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not occur at all in the D_2O system, but the difference of volume between L and VI is convex toward the temperature axis over the entire measured range. The situation is reversed with regard to the phase I. In the H_2O system Δv is linear against temperature, whereas in the D_2O system it is abnormally concave toward the temperature axis. It is to be questioned, however, whether H_2O is not really more abnormal on its L–I line than D_2O, since the numerical magnitude of the variation of Δv is very much greater in H_2O. An accompaniment of this is a much greater variation of the latent heat along the L–I line for H_2O than for D_2O.

The greatest qualitative difference with regard to volume is shown by the phases I and III. At the triple point L–I–III the decrease of volume when I changes to III is 9 percent greater in the D_2O system, whereas at the I–II–III triple point, only 12° lower, it is 1 percent less. The variation is perhaps in small part due to experimental error, the volume determinations on the I–III line being the most uncertain of the measurements, but the triple point conditions did not seem to allow any important divergence from the values given, and the difference must be mostly real.

The conclusion seems forced, I believe, by this detailed examination of the differences in the two systems that abnormalities occur not only in the liquid but also in the solid phases, and particularly in the phases I and III. In fact, I have been of the opinion ever since making the original measurements in 1912 on the H_2O system that the p–τ–v surface of ice I would be found to deviate markedly from that of a normal solid, particularly in the neighborhood of the L–I–III triple point. This subject has never been investigated experimentally, and would, I believe, be well worth while. Measurements should be made if possible on single crystals. Not only is it highly probable that the ices I and III are abnormal, but the abnormalities must differ in the D_2O and the H_2O systems. More elaborate considerations than simply zero-point energy appear to be necessary to satisfactorily explain the situation.

Precision Determination of Lattice Constants

ERIC R. JETTE AND FRANK FOOTE, *School of Mines, Columbia University*

In Part I the theoretical and experimental conditions which must be satisfied in order to determine lattice constants with a precision of a few parts per hundred thousand are discussed with particular application to the symmetrical focusing type of camera. Cohen's method of calculation of lattice constants for the elimination of "drift" and experimental errors is applied. Methods are developed for the evaluation of standard errors and fiduciary limits of results from a single film and from a set of films. The usefulness of x-ray targets made of alloys rather than pure elements for the purpose of securing a larger number and better distribution of lines is indicated. The influence of the number and Miller indices of diffraction lines on the values of lattice constants in noncubic systems is shown. The importance of the methods of sample preparation for precision work is emphasized. In Part II, precision measurements on Al, Ni, Ag, Au, Si, Fe, Mo, W, Mg, Zn, Cd, Sb, Bi and Sn are reported for materials of a high degree of purity. The fiduciary limits of these lattice constants vary between 2 and 7 parts per hundred thousand and are so chosen that the probability of the correct value lying between the stated limits is 19 out of 20.

Part I. Theoretical and Experimental Conditions

INTRODUCTION

DURING the last few years the determination of precise values of lattice constants has become more and more important. In many cases the problem consists mainly in determining comparatively small changes in lattice constants due to changes in the compositions or nature of the sample investigated. This is the case in one

of the most important fields of x-ray investigation, namely, the study of solid solutions and solubility limits in the solid state. Since the nature of the x-ray technique is such as to preclude the direct determination of these differences, it is necessary to obtain the individual values of the lattice constants with a precision of 0.01 percent or better.

The precision problem in this field may be divided into four distinct but equally important parts. (A) A theoretical study of the diffraction camera used to discover the sources of error inherent in it and their possible magnitude. (B) The development of an adequate method of calculating the experimental results. (C) The development of an experimental technique which in view of the preceding is capable of yielding results of high precision. (D) The development of a technique of preparing the samples to be measured so that it is worth while to apply the precision x-ray technique.

We shall confine our attention to measurements made on finely divided material by means of the so-called focusing type cameras of the symmetrical type which have the advantage of not requiring the use of a calibrating substance.[1]

A. Errors Inherent in the Symmetrical Focusing Camera

The principle on which the focusing camera depends[2] demands that the slit (or in some constructions the focal spot of the x-ray tube), the sample and the film be located on the same circumference and that the part of the sample exposed be very narrow in the direction parallel to the cylinder axis of the camera. These conditions can never be completely satisfied. In addition, the fact that photographic film must be used introduces an error due to film shrinkage which our experience indicates cannot be completely eliminated by the use of fiducial points. Further, if the camera is to be used as an absolute instrument and thus be free from the use of calibrating substances, the lattice constants will be subject to errors in measuring the camera radius. Finally, of course, errors of the ordinary accidental sort in determining the line positions will occur.

These errors just enumerated have been described in the articles by Saini[3] and Cohen[4] so that detailed discussion of them are unnecessary here. The systematic errors may be combined in the following equation

$$\Delta \sin^2 \theta = \left(\frac{\Delta S}{L} + \frac{\Delta R_3 - \Delta R_1}{R}\right)\phi \sin 2\phi + \left(\frac{\Delta R_2 - \Delta R_3 + k_4 \Delta R_4}{4R} + \frac{1}{4}\left(\frac{h}{R}\right)^2\right) \tan 2\phi \sin 2\phi, \qquad (1)$$

where L = measured distance between reflections from the same plane on the opposite sides of the film;
   R = camera radius
   θ = glancing angle from a plane of indices hkl
   $\phi = \pi/2 - \theta = L/8R$
   ΔS = error in shrinkage correction applied
   ΔR_1 = error in measuring camera radius
   ΔR_2 = error due to sample being off the circumference
   ΔR_3 = error due to film being off the circumference
   $k_4 \Delta R_4$ = error due to thickness of sample, k_4 is not known
   h = vertical divergence of beam.[4]

