

end-point was obtained with concentrations above 2 cc. for each 100 cc. of solution, although the color end-points were obtained when the uranium was completely oxidized.

### Summary

When solutions of uranyl sulfate, reduced with zinc, are titrated electrometrically with permanganate, or when chloride solutions are titrated with dichromate, one change in the oxidation potential occurs when the trivalent uranium is oxidized to the tetravalent and another when the latter is oxidized to the hexavalent form. Thus the total amount of uranium may be calculated.

A third end-point is obtained when iron is present.

EAST LANSING, MICHIGAN

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## THE CRYSTAL STRUCTURE OF PHOSPHONIUM IODIDE

BY ROSCOE G. DICKINSON<sup>1</sup>

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### Introduction

The structure of ammonium chloride has been found<sup>2</sup> to be such that each nitrogen atom is surrounded by 8 chlorine atoms at the corners of a cube and each chlorine atom similarly surrounded by nitrogen atoms. Above<sup>3</sup> 184.3° ammonium chloride crystallizes in a second cubic modification which has been found<sup>4</sup> to have the sodium chloride structure. The same relations are true for ammonium bromide whose transition temperature is 137.8°. Ammonium iodide undergoes transition at -17.6°, and above this temperature has the sodium chloride structure.

Phosphonium iodide,  $\text{PH}_4\text{I}$ , readily sublimates, yielding colorless crystals that are cube-like in appearance, but which optical examination has shown<sup>5</sup> to be tetragonal so that the cube-like habit is considered a combination of  $\{110\}$  and  $\{001\}$ . The axial ratio could not be measured. A study of the crystal structure of this substance was undertaken partly with the object of determining whether it bore any relation to either of the structures of the ammonium halides. It has been found possible to account for the X-ray data with a structure which may be considered a modification of

<sup>1</sup> National Research Fellow in Chemistry.

<sup>2</sup> W. H. and W. L. Bragg, "X-rays and Crystal Structure," G. Bell and Sons, Ltd., London, 1916, pp. 110, 158.

<sup>3</sup> The transition temperatures are from Bridgman, *Proc. Am. Acad. Arts Sci.*, **52**, 133 (1916).

<sup>4</sup> Bartlett and Langmuir, *THIS JOURNAL*, **43**, 84 (1921).

<sup>5</sup> Wagner, *Z. Kryst. Mineralog.*, **50**, 47 (1911).

that of the lower temperature form of the ammonium halides. The purpose of this paper will be to show how fully the X-ray data are accounted for, and to show that no simpler structure is capable of accounting for them.

### Method of Experimentation

The phosphonium iodide was kindly prepared by Mr. G. L. Garver using the method of Baeyer.<sup>6</sup> The crystals were formed by sublimation in a closed tube, one end of which was at about 35° and the other at room temperature. By examination between crossed nicols suitable small specimens were selected. They were mounted in wax on microscope cover glasses, the manipulation being made through rubber gloves in a desiccated chamber.

The X-ray methods and routine treatment of data were much the same as previously used.<sup>7</sup> The spectral photographs were obtained by transmission of the incident beam through the crystals rather than by the use of developed faces; the reference crystal was rock salt. Several unsymmetrical Laue photographs were made with 3 different specimens with the incident beam at various inclinations from the perpendicular to (001) and to (110). In spite of the ease with which the compound breaks up, very good photographs were obtained without difficulty, those through the basal plane showing 200 or more spots.

### Derivation of the Structure

The rhodium K  $\alpha$  radiation (wave length,  $\lambda$ , 0.614 Å.) was found to be reflected from (110) at the angles 3° 55½' and 7° 52'. Application of the equation  $\theta n\lambda = 2 d \sin \theta$  shows that  $d_{110}$  is 4.484 Å. or an integral multiple of this value. Similarly reflections from (001) were found at 3° 49' and 7° 38'; from these  $d_{001}$  is 4.62 Å. or a multiple of this value.

