. R_1 is the distance AO and R_2 the distance AB . r_1 and r_2 are the least and greatest radii respectively of the cam, and r is the radius of the cam at an angle α with the least radius r_1 . The angle from OA to r_1 is ωt where ω is the angular velocity of the cam and t the time measured from the coincidence of r_1 with OA . The meaning of the angles θ and φ is clear from the figure.

It is evident from the figure that

$$r^2 = R_1^2 + R_2^2 - 2R_1R_2\cos\theta \quad (1)$$

from which

$$\cos\theta = \frac{R_1^2 + R_2^2 - r^2}{2R_1R_2} \quad (2)$$

The smallest angle θ_1 occurs when the cosine is greatest, that is, when r is least, and the largest angle θ_2 when the cosine is the smallest, that is, when r is largest (as long as θ is less than 180°).

¹ R. W. G. Wyckoff, *The Structure of Crystals*, p. 163.

$$\cos \theta_1 = \frac{R_1^2 + R_2^2 - r_1^2}{2R_1R_2} \quad (3)$$

$$\cos \theta_2 = \frac{R_1^2 + R_2^2 - r_2^2}{2R_1R_2} \quad (4)$$

The angle β through which the crystal holder rotates is then given by the relation

$$\beta = \theta_2 - \theta_1 \quad (5)$$

When convenient values of R_1 , R_2 and r_1 have been chosen, θ_1 can be determined from equation (3) and r_2 can then be calculated from equation (4) by putting $\theta_2 = \theta_1 + \beta$ where β is the angle through which it is desired to rotate the crystal holder.

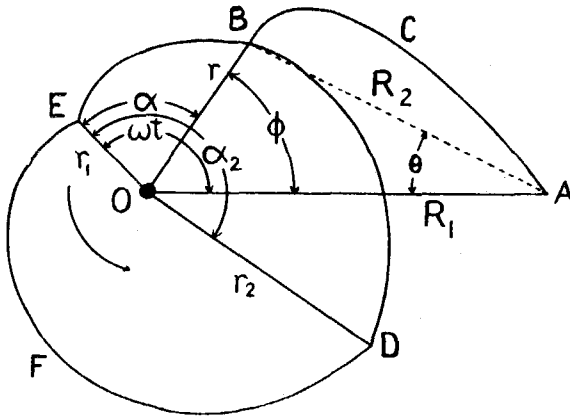


FIG. 1.

Differentiating equation (2) gives

$$-\sin \theta \frac{d\theta}{dt} = -\frac{2r \frac{dr}{dt}}{2R_1R_2} \quad (6)$$

which can be written

$$\sin \theta \frac{d\theta}{dt} = \frac{r}{R_1R_2} \frac{dr}{d\alpha} \frac{d\alpha}{dt} \quad (7)$$

But it is clear from the figure that $\alpha = \omega t - \phi$ which gives when differentiated

$$\frac{d\alpha}{dt} = \omega - \frac{d\phi}{dt} \quad (8)$$

so that equation (7) becomes

$$\sin \theta \frac{d\theta}{dt} = \frac{r}{R_1 R_2} \frac{dr}{d\alpha} \left(\omega - \frac{d\varphi}{dt} \right) \quad (9)$$

The quantity $\frac{d\varphi}{dt}$ can be expressed in terms of $\frac{d\theta}{dt}$ in the following manner. It is evident that

$$R_2^2 = R_1^2 + r^2 - 2rR_1 \cos \varphi$$

giving

$$\cos \varphi = \frac{R_1^2 - R_2^2 + r^2}{2rR_1} \quad (10)$$

Differentiating this gives

$$\sin \varphi \frac{d\varphi}{dt} = \left(\frac{R_1^2 - R_2^2}{2r^2 R_1} - \frac{1}{2R_1} \right) \frac{dr}{dt} \quad (11)$$

But

$$\sin \varphi = \frac{R_2}{r} \sin \theta$$

while equation (6) gives

$$\frac{dr}{dt} = \frac{R_1 R_2}{r} \sin \theta \frac{d\theta}{dt}$$

Substitution of these values in equation (11) then gives

$$\frac{d\varphi}{dt} = \left(\frac{R_1^2 - R_2^2}{2r^2} - \frac{1}{2} \right) \frac{d\theta}{dt} \quad (12)$$

When this value of $\frac{d\varphi}{dt}$ is put into equation (9) the result is

$$\sin \theta \frac{d\theta}{dt} = \frac{r}{R_1 R_2} \frac{dr}{d\alpha} \left[\omega - \left(\frac{R_1^2 - R_2^2}{2r^2} - \frac{1}{2} \right) \frac{d\theta}{dt} \right]. \quad (13)$$