The accidental errors in determining the line position may be expressed by the equation

$$\Delta \sin^2 \theta = (\Delta L/L)\phi \sin 2\phi. \qquad (2)$$

An exhaustive and laborious investigation in this laboratory has shown (1) that while some of the values for the individual errors may be estimated with a fair degree of assurance, others

cannot, (2) that there is no way of predicting as to either quantity or sign the resultant effect of the errors on an individual film, (3) that with the technique as used in this laboratory and others the systematic error largely outweighs the accidental errors of measurement, (4) that while a fictitious value for the radius can be found for a single film which will make the resultant of all the terms in the above equation zero (assuming $\Delta S/L$ to be constant over the whole film) this radius will not serve for another film, (5) that the use of calibrating substances of known lattice constants mixed with the samples was in general unsatisfactory and no one such substance was suitable for the range of materials under investigation in this laboratory.

[1] W. F. De Jong, Physica 7, 23 (1927); M. Gayler and C. D. Preston, J. Inst. Metals (Lond.) 41, 191 (1929).

[2] H. Seeman, Ann. d. Physik 59, 455 (1919); H. Bohlin, ibid. 61, 421 (1920).
[3] H. Saini, Helv. Phys. Acta 6, 597 (1933).
[4] M. U. Cohen, Rev. Sci. Inst. 6, 68–74 (1935).

B. Calculation of Lattice Constants, the "Drift Constant" and Errors

The resultant effect of the errors included in Eq. (1) is to yield lattice constants which depend upon the angles used for calculating them. This is shown clearly for cubic substances where a value of the lattice constant can be secured for each diffraction line measured. The constants determined from the lines at lower angles differ from those from higher angles by amounts well beyond experimental error in the line positions. This "drift" arising from the systematic errors is the most serious source of error in the vast majority of lattice constant measurements available in the literature at present because not only the focusing methods but likewise Debye-Hull powder methods and back reflection methods of various types are subject to similar errors.

That the existence of this drift has been recognized is evidenced by the various graphical and analytical methods proposed to eliminate it among which may be mentioned those discussed by Bradley and Jay,[5] Stentzel and Weerts,[6] and Weigle.[7] While graphical methods involving plots of the lattice constant as a function of $\cos^2 \theta$, $\phi \tan \phi$ or $\sin^2 \theta$ with extrapolation to $\theta = 90°$ or to $\phi = 0$ are suitable for cubic substances, they become extremely complicated for other systems. During the course of our own investigations we developed graphical methods for hexagonal and tetragonal systems. All of these methods, how-ever, are inexact and cumbersome in comparison with the analytical method by Cohen.[4]

For purpose of orientation, it may be mentioned at this point that what Cohen does is to assume that the errors in $\sin^2 \theta$ will be proportional to $\phi \sin 2\phi$ and adds a term $D\phi \sin 2\phi$ to the quadratic form for the crystallographic system to which the substance belongs. Thus for the hexagonal system he uses the equation

$$\sin^2 \theta = \frac{\lambda^2}{3a^2}(h^2+k^2+hk) + \frac{\lambda^2 l^2}{4c^2} + D\phi \sin 2\phi \quad (3)$$

or $\sin^2 \theta = A(h^2+k^2+hk) + Bl^2 + D\phi \sin 2\phi$.

By knowing the values of the indices hkl and the angles θ and ϕ, the set of measured $\sin^2 \theta$ values is solved by least squares methods to find A, B and the "drift constant" D. It is evident from Eq. (1) that setting $\Delta \sin^2 \theta = D\phi \sin 2\phi$ involves an approximation. Cohen's experience, frequently confirmed in this laboratory, shows that any error arising from this source is unimportant in cameras of 10 and 15 centimeter diameter (cf. Table I). For larger cameras it may be necessary to use two correction terms as indicated by Eq. (1).

The method of calculation here used makes possible the evaluation of the errors of the lattice constants determined from an individual film. For the case of cubic crystals, the weight of $A (A = \lambda^2/4a_0^2)$ is given by $W_A = C/C_A$, where C is the determinant of the coefficients of the normal equation[4]

$$C = \begin{vmatrix} \Sigma(h^2+k^2+l^2)^2 & \Sigma(h^2+k^2+l^2)(\phi \sin 2\phi) \\ \Sigma(h^2+k^2+l^2)(\phi \sin 2\phi) & \Sigma(\phi \sin 2\phi)^2 \end{vmatrix}$$

and C_A is the minor of the $\Sigma(h^2+k^2+l^2)^2$ element in the above determinant.

$$C_A = \Sigma(\phi \sin 2\phi)^2.$$

Back calculation yields a set of $\Delta \sin^2 \theta$ terms and from these the variance, S^2, of $\sin^2 \theta$ is obtained by:

$$S^2 = (\Sigma(\Delta \sin^2 \theta)^2)/(N-w),$$

where N = number of lines, w = number of con-stants to be determined, in the cubic case, $w = 2$; $N-w$ = degrees of freedom. The variance S_A^2 of the quadratic equation constant A, is given by $S_A^2 = S^2 \cdot C_A/C$ and the standard error, S_{a_0}, of the lattice constant (a_0) by

$$S_{a_0} = a_0 S_A/2A. \quad (4)$$

The hexagonal case is a simple extension of the cubic case. The C determinant becomes

$$C = \begin{vmatrix} \Sigma(h^2+k^2+hk)^2 & \Sigma(h^2+k^2+hk)(l^2) & \Sigma(h^2+k^2+hk)(\phi \sin 2\phi) \\ \Sigma(h^2+k^2+hk)(l^2) & \Sigma(l^2)^2 & \Sigma(l^2)(\phi \sin 2\phi) \\ \Sigma(h^2+k^2+hk)(\phi \sin 2\phi) & \Sigma(l^2)(\phi \sin 2\phi) & \Sigma(\phi \sin 2\phi)^2 \end{vmatrix}$$

[5] A. J. Bradley and A. H. Jay, Proc. Phys. Soc. London 44, 563 (1932).
[6] W. Stentzel and J. Weerts, Zeits. f. Krist. A84, 20 (1933).
[7] J. Weigle, Helv. Phys. Acta 7, 46–50, 51–56 (1934).