The smallest unit of structure compatible with the mere presence of observed reflections will first be found. The number of molecules  $m$ , associated with a tetragonal unit of structure is given by  $m = \frac{\rho N d_{100}^2 d_{001}}{M}$  where  $\rho$  is the density (2.86 in the present case<sup>5</sup>),  $M$  the molecular weight, and  $N$  the Avogadro number. The value of  $m$  for a unit  $4.484 \times 4.484 \times 4.62$  is found to be 0.995. This unit evidently corresponds to such a transformation of the axes that the original (110) becomes (100). If, however, the spots on the Laue photographs are assigned indices referred to the axes of this unit, and values of  $n\lambda$  calculated<sup>8</sup> for them, values

<sup>6</sup> Baeyer, *Ann.*, **155**, 269 (1870).

<sup>7</sup> Dickinson, *THIS JOURNAL*, **44**, 276 (1922).

<sup>8</sup> In the case of a tetragonal crystal the formula for this calculation becomes

$$n\lambda = \frac{2d_{001} \sin \theta_{hkl}}{\sqrt{(h^2 + k^2)c^2 + l^2}} \quad \text{where } c = \frac{d_{001}}{d_{100}}.$$

as low as  $0.15 \text{ \AA}$ . are obtained. As the photographs were taken with a voltage of about 53,000 and the spectrum could, therefore, contain no wave lengths below about  $0.23 \text{ \AA}$ ., this unit must be regarded as impossible. Any larger unit differing from this one only by having  $d_{001}$  a multiple of  $4.62 \text{ \AA}$ . is impossible for the same reason. A unit having  $d_{100}$  equal to  $4.48^4\sqrt{2} = 6.34$  and  $d_{001}$  equal to  $4.62 \text{ \AA}$ . contains two molecules; its axes are coincident with the original axes. No impossible values of  $n\lambda$  have been found with the indices referred to this unit as has been done in the gnomonic projection shown in Fig. 1. This unit is accordingly the smallest one requiring further investigation.

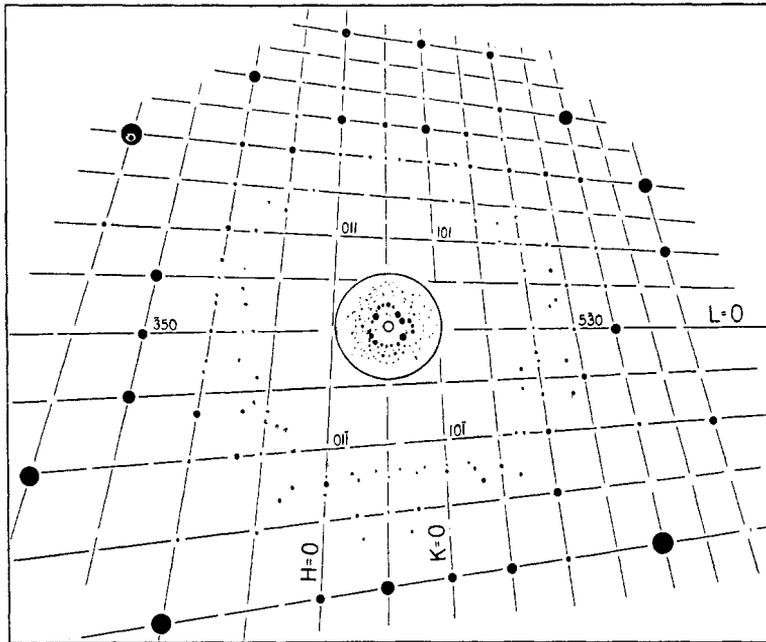


Fig. 1.—Gnomonic projection of Laue photograph made with incident beam inclined about  $3^\circ$  from normal to (110); distance from crystal to plate, 5 cm. The scale is obtainable from the fact that the circle around the diagrammatic Laue photograph has a diameter of 10 cm.

The manner in which the phosphorus and iodine atoms may be situated in this unit will next be considered. It will be assumed that all of the phosphorus atoms occupy equivalent positions and likewise all of the iodine atoms. The reflecting power of the hydrogen atoms will be considered to be negligible. All of the positions<sup>9</sup> for two equivalent atoms, not in-

<sup>9</sup> The coördinates used in this discussion are based in part upon a tabulation by Niggli, "Geometrische Krystallographie des Diskontinuums," Gebrüder Bornträger, Leipzig, 1919, p. 418, and partly on a tabulation by Wyckoff, contained in "An Analytical Expression of the Theory of Space-Groups" now in press.