It is desired to have the angular velocity of the crystal holder constant and of the same magnitude in both directions. Consequently, the crystal holder must rotate through the angle β (measured in degrees) while the cam rotates through 180° . Since the two angular velocities

are constant they must be in the same ratio as the angles through which the crystal holder and the cam rotate in the same time. Hence,

$$\frac{d\theta}{dt} = \frac{\beta}{180}$$

and

$$\frac{d\theta}{dt} = \frac{\beta\omega}{180} \quad (14)$$

Substituting this value for $d\theta$ in equation (13) and making a few simplifications we have

$$\sin \theta = \frac{r}{R_1 R_2} \frac{dr}{d\alpha} \left(\frac{180}{\beta} + \frac{1}{2} - \frac{R_1^2 - R_2^2}{2r^2} \right) \quad (15)$$

When the value of $\sin \theta$ in terms of r is introduced by using $\sin \theta = \sqrt{1 - \cos^2 \theta}$ there results

$$R_1 R_2 d\alpha = \frac{r dr \left(\frac{180}{\beta} + \frac{1}{2} - \frac{R_1^2 - R_2^2}{2r^2} \right)}{\sqrt{1 - \left(\frac{R_1^2 + R_2^2 - r^2}{2R_1 R_2} \right)^2}} \quad (16)$$

as the differential equation giving the relation between r and α for the part EBD of the cam. The introduction of the substitution

$$\mu = \frac{R_1^2 + R_2^2 - r^2}{2R_1 R_2}$$

reduces the integrals to forms which can be found in the tables. The result of the integration is

$$\alpha + C = \left(\frac{180}{\beta} + \frac{1}{2} \right) \cos^{-1} \frac{R_1^2 + R_2^2 - r^2}{2R_1 R_2} + \frac{1}{2} \sin^{-1} \frac{(R_1^2 - R_2^2)^2 - (R_1^2 + R_2^2)r^2}{2R_1 R_2 r^2} \quad (17)$$

The constant of integration C can be determined from the condition that $r = r_1$, when $\alpha = 0$ and is found to be

$$C = \left(\frac{180}{\beta} + \frac{1}{2} \right) \theta_1 + \frac{1}{2} \sin^{-1} \frac{(R_1^2 - R_2^2)^2 - (R_1^2 + R_2^2)r_1^2}{2R_1 R_2 r_1^2} \quad (18)$$

The constant of integration having been determined, equation (17) can be used to calculate values of the angle α corresponding to different values of r and the profile of the cam for the part EBD can be drawn. The angle α_2 corresponding to the greatest radius r_2 is found to be

$$\alpha_2 = 180 + \frac{\beta}{2} + \frac{1}{2} \sin^{-1} \frac{(R_1^2 - R_2^2)^2 - (R_1^2 + R_2^2)r_2^2}{2R_1R_2r_2^2} - \frac{1}{2} \sin^{-1} \frac{(R_1^2 - R_2^2)^2 - (R_1^2 + R_2^2)r_1^2}{2R_1R_2r_1^2} \tag{19}$$

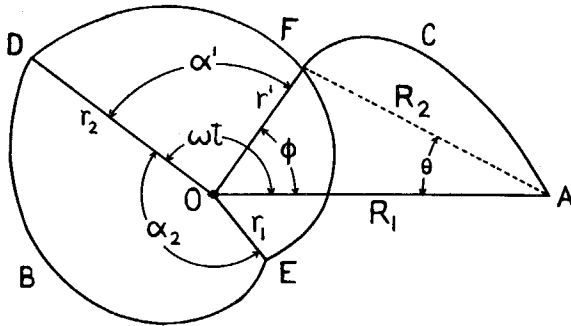


FIG. 2

The profile of the remainder of the cam can be determined in a similar way. In Fig. 2 r' represents the radius of the cam at an angle α' with the greatest radius r_2 . The only difference with the preceding case is that $\frac{d\theta}{dt}$ is now negative

$$\frac{d\theta}{dt} = -\frac{\beta\omega}{180}$$

When this is substituted in equation (13) the resulting differential equation is

$$R_1R_2da' = \frac{r'dr' \left(\frac{180}{\beta} - \frac{1}{2} + \frac{R_1^2 - R_2^2}{2r'^2} \right)}{\sqrt{1 - \left(\frac{R_1^2 + R_2^2 - r'^2}{2R_1R_2} \right)^2}} \tag{20}$$

Integration gives

$$C' - a' = \left(\frac{180}{\beta} - \frac{1}{2} \right) \cos^{-1} \frac{R_1^2 + R_2^2 - r'^2}{2R_1R_2} - \frac{1}{2} \sin^{-1} \frac{(R_1^2 - R_2^2)^2 - (R_1^2 + R_2^2)r'^2}{2R_1R_2r'^2} \tag{21}$$

where the constant of integration C' determined from the condition that $r' = r_2$ when $\alpha' = 0$ is found to be

$$C' = \left(\frac{180}{\beta} - \frac{1}{2} \right) \theta_2 - \frac{1}{2} \sin^{-1} \frac{(R_1^2 - R_2^2)^2 - (R_1^2 + R_2^2)r_2^2}{2R_1R_2r_2^2} \quad (22)$$

The values of α' for different values of r' can now be calculated and the complete profile of the cam drawn. It is evident that α' must be equal to $360 - \alpha_2$ when $r' = r_1$ and this is found to be the case by equation (21).