C_A is the minor of the $\Sigma(h^2+k^2+hk)^2$ element in the C determinant

$$C_A = \begin{vmatrix} \Sigma(l^2)^2 & \Sigma(l^2)\ (\phi\sin 2\phi) \\ \Sigma(l^2)\ (\phi\sin 2\phi) & \Sigma(\phi\sin 2\phi)^2 \end{vmatrix}.$$

C_B is the minor of the $\Sigma(l^2)^2$ element in the C determinant.

$$C_B = \begin{vmatrix} \Sigma(h^2+k^2+hk)^2 & \Sigma(h^2+k^2+hk)\ (\phi\sin 2\phi) \\ \Sigma(h^2+k^2+hk)\ (\phi\sin 2\phi) & \Sigma(\phi\sin 2\phi)^2 \end{vmatrix}$$

the ratios C/C_A and C/C_B give the weights of A and B, respectively. As before the variance of $\sin^2\theta$, S^2, is given by

$$S^2 = (\Sigma(\Delta\sin^2\theta))/(N-w)$$

and in the hexagonal case $w=3$. The variances of A and B are given by

$$S_A{}^2 = S^2\,C_A/C, \quad S_B{}^2 = S^2\,C_B/C$$

and the standard errors of the lattice constants a and c by

$$S_a = aS_A/2A, \quad S_c = cS_B/2B. \tag{5}$$

The modifications necessary to treat tetragonal crystals and the extension to the orthorhombic case are obvious.

The standard errors as calculated above put rather narrow limits on the lattice constants since it corresponds to a probability of only 0.5 that the true values of the constants lie within these limits. To increase the probability that the true value of a calculated constant lies within

the limits of error reported, use is made of fiduciary limits. Tables[8] have been set up giving the factor by which the standard error must be multiplied in order to obtain the desired limits. In our work we have taken a probability of 0.05 as our desired limit. This corresponds to the probability of 19 in 20 that the true value lies inside the limits thus set. The factor by which the standard error is multiplied varies with the number of degrees of freedom and is greater, the fewer the degrees of freedom.

When a series of films of the same material are taken the standard errors are, in general, not the same for the whole set. Further, if different radiations are used the degrees of freedom are often quite different for different films. Some method of averaging is desirable which takes account of these effects.

The most rigorous method is the following:

For cubic crystals, we obtain from quantities already computed the weight of a_0 for each film. $W_{a_0} = 4\cdot(A^2/a_0{}^2)C/C_A$; $a_0 =$ lattice constant; $A = \lambda^2/4a_0{}^2$; C and C_A are the determinants defined above. The weighted average of a_0, namely $\bar{a}_0$, is

$$\bar{a}_0 = \Sigma(W_{a_0}\cdot a_0)/\Sigma(W_{a_0}). \tag{6}$$

To obtain the standard error in $\bar{a}_0$, we calculate the variance, $S_t{}^2$, for the whole set of films

$$S_t{}^2 = \frac{\Sigma n S^2}{\Sigma n} = \frac{\Sigma(\Sigma(\Delta\sin^2\theta)^2)}{\Sigma n}. \tag{7}$$

[8] R. A. Fisher, *Statistical Methods for Research Workers*, fourth edition (Oliver & Boyd, London, 1932), p. 151.

TABLE I.

Ag	Film VII-174			Co-Ni rad.	$t=28.0°$		$\Delta\sin^2\theta\cdot 10^6$		$(1)-(2)$ to ΔL
			$\sin^2\theta$						
LINE	(1)	(2)	(3)	(4)	$(1)-(2)$	$(1)-(3)$	$(1)-(4)$		(mm)
$19\alpha_2$Ni	0.781460	0.781413	0.781391	0.781422	$+47$	$+69$	$+38$		-0.02
$20\alpha_1$Ni	.822617	.822624	.822632	.822621	-7	-15	-4		0
$20\alpha_2$Ni	.822553	.822632	.822642	.822629	-79	-89	-76		$+0.04$
$19\alpha_1$Co	.781711	.781662	.781679	.781655	$+48$	$+32$	$+56$		$-.04$
$19\alpha_2$Co	.781690	.781669	.781686	.781662	$+21$	$+4$	$+28$		$-.02$
$20\alpha_1$Co	.822919	.822890	.822893	.822889	$+29$	$+26$	$+30$		$-.03$
$20\alpha_2$Co	.822849	.822897	.822898	.822896	-48	-49	-47		$+.06$
$24\alpha_1$Ni	.987509	.987529	.987516	.987534	-20	-7	-25		$+.02$
$24\alpha_2$Ni	.987553	.987539	.987523	.987544	$+14$	$+30$	$+9$		$-.03$

$$S^2 = (\Sigma(\Delta\sin^2\theta)^2)/(N-2) \qquad\qquad S^2\cdot 10^{12} = 2140.7 \qquad 2567.6 \qquad 2138.7$$

(1) Experimental value from line measurements $\phi=(1/8R)\cdot L$, $1/8R=0.0024469$. Corrected for refraction and converted to Niα_1 as common wave-length.