volving undetermined parameters, given by any tetragonal space group may be reduced to one of the following by a suitable movement of the origin: (a) (000)  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ ; (b), (000)  $(00\frac{1}{2})$ ; (c) (000)  $(\frac{1}{2}\frac{1}{2}0)$ . Neither (a) nor (b) nor any combination of them would produce the observed reflection from (001). The arrangement (c) could produce no reflections not produced by a structure having one molecule in the unit and shown above to be impossible. Moreover, no combination of (c) with (a) or (b) occurs in any space group. The arrangement of the phosphorus and iodine atoms must then involve at least one undetermined parameter.<sup>10</sup>

With two molecules in the unit, and with the assumptions that have been made concerning equivalence of atoms, only two distinct arrangements of two kinds of atoms involving only one undetermined parameter can result from any tetragonal space group.<sup>11</sup>

- (A) I,  $(0\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}0\frac{1}{2})$ ; II, (00u) 00 $\bar{u}$   
 (B) III, (000)  $(\frac{1}{2}\frac{1}{2}0)$ ; IV,  $(0\frac{1}{2}u)$   $(\frac{1}{2}0\bar{u})$

In either case all distinct values of  $u$  lie between zero and one-half.

For the first order reflections from planes having  $h$  and  $k$  one even and one odd and  $l = 0$ , the value of  $\sqrt{A^2 + B^2}$  is  $2\bar{R}$  for arrangement (A) and zero for (B);  $\bar{R}$  is the reflecting power of the kind of atom occupying positions II. A Laue photograph made with the incident beam at a considerable inclination (about  $17^\circ$ ) from perpendicular to (001) permitted reflections from a number of planes in the zone [001]. Of these none having  $h$  and  $k$  one even and one odd appeared in the first order although a number had equal or better opportunity than planes which did reflect. This fact eliminates arrangement (A).

The values of  $\sqrt{A^2 + B^2}$  for first order reflections from arrangement (B) are

- |  |  |                             |
|--|--|-----------------------------|
| Class 1, $h$ and $k$ both odd;             | $A = 2\bar{P} - 2\bar{I} \cos 2\pi lu$ | $B = 0$                     |
| Class 2, $h$ and $k$ both even;            | $A = 2\bar{P} + 2\bar{I} \cos 2\pi lu$ | $B = 0$                     |
| Class 3, $h$ and $k$ one even and one odd; | $A = 0$ ;                              | $B = 2\bar{I} \sin 2\pi lu$ |

These equations are for the phosphorus at III and the iodine at IV; for the reverse case  $\bar{P}$  and  $\bar{I}$  must be interchanged.

All planes of any one class having the same value of  $l$  evidently have the same value of  $\sqrt{A^2 + B^2}$ . Hence, among such planes there should occur no instances where one plane with the same or a smaller spacing than a

<sup>10</sup> There are also tetragonal space groups providing more than one set of 4-fold or 8-fold positions not requiring the determination of parameters. It is evidently possible to specify the dimensions and orientations of all the possible units of structure which contain either 4 or 8 molecules of  $\text{PH}_4\text{I}$ . The non-variant arrangements of 4 or 8 phosphorus and iodine atoms may then be examined with reference to these units in a manner similar to that carried out in the case of 2 phosphorus and iodine atoms. This has been done and the non-variant arrangements with the larger units found to be impossible.

<sup>11</sup> Arrangement (A) may be derived from the space groups:  $D_{4h}^1$ ,  $D_{4h}^2$ ,  $V_{4d}^1$ ,  $C_{4h}^1$ ; arrangement (B) from:  $D_{4h}^2$ ,  $D_{4h}^3$ ,  $V_{4d}^2$ ,  $C_{4h}^2$ .

second, reflects under comparable conditions of wave length more strongly than the second. A systematic examination of all the planes appearing on 3 quite different photographs revealed no such intensity difference, although many were found among planes with different values of  $l$ .