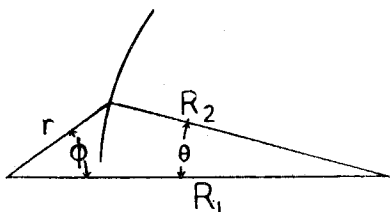


FIG. 3

The equations show clearly that the cam is unsymmetrical and that in general the angle between the least and greatest radii is not equal to 180° . The reason for this is due to the fact that as θ changes the angle ϕ also changes and the line OB accordingly moves forward or backward. It is desired that the change from the least angle θ_1 to the greatest take place while the cam rotates through 180° . Consequently,

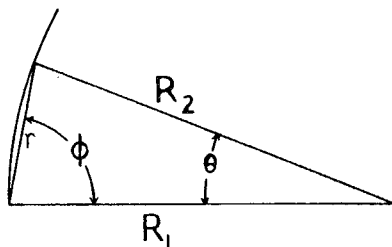


FIG. 4

the point B of the lever must make contact with the greatest radius r_2 when the cam has turned 180° from the initial position in which B makes contact with the least radius r_1 . If ϕ has decreased by the amount ϕ_0 in this half revolution of the cam, the angle α_2 from the least to the greatest radius must be $180^\circ + \phi_0$ measured in the direction EBD , while if ϕ has increased by the amount ϕ_0' the angle α_2 must be $180^\circ - \phi_0'$. As shown in Figs. 3, 4 and 5 the locus of B is on a circle

having a radius R_1 and a center at A . When $R_2 > R_1$ as in Fig. 5, or when $R_2 = R_1$ as in Fig. 4 it is evident from the figures that φ decreases as θ increases. The angle α_2 is therefore greater than 180° for these cases. But when $R_2 < R_1$ as in Fig. 3 it is clear that starting from the initial position shown in the figure, φ at first increases to a maximum and then decreases as θ increases. In this case α_2 may be either greater or less than 180° depending upon the values chosen for R_1 , R_2 , r_1 and β , the angle through which the crystal holder is to be rotated. The cam drawn in Figs. 1 and 2 is calculated to rotate the crystal holder through 30° . R_1 , R_2 and r_1 were chosen to be 12, 10 and 3 cm respectively. In this case α_2 is less than 180° being equal to 166.9° . $r_2 = 8.05$ cm.

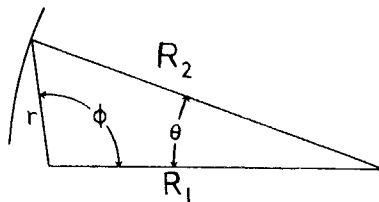


FIG. 5

The equations given make it possible to determine the proper profile to be given to the cam for general values of R_1 and R_2 . When the apparatus can be so constructed that R_1 and R_2 can be made equal, the equations become much simpler and the computation of the profile is much facilitated. When $R_1 = R_2 = R$ equation (17) reduces to

$$a + C = \left(\frac{180}{\beta} + \frac{1}{2} \right) \cos^{-1} \frac{2R^2 - r^2}{2R^2} + \frac{1}{2} \sin^{-1} \left(- \frac{2R^2}{2R^2} \right) \quad (23)$$

The second term on the right hand side is a constant and can be combined with C so that if

$$C_1 = C - \frac{1}{2} \sin^{-1}(-1)$$

we have

$$a + C_1 = \left(\frac{180}{\beta} + \frac{1}{2} \right) \cos^{-1} \frac{2R^2 - r^2}{2R^2} \quad (24)$$

This gives

$$1 - \frac{r^2}{2R^2} = \cos \frac{a + C_1}{\frac{180}{\beta} + \frac{1}{2}}$$

or

$$r = 2R \sin \frac{\alpha + C_1}{2 \left(\frac{180}{\beta} + \frac{1}{2} \right)} \quad (25)$$

C_1 is determined from the condition that $r = r_1$ when $\alpha = 0$ and is found to be

$$C_1 = \left(\frac{180}{\beta} + \frac{1}{2} \right) \theta_1 \quad (26)$$

The angle α_2 from the least to the greatest radius is found to be

$$\alpha_2 = 180 + \frac{\beta}{2}$$

from equation (19). The expression (21) for the profile of the remainder of the cam simplifies to

$$r' = 2R \sin \frac{C_1' - \alpha'}{2 \left(\frac{180}{\beta} - \frac{1}{2} \right)} \quad (27)$$

with

$$C_1' = \left(\frac{180}{\beta} - \frac{1}{2} \right) \theta_2 \quad (28)$$

BUREAU OF METALLURGICAL RESEARCH,
 CARNEGIE INSTITUTE OF TECHNOLOGY,
 PITTSBURGH, PENNSYLVANIA,
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