(2) Calculated from the fitted equation:
$\sin^2\theta = 0.04114809\ (h^2+k^2+l^2) - 0.00101825\ (\phi\sin 2\phi)$
from which $a_0 = 4.0779_1 \pm 0.0000_6$ at 25°.

(3) Calculated from the fitted equation:
$\sin^2\theta = 0.04114723\ (h^2+k^2+l^2) - 0.00034556\ (\sin 2\phi\tan 2\phi)$
from which $a_{0_3} = 4.0779_5 \pm 0.0000_6$ at 25°.

(4) Calculated from the fitted equation:
$\sin^2\theta = 0.04114839\quad (h^2+k^2+l^2) - 0.00140727\quad (\phi\sin 2\phi) + 0.00013361\ (\sin 2\phi\tan 2\phi)$ from which $a_0 = 4.0778_9 \pm 0.0000_7$.

Then the variance of the mean $\bar{a}_0$ is

$$S_{\bar{a}_0}^2 = S_i{}^2/\Sigma W_{a_0}, \qquad (7a)$$

where $n =$ degrees of freedom for each film; $\Sigma(\Delta \sin^2 \theta)^2 =$ sum of the squares of the deviations for each film; $W_{a_0} =$ weight of a_0.

The fiduciary limit of the average, $\bar{a}_0$, is obtained from the standard error $S_{\bar{a}_0}$ by using the factor for probability $= 0.05$ corresponding to Σn degrees of freedom.

For other systems the treatment is similar, the same set of operations merely being repeated for each of the lattice constants. Actually the calculations are rather less cumbersome than would appear at first sight because most of the required quantities have been determined previously.

C. THE EXPERIMENTAL TECHNIQUE

Concerning the main features of construction of the symmetrical focusing cameras there is little to be said. Cohen's method of calculation makes it unnecessary to use meticulous care in keeping slit, sample and film on the same circumference. It is obvious that large values of the drift constant are undesirable on general principles so that reasonable accuracy in keeping the camera a true cylinder is indicated.

It is necessary in practically all cases to keep the sample moving during the exposure, otherwise the diffraction lines are apt to be spotty which is a serious handicap to accurate measurement. Of the various constructions possible, the one adopted in this laboratory is to mount the sample on a segment of the cylinder supported by a conical bearing accurately centered with respect to the cylinder axis. The precaution was taken of mounting the entire structure in a lathe by means of a bar through the central axis and trueing the cylinder with the slit and movable segment in position by a grinding operation. The movable segment is oscillated over a path approximately 0.5 cm on the circumference by a cam device with a worm gear and pulley to reduce the speed of the motor drive. It was found that unless the entire oscillating mechanism was made to move quite freely, friction caused a steady increase in camera and sample temperature during the exposure with deleterious effects on the final results (see below).

Diaphragming the divergent beam is an important detail. Since the focal spot of the target is used either as a point or a line source, the beam diverges in both horizontal and vertical directions, the cylinder axis of the camera being almost perpendicular to the target face plane in multiple window x-ray tubes or to the main plane of the x-ray beam with tubes with 45° targets. In the horizontal direction the beam must be restricted so that it stays within the sample area at all positions of the sample holder. In the vertical direction it must be restricted so that the beam is symmetrical with respect to a plane bisecting the opening between the upper and lower plates of the camera. It must be further restricted so that the direct beam itself nowhere strikes the plates else excessive background darkening is produced on the film which may obscure some of the weaker lines. With a camera of 10 cm diameter and 1 cm opening between the plates we have found it satisfactory to use beams which covered a sample area of approximately 25–30 mm long and 4–6 mm high; the slit width is 0.1 mm.

We have found no completely satisfactory way of printing fiducial points on a film during the x-ray exposure but our investigation on this point was not exhaustive. While strictly speaking it is unnecessary to have such reference points on the film if Cohen's method of calculation is used, it is desirable to make an approximate correction to keep the value of D low. Since most of the change in film length occurs during and after development, we have adopted the scheme of printing reference lines on the film after exposure to the x-rays but prior to development. This is done by means of a heavily blackened photographic plate with very fine lines ruled on it at points just beyond the darkened portion of the film; a special printing frame is used for the purpose. When it is necessary to keep the camera evacuated or filled with a thoroughly dried gas during exposure some other means might be necessary to obtain an approximate shrinkage correction since the film length is particularly sensitive of changes in moisture content of the film.

Temperature affects the precision determination of lattice constants in several ways. It is necessary that the camera temperature be con-

stant within 1°C and that the sample be allowed time to reach the camera temperature. Correction to a standard temperature by one of the obvious methods must be made if precision work by various investigators is to be compared. Constancy of temperature during the exposure is very important. It may be shown that the effect of changes in camera dimensions is negligible for cameras made of brass, bronze or steel even with changes as great as 5° during exposure. The effect of changing sample temperature is more significant for the position of the diffraction lines shift according to the relation:

$$\Delta L = 8R\alpha\Delta t \cot \phi = 8R\alpha\Delta t \tan \theta$$

with an expansion coefficient $\alpha = 2 \times 10^{-5}$ and $\Delta t = 3°C$ each line will be broadened (i.e., $\Delta L/2$) from 0.04 to 0.1 mm depending upon the angle. With varying temperature during exposure this broadening may be unsymmetrical and lead to false values for the lattice constants. It is for this reason that friction in the oscillating mechanism must be kept very low. We have occasionally observed temperature rises of 8 to 10°C when this detail was not cared for.