The reflections of Class 3, since they are due to only one kind of atom, are best suited to the evaluation of  $u$ . In this class, planes having  $l = 2$  or 3 gave the strongest reflections; those having  $l = 5$  were exceedingly weak; those having  $l = 1, 4,$  or 6 were intermediate. By plotting  $\sin 2\pi lu$  against  $u$  for the various values of  $l$ , or otherwise, it can readily be shown that the only values of  $u$  which are capable of accounting for these reflections are close to either 0.10 or 0.40. At these values of  $u$ ,  $\sin 2\pi lu$  is equal to the following:  $l = 1, 0.588$ ;  $l = 2, 0.951$ ;  $l = 3, 0.951$ ;  $l = 4, 0.588$ ;  $l = 5, 0$ ;  $l = 6, 0.588$ . The rapidity with which the last three values change with  $u$  makes it hardly possible for  $u$  to be in error by as much as 0.01; but the appearance at all of planes having  $l = 5$  indicates that  $u$  is not precisely 0.10 or 0.40. It has not been found possible to determine with certainty whether it is slightly greater or slightly less. It is necessary to consider another class of planes in order to choose between 0.10 and 0.40 and to determine which kind of atom is to be placed in this position.

Planes of Class 1 having  $l = 3$  gave reflections too weak to be detected with certainty. If the reflecting powers of the phosphorus and iodine atoms are assumed to be proportional to their atomic numbers 15 and 53, respectively, the following values of  $\sqrt{A^2 + B^2}$  result for the four possibilities.

Position of phosphorus:	III	III	IV	IV
Position of iodine:	IV	IV	III	III
Value of $u$ :	0.10	0.40	0.10	0.40
Value of $\sqrt{A^2 + B^2}$ :	63	3	115	63

Granting that the assumed reflecting powers may be somewhat in error, the evidence is still clearly in favor of giving the iodine atoms Arrangement IV and  $u$  the value 0.40.

Since the analysis by which the above structure was arrived at was directed toward the derivation of the simplest possible structure, *i. e.*, the one having the smallest unit and fewest undetermined parameters, it is especially desirable to test it with the numerous other abnormal intensity relations to be found on the Laue photographs and not used in the derivation. In general in making such tests it is desirable to avoid comparisons which involve calculated values of  $\sqrt{A^2 + B^2}$  whose order of inequality may be reversed by small changes in the assumed reflecting powers. However, in the present instance no abnormalities were found which were not qualitatively accounted for by the above structure on the

assumption of proportionality of reflecting power to atomic number. A variety of examples is afforded by the Laue photographic data of Tables

TABLE I  
Incident beam  $3^\circ$  from perpendicular to (001)

Plane	Spacing	$n\lambda$	Estimated intensity	$\sqrt{A^2 + B^2}$
251	1.14	0.45	4.	62
{ 351	1.06	0.43	9.	116
{ 531	1.06	0.47	9.	116
{ 531	1.06	0.50	4.	116
601	1.03	0.42	1.4	56
611	1.02	0.42	1.8	62
621	0.98	0.43	1.1	56
171	0.88	0.41	2.5	116
{ 551	0.88	0.37	0.2	116
{ 551	0.88	0.42	2.5	116
461	0.87	0.41	0.5	56
372	0.78	0.45	0.0	3
652	0.77	0.44	0.7	101
742	0.75	0.42	0.5	101
472	0.75	0.44	0.6	101
812	0.75	0.44	0.5	101
832	0.71	0.44	0.35	101
752	0.70	0.44	0.0	3
902	0.67	0.42	0.2	101
912	0.67	0.42	0.0	3
922	0.66	0.44	0.15	101
852	0.65	0.42	0.1	101
392	0.64	0.42	0.0	3
10.1.3	0.58	0.41	0.05	101

TABLE II  
Incident beam  $17^\circ$  from perpendicular to (001)

Plane	Spacing	$n\lambda$	Estimated intensity	$\sqrt{A^2 + B^2}$
230	1.76	0.42	0.0	0
321	1.64	0.44	strong	62
340	1.27	0.54	0.0	0
251	1.14	0.39	2.5	62
512	1.10	0.45	0.0	3
{ 350	1.09	0.24	faint	76
{ 350	1.09	0.42	3.0	76
{ 530	1.09	0.49	1.3	76
{ 530	1.09	0.60	0.4	76
522	1.05	0.43	6.0	101
161	1.02	0.43	1.3	62
450	0.99	0.44	0.0	0
352	0.98	0.46	0.0	3
452	0.91	0.44	2.0	101
720	0.87	0.46	0.0	0
172	0.84	0.44	0.0	3