In this laboratory we have found it desirable to measure the line positions by means of a simple photometer. Light from a 6-volt, 108-watt Mazda ribbon filament lamp is passed through a lens system at the end of which is low power microscope. This is adjusted to give a very highly concentrated scanning beam of approximately 2.0×0.2 mm in area focused on the film. Light passing through the film strikes a Weston photronic cell. A portion of the light beam is split off ahead of the microscope and passes into a similar photronic cell. The two cells are opposed through a galvanometer. After the light has operated for 10 or 15 minutes, the deflections are virtually independent of variations in line voltage, etc. Intense lines produce galvanometer deflections of 20 to 30 cm. The film is firmly mounted on a carriage moved by a precision screw. A scale and drum is provided for making exact readings. Any systematic variation in the pitch of the screw is eliminated by the method of calculation. Irregular variations were found to be well within the other limits of error.

In our focusing cameras the range covered is

from $\sin^2 \theta = 0.78$ to 0.995. At the lower angles the two reflections of a $K\alpha_{1,2}$ doublet of iron radiation are separated about 0.5 mm; at the high angles by 6–7 mm. The high angle reflections, however, are rather broad while low angle reflections are sharp. Use of the photometer enables full use to be made of the sharpness of these low angle reflections as well as the high dispersion of the outer range of the camera. Lattice constants for a cubic substance calculated from the two lines of a doublet at low angles thus agree with each other quite as well as values from a doublet at high angles in spite of the difference in dispersion. The values obtained from the two doublets will not in general agree with each other because of the drift factor. The measurements over the entire film are, therefore, more consistent and if (for a cubic crystal) a graphical extrapolation such as a_0 vs. $\phi \tan \phi$ is used the scattering of the individual points about the best straight line representing them is nearly uniform over the entire range. The agreement between the measured and calculated line positions is shown by the last column of Table I. Similar results have been obtained for noncubic substances.

Cohen's method of calculating films is essentially an analytical extrapolation to $\phi = 0$. As such, the films must satisfy two important conditions if full value of the method is to be obtained. In the first place the film must show diffraction lines from at least two sets of planes for a cubic crystal, from three sets for hexagonal and tetragonal crystals, and from four sets for orthorhombic crystals. In the second place, these reflections must be properly distributed over the range of angles covered and at least one set of reflections should occur at $\sin^2 \theta > 0.90$ otherwise the extrapolation must be carried too far. With the more complicated structures it is usually not difficult to satisfy both conditions. The simpler metallic elements, however, yield relatively few lines and even when a number of different x-ray targets are available it is frequently impossible to obtain the necessary number and desired distribution of lines. Since the attainment of high precision is frequently required in these cases when solid solution limits are to be determined or deviations from some ideal law are to be studied, we have frequently

adopted the expedient of using a metallic alloy as a target, usually two elements in a 50 atomic percent mixture. Alloy targets of Fe-Mn, Fe-Ni, Fe-Cr, Cu-Ni, Fe-Co, Ni-Cr, Ni-Co and Cu-Mn all have been found to work satisfactorily. It is to be emphasized that one does not obtain the same result by exposing the same sample to the two different radiations on different films since the "drift constants" will not be the same except by chance.

The use of a refraction correction in lattice constant measurements has been discussed by several writers with the general conclusion that it was of uncertain validity and unnecessary in view of the attainable precision. The use of alloy targets and the attainment of higher precision makes it necessary to reconsider the matter. Without going into the theory of the subject, it may be said that in the few cases suitable for investigating the point, e.g., using radiation from a Ni-Cr target on a metal of high density, the results over the entire film were somewhat more consistent when a refraction correction was applied to each line measured. We have therefore applied such corrections in all the experimental work which follows in a later section. For convenience we have transformed Siegbahn's equation[9] and introduced a minor correction of 0.9 for anomalous dispersion as suggested by Weigle[7] which result in the following relation:

$$\Delta \sin^2 \theta = \frac{19.58 \rho Z}{M} \cdot \frac{\lambda^2}{4} \cdot 10^{-6}, \qquad (8)$$

where ρ = density, Z = atomic number, M = atomic weight and λ = wave-length in Angstroms. Care must be used in comparing precision results of various investigators because there is as yet no complete agreement on this point.

In systems other than cubic, there is an important source of variation in lattice constant data which, to our knowledge, has not been adequately considered elsewhere. This is the choice of planes whose reflections are to be used in the calculation.

To find the conditions which must be satisfied if the relative errors in a and c are to be the same, we may start with the equation for the standard errors, Eq. (5). Since $S_a/a = S_A/2A$ and S_c/c

[9] M. Siegbahn, *Spectroscopie der Röntgenstrahlen* (Springer, Berlin, 1931), pp. 36–42.