{ $\overline{730}$	0.83	0.43	0.4	76
{ $\overline{730}$	0.83	0.48	0.3	76
$\overline{740}$	0.79	0.43	0.0	0
$\overline{553}$	0.77	0.43	0.0	3
$\overline{471}$	0.77	0.40	0.25	62
$\overline{643}$	0.76	0.43	0.2	63
$\overline{281}$	0.76	0.42	0.1	56
{ $\overline{182}$	0.75	0.44	0.4	101
{ $\overline{182}$	0.75	0.47	0.4	101
$\overline{381}$	0.73	0.43	0.1	62
$\overline{373}$	0.73	0.46	0.0	∴
$\overline{563}$	0.72	0.45	0.25	101
$\overline{481}$	0.71	0.44	0.05	56
$\overline{283}$	0.69	0.44	0.05	63
$\overline{734}$	0.68	0.44	0.2	116

TABLE III

Incident beam  $4^\circ$  from perpendicular to (110)

Plane	Spacing	$n\lambda$	Estimated intensity	$\sqrt{A^2 + B^2}$
$\overline{231}$	1.64	0.44	8.0	62
$\overline{232}$	1.40	0.45	10.0	101
$\overline{431}$	1.22	0.44	2.5	62
$\overline{323}$	1.16	0.44	4.0	101
014	1.14	0.40	1.4	62
$\overline{432}$	1.11	0.40	4.0	101
$\overline{350}$	1.09	0.46	1.8	76
{ $\overline{351}$	1.06	0.41	3.5	116
{ $\overline{351}$	1.06	0.46	3.0	116
$\overline{423}$	1.04	0.45	1.0	63
$\overline{144}$	0.92	0.46	0.3	62
115	0.91	0.46	0.6	76
$\overline{533}$	0.89	0.45	0.0	3
205	0.89	0.45	1.6	136
$\overline{215}$	0.88	0.44	faint	0
$\overline{362}$	0.88	0.43	1.0	101
$\overline{305}$	0.85	0.41	0.0	0
$\overline{315}$	0.84	0.41	0.5	76
$\overline{524}$	0.83	0.43	0.1	62
$\overline{741}$	0.78	0.44	0.1	62
$\overline{742}$	0.75	0.44	0.3	101
126	0.74	0.44	0.15	62
$\overline{515}$	0.74	0.45	0.15	76
$\overline{634}$	0.73	0.44	0.1	62
$\overline{265}$	0.68	0.44	0.2	136
$\overline{383}$	0.67	0.43	0.1	101

I, II, and III; on account of the large number of reflections examined, the tables are not complete, but effort has been made to make them representative. Examination of planes of one form showed, with increasing values of  $n\lambda$ , a sharp increase of intensity at the critical absorption wave length of iodine (0.37 Å.) and a decrease at the critical absorption of silver

(0.48 Å.); but between 0.41 and 0.47 all wave lengths were roughly equally effective.

### Discussion of the Structure

The arrangement of the phosphorus and iodine atoms found in phosphonium iodide is shown in Fig. 2*a*; OA, OA, and OC are the axes of the unit. In Fig. 2*b* is shown the arrangement of the nitrogen and chlorine atoms in ammonium chloride oriented for comparison with 2*a*; the lines

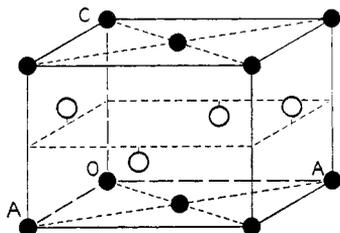


Fig. 2*a*.

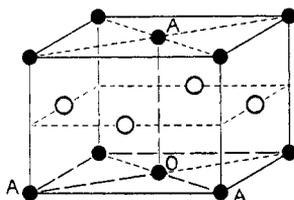


Fig. 2*b*.

Fig. 2.—2*a* shows the arrangement of phosphorus and iodine atoms in  $\text{PH}_4\text{I}$ . 2*b* is drawn to the same scale, and shows the arrangement of nitrogen and chlorine in  $\text{NH}_4\text{Cl}$  so oriented as to correspond to 2*a*. The black circles represent the phosphorus or nitrogen atoms and the white circles the halogen.

OA are the cubic axes. The difference between the two arrangements lies chiefly in the small displacement given to the iodine atoms. As a result of this displacement, each phosphorus atom instead of having 8 iodine atoms equidistant from it has 4 at a distance of 3.67 Å. and 4 at a distance of 4.21 Å. But the structure is still to be considered ionic in that no grouping of the phosphorus and iodine atoms can be made.