TABLE II. *Zinc.*

FILM	C_A	C_B	ACTUAL $\left(\frac{C_A}{C_B}\right)$	$\dfrac{\frac{C_A}{C_B}(\text{ACTUAL})}{21.11}$	$\dfrac{Sa/a}{Sc/c}$ MEAS.
VIII-35	279.37	1.7663	158.16	7.49	2.91
VIII-6	590.42	15.2077	38.82	1.84	1.36
VIII-8	590.45	15.2078	38.83	1.84	1.50
VII-229	227.90	6.9128	32.97	1.56	1.18

$$c/a = 1.856 \qquad (16/9)(c/a)^4 = 21.11 = C_A/C_B. \qquad (9)$$

$= S_B/2B$, we obtain by setting: $S_a/a = S_c/c = S_A/2A = S_B/2B$ the equation:

$$(16/9)(c/a)^4 = C_A/C_B. \qquad (9)$$

It will seldom be possible to satisfy this condition but excessive deviations from the equality can be avoided by proper choice of wave-lengths. The effect is illustrated by the results in zinc (see Table II). All of the films were taken with Fe-Co radiation. On film VIII-35 it was impossible to measure the reflections from the 104 planes which occur close to the low angle limit in the camera. On film VII-229 the reflections of $K\alpha_2$ radiation from the 104, 202, and 105 planes were too weak for measurement. Because of the distribution of the lines omitted in the second case, (VII-229) Eq. (9) is more closely satisfied than any of the other films tabulated while in the case of film VIII-35 the deviation from the equation is the largest although the lines dropped are those which have the least effect on the extrapolation.

While Eq. (9) appears cumbersome to use actually all the summations can be determined rather easily and the axial ratio c/a need not be known to more than three significant figures. Thus a preliminary value of the axial ratio and a knowledge of the reflection lines available from a given set of wave-lengths in a given camera are all that are needed to determine the best set of planes.

The application of this equation will frequently clear up otherwise puzzling discrepancies in the accuracies of results of different investigators and among different films obtained in a single investigation. Further it is occasionally important in solid solution investigations when, because of changing lattice parameters, certain lines move into or out of the range of the camera and the relative accuracy of several points on a lattice parameter *vs.* composition curve must be taken into consideration.

D. Preparation of the Sample

With increasingly high dispersion in diffraction cameras and precision in measurement of lattice constants, the preparation of the material to be studied by the x-ray methods becomes a problem of major importance. A lattice constant measurement or a description of a phase in terms of its lattice structure is virtually useless unless the substance has been prepared with sufficient care and its composition and method of preparation adequately described. This fact, although obvious, has not received the attention it deserves and many x-ray results reported in the literature, particularly in the fields of alloy structures and phase diagram studies, are seriously marred by failure to consider this important feature of x-ray work.

While practically every substance presents its own problems on this matter of adequate sample preparation, a few guiding principles can be stated which generally, but by no means always, bring about satisfactory results. From the technical side, every effort must be made (1) to be certain that the diffraction lines found on the photographic film correspond to the phase or phases present under the conditions postulated and (2) to secure sharp diffraction lines from each phase. Essentially the problem is one of bringing the substance into equilibrium under a definite set of conditions and retaining it unchanged until after the x-ray exposure has been made. This means, of course, that the methods used to attain equilibrium in heterogeneous systems must be applied. The attainment of equilibrium may, however, be a very slow process. We have frequently found it necessary to anneal metallic alloys for a month at temperatures of 450°C or higher before equilibrium was reached and occasionally for 4–6 months. One case has been reported where the annealing time was a year at 100°C.[10] On the other hand, annealing for as little as one hour occasionally permits such excessive grain growth that the films contain discontinuous spots instead of uniform lines. Spotty films cannot be successfully measured by photometric measurements since the diffraction lines are generally curved and

the spots are unsymmetrically distributed with respect to the median line of the films. For severely cold-worked specimens annealing for a few minutes at temperatures not far from their melting points is sufficient to secure equilibrium.

Most of the work in this laboratory concerns metallic alloys. The usual technique is to anneal the original ingot at the highest permissible temperature for 5–10 days to secure homogeneity of composition by eliminating "coring" and segregation. The ingot is then ground or filed to secure finely divided material for the x-ray work. These operations so frequently cause internal changes in the substance aside from the effect of the cold work that annealing of the powder is necessary. This final annealing is carried out at a definitely determined temperature and is followed by quenching so that the powder is brought to room temperature in a very short time, usually a small fraction of a second. Both annealing operations are usually carried out in vacuum but sometimes a hydrogen atmosphere is used. The latter has been found necessary if one of the elements is volatile in which case surprisingly small temperature gradients in the furnace may produce very marked effects. In the case of certain magnesium alloys, this element would distill out and partially react with the glass or quartz tube containing the powder. If sufficient time was allowed, a new equilibrium would be reached between the main portion of the powder and the material on the walls of the tube but, of course, the original analysis of the powder then became meaningless. By filling the tube with hydrogen so that at the annealing temperature the pressure inside would be approximately one atmosphere, distillation was hindered to such an extent that the powder remained unchanged in composition and the diffraction lines were quite sharp.

Variations in the composition of a phase produce variations in lattice parameter which will show up on the films either as a multiplicity of lines where only one line should occur or a broadening and blurring of the lines. The effect of small variations of lattice constant on line position is given by

$$\Delta L = 8R \cot \phi (\Delta a/a).$$

For a cubic substance with $a = 3.0$A in a camera

[10] E. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda, Trans. Am. Inst. Min. Met. Eng. 111, 264 (1934).

of 50-mm radius ΔL varies from 0.075 at $\phi = 28°$ to 0.75 at $\phi = 3°$ when $\Delta a/a = 0.0001$. There are many systems where such a variation in lattice constant is produced by relatively small composition changes.

Direct experimental test is the only way to determine whether a sample prepared under a given set of conditions can be retained without change under the conditions in the x-ray camera. In general there are three possibilities which must be considered. (1) The substance reacts with the atmosphere in the camera. This is comparatively rare and experimental means can usually be found to eliminate it. (2) The substance undergoes an allotropic change with greater or less rapidity, e.g., the transformation from γ to α iron which is exceedingly rapid or the transformation of sulfur from the monoclinic to the rhombic form which is comparatively slow. It is one of the serious disadvantages of the x-ray technique that in working with cameras at room temperature such transformations may be entirely missed. The $\gamma - \alpha$ transformation of pure iron could not have been found by ordinary x-ray methods. It was found by special cameras built for high temperature work.[11] No precision x-ray work has been done at temperature above 600°C and very little between 100° and 600°C.[12] Unfortunately very little can be done with x-ray methods alone to establish the existence or nonexistence of allotropic modifications when the investigation is restricted to pure substances at room temperatures. If a binary or more complex system involving such a substance is studied the chances of finding both modifications or of at

least suspecting that there is more than one modification are greatly improved. For example, in a two-phase region where one of the modifications is in equilibrium with another phase it is very rare that both are pure compounds. In other words, one of the phases is a solid solution. That the equilibrium concentrations of each of the modifications with this other phase should be the same is also a rare occurrence. Thus, if the high temperature modification has been brought into equilibrium with the neighboring phase and transforms during cooling to room temperature, the diffraction lines of at least one of the phases will be badly blurred because of lack of chemical homogeneity. While such a criterion is by no means infallible, it has frequently proved to be exceedingly useful in this laboratory and has made it possible to locate certain phase boundary regions with a fair degree of correctness. The higher the cooling or quenching rates, the better this criterion can be applied. Slowly cooled samples yield untrustworthy indications because the time of cooling permits adjustments in composition which result in sharper lines. (3) During quenching the substance becomes strained due to unequal cooling rates in different directions. It has been shown by Phillips and Brick[13] that with powders, fine wires and very thin foils such strains do not arise on quenching to such an extent that lattice constants are measurably affected. With larger sized material including the small quenched ingots frequently used in back reflection cameras such as the Sachs type, the results may be in error by amounts far exceeding the experimental errors enumerated in Part A.

[11] A. Westgren and G. Phragmen, J. Iron and Steel Inst. 105, 241 (1922).
[12] Cf. E. A. Owen and E. L. Yates, Phil. Mag. (7) 17, 113 (1934).

[13] A. Phillips and R. M. Brick, Trans. Am. Inst. Min. Met. Eng. Inst. of Metals Division 111, 94 (1934).

Part II. Experimental Results on Fourteen Metallic Elements

The theory and technique outlined in Part I have been applied to fourteen metallic elements of cubic, hexagonal and tetragonal symmetry. The cameras used were of the symmetrical focusing type of 10-cm diameter. Further details are concerned merely with the preparation and purity of the samples which will be given in connection with each element. Corrections for the temperature of the sample were made by

the use of the ordinary expansion formula using expansion data given in *International Critical Tables*. In noncubic systems the coefficients appropriate to each axis were used. All lattice constants have been corrected to 25°C. It should be mentioned again that the values have been corrected for refraction.

It is interesting to note that for but one of the elements investigated (iron) does a very small

amount of impurity have a marked effect and the only reported impurity which has such an effect is carbon. Carbon enters the alpha-iron lattice in the interstices and expands the lattice. Further, since the atomic weight is low in comparison with iron the weight percentage is a misleading way of giving the amount of impurity. There seems to be good reasons to believe that of the impurities contained in readily available "pure" metals the only ones which need be feared in regard to their direct effect upon the lattice constants are those of low atomic weight which form the interstitial type of solid solution. While interstitial solid solution in lattices of metallic elements is a rather rare phenomenon the elements which are most likely to go into this form of solid solution are carbon, hydrogen,

TABLE III. *Aluminum—face-centered cubic.*

SAMPLE	a_0	$Sa_0 \cdot 10^5$	NO. OF LINES	RAD.
1	4.0417$_9$	10	5	Cr
1	4.0412$_7$	11	4	Cu
1	4.0412$_2$	11	4	Cu
2	4.0414$_2$	3	4	Cu
2	4.0414$_6$	7	4	Cu
2	4.0412$_9$	15	8	Cr-Ni
	Mean	$a_0 = 4.0413_9 \pm 0.0000_8$		

Sample No. 1. 99.971%. Aluminum Co. of America. Analysis: Si—0.009; Fe—0.016; Cu—0.004.
Sample No. 2. Another sample of the above.

TABLE IV. *Nickel—face-centered cubic.*

SAMPLE	a_0	$Sa_0 \cdot 10^5$	NO. OF LINES	RAD.
1	3.5167$_2$	8	6	Fe-Mn
1	3.5168$_1$	7	6	"
2	3.5168$_9$	6	6	"
3	3.5168$_9$	11	6	"
4	3.5168$_8$	9	6	"
	Mean	$a_0 = 3.5168_1 \pm 0.0000_8$		

Sample No. 1. Spectroscopic traces of Cu. Prepared by C. G. Fink and F. A. Rohrman (Trans. Electrochem. Soc. **59**, 359 (1931)). 16 hr.—525°.
Sample No. 2. Electrolytic. 51 hr.—525°. Fe =0.013%; Co =0.11%; Si and S, traces.
Sample No. 3. 99.99%. Obtained from E. Fetz. 1 hr.—700°.
Sample No. 4. Prepared from NiCl₂·6H₂O by reduction with pure, dry hydrogen. Analysis of NiCl₂·6H₂O (J. T. Baker & Co.) SO₄—0.001; Fe—0.000; N compds. (as N)—0.04; Zn—0.00; Pb—0.00; Earths & alkalis, 0.15; Cu—0.004; Co—0.00. 71 hr.—550°.