It is compatible with the symmetry of the phosphonium iodide arrangement to group the hydrogen atoms tetrahedrally about the phosphorus atoms in such a way that the hydrogen atoms will all be equivalent;<sup>12</sup> these tetrahedra may but need not be regular. It seems likely that tetramethyl phosphonium iodide, which is also tetragonal<sup>6</sup> and whose axial ratio is 1:0.7310 as compared with 1:0.729 found here for phosphonium iodide, is structurally similar to the latter compound. If this proves to be the case, the type of arrangement of the hydrogen atoms can be inferred from that of the substituting methyl groups.

### Summary

The structure of crystals of tetragonal phosphonium iodide has been investigated by means of X-rays, using chiefly Laue photographs. It is shown that the X-ray data are satisfactorily accounted for by a structure obtained by placing in a unit of the dimensions  $6.34 \times 6.34 \times 4.62$  Å.,

<sup>12</sup> For instance the space group  $D_{2d}^{14}$  gives the following set of equivalent positions: (uov) ( $\bar{u}ov$ ) (ou $\bar{v}$ ), (o $\bar{u}\bar{v}$ ) ( $\frac{1}{2} + u, \frac{1}{2}, \bar{v}$ ) ( $\frac{1}{2} - u, \frac{1}{2}, \bar{v}$ ) ( $\frac{1}{2}, \frac{1}{2} + u, v$ ) ( $\frac{1}{2}, \frac{1}{2} - u, v$ ).

phosphorus atoms at (000) and  $(\frac{1}{2}\frac{1}{2}0)$  and iodine atoms at  $(0\frac{1}{2}u)$  and  $(\frac{1}{2}0\bar{u})$  where  $u$  is very close to 0.40; and it is shown that no simpler structure is capable of accounting for the data. The close relation between this structure and that of the lower temperature form of ammonium chloride is shown.

PASADENA, CALIFORNIA

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#### NOTE

**The Sizes of Atoms in Diamond-Type Crystals.**—It has recently been shown that the interatomic distances for substances crystallizing in the diamond type of lattice can be satisfactorily represented in terms of atomic "radii" characteristic only of the rare-gas types of atoms involved.<sup>1</sup> For the argon type, the value for silicon derived from the density (1.15 Å. U.) rather than that given by Debye and Scherrer<sup>2</sup> (1.18 Å. U.) was taken. Gerlach<sup>3</sup> has recently made a careful re-determination of this constant and finds its value to be 1.17 Å. U. It, therefore, seems that this value rather than the lower one derived from the density should be adopted. For the radius of atoms of the krypton type, one-half the value for the distance between the copper and bromine atoms in cuprous bromide (1.26 Å. U.) was taken. Hull<sup>4</sup> has recently found that the element germanium, which is of the krypton type, also crystallizes in the diamond lattice, the value for the atomic radius being 1.22 Å. U. The rather close agreement between the interatomic distances in gray tin and silver iodide (2.80 and 2.83 Å. U., respectively), all the atoms being of the same (xenon) type, would lead one to expect better agreement between cuprous bromide and germanium (2.52 and 2.44 Å. U., resp.). Inasmuch as cuprous bromide is undoubtedly the more difficult of the two to prepare in a pure state owing to its tendency to be decomposed by light and as the germanium value gives a little better agreement with the data (with the exception, of course, of the value for cuprous bromide), it seems best to adopt the value derived from germanium (1.22 Å. U.) as the atomic "radius" of krypton-type atoms in the diamond type of lattice. This, moreover, results in the constants all being determined from elementary substances.

The revised set of constants and the resulting values calculated for the various substances are given below.

Type		Atomic radius Å. U.
Neon	Diamond	0.77
Argon	Silicon (S, Cl)	1.17
Krypton	Germanium (Cu, Zn, Br)	1.22
Xenon	Gray tin (Ag, I)	1.40

<sup>1</sup> Pease, *THIS JOURNAL*, **44**, 769 (1922).

<sup>2</sup> Debye and Scherrer, *Physik. Z.*, **17**, 277 (1916).

<sup>3</sup> Gerlach, *ibid.*, **22**, 557 (1921); **23**, 114 (1922).

<sup>4</sup> Hull, American Physical Society Meeting at Washington, April 22, 1922.