TABLE V. *Silver—face-centered cubic.*

SAMPLE	a_0	$Sa_0 \cdot 10^5$	NO. OF LINES	RAD.
1	4.0779$_0$	6	9	Co-Ni
1	4.0778$_5$	8	11	Co-Ni
1	4.0776$_5$	5	4	Cu
1	4.0777$_5$	20	4	Cu
1	4.0778$_9$	5	9	Cr-Ni
1	4.0779$_6$	13	9	Cu-Ni
	Mean	$a_0 = 4.0778_7 \pm 0.0000_8$		

Sample No. 1. Proof silver—99.999+%. U. S. Metals Refining Co. Melted in an alundum crucible under vacuum in high frequency furnace. 24 hr.—600°.

TABLE VI. *Gold—face-centered cubic.*

SAMPLE	a_0	$Sa_0 \cdot 10^5$	NO. OF LINES	RAD.
1	4.0704$_4$	5	8	Cu-Ni
1	4.0703$_5$	5	9	Co-Ni
1	4.0703$_3$	8	9	Co-Ni
1a*	4.0705$_2$	7	8	Cr-Ni
1b*	4.0705$_6$	5	8	Cr-Ni
	Mean	$a_0 = 4.0704_2 \pm 0.0000_6$		

* Two measurements on same film.
Sample No. 1. Prepared by double precipitation with SO₂. 15 hr.—500°.

TABLE VII. *Silicon—diamond type cubic.*

SAMPLE	a_0	$Sa_0 \cdot 10^5$	NO. OF LINES	RAD.
1	5.4199$_5$	23	6	Fe-Co
1	5.4196$_8$	4	4	Ni
	Mean	$a_0 = 5.4198_2 \pm 0.0003_4$*		

* Silicon gives rather spotty films which accounts for the rather high value for the fiduciary limits.
Sample No. 1. 99.84%. Electro Metallurgical Co. Analysis: C—0.025; Mn—0.001; Fe—0.020; N₂—0.006; Al—0.016; O₂—0.034; Ca—0.005; H₂—0.006. 36 hr.—600°.

TABLE VIII. *α-Iron—body-centered cubic.*

SAMPLE	a_0	$Sa_0 \cdot 10^5$	a_0 (corr.)	FIDUCIARY LIMIT	NO. LINES	RAD.
1	2.8607$_8$	4	2.8604$_2$	$17 \cdot 10^{-5}$	4	Fe-Co
2	2.8607$_1$	5	—	22	4	"
3	2.8607$_1$	13	—	56	4	"
4	2.8607$_6$	11	2.8604$_9$	47	4	"
	Mean		2.8604$_6$			

Powders of samples 1 and 2 were annealed for 71 hours at 550°C; samples 3 and 4 for 13 hours at 570°C.
Sample No. 1 was German carbonyl iron. Analyses by the Union Carbide and Carbon Research Laboratories gave C, 0.007; Mn, trace; Si, 0.004; S, 0.004; P, nil; O, 0.004. The oxygen was determined by the iodine extraction method and was therefore not dissolved oxygen.
Sample No. 2 was some of Merck's "Iron by hydrogen" lot #33400 which had been further treated by heating 15 hours in pure dry H₂ at 500°C. "Maximum impurities," as stated on the label, were: substances insoluble in sulphuric acid, 0.500%; water-soluble substances, 0.05%; nitrogen, 0.003%; sulphide, 0.030%; arsenic, 0.0015%. The "insoluble in sulphuric acid" material is probably mostly SiO₂ which would not affect the lattice constant.
Sample No. 3 was a small piece received from Dr. J. B. Austin of the U. S. Steel Corporation Research Laboratories. It was made by P. P. Cioffi of the Bell Telephone Laboratories by heating in pure dry hydrogen at 1490°C for 24 hours. This sample is now being analyzed by the Bureau of Standards.
Sample No. 4 was from the same original source (Cioffi) but had been heated in moist hydrogen at 1500°C for 18 hours. The American Rolling Mills Co. reported the following analysis: C, 0.005; Mn, 0.03; S, 0.003; P, 0.004; Si, 0.01; O, 0.002; N, 0.0001.

Corrections. The measured values of a_0 were corrected for the effects of the impurities present insofar as these effects are known. It is certain that carbon, manganese, silicon and nitrogen enter into the alpha-iron lattice and change its dimensions. To what extent oxygen, sulphur and phosphorus enter the lattice and how much they affect the dimensions is, as yet, unknown. No correction is possible for these last three elements at the present time.
Silicon decreases the lattice constant of iron at the rate of 6.5×10^{-4}A per atomic percent[14] when the silicon is less than 9 atomic percent. Manganese increases the lattice dimensions. For small amounts of Mn we may assume the additivity of atomic radii (Vegard's rule) which gives a change of 8×10^{-4}A per atomic percent Mn if the radius of the latter is taken as 1.27A. This change is roughly checked by the work of W. Schmidt[15] who used very impure manganese in making his alloys.
J. L. Burns[16] showed that carbon enters the iron lattice at the rate of 0.0515A per *weight* percent carbon.
It should be pointed out that the analyses of the samples are probably not complete. Because of the uncertainties in the corrections no fiduciary limits are given for this element.

[14] E. R. Jette and E. S. Greiner, Trans. Am. Inst. Min. Met. Eng. **105**, 259 (1933).
[15] W. Schmidt, Stahl and Eisen, **49**, 1696 (1929).
[16] J. L. Burns, Trans. Inst. Min. Met. Eng. **113**, 239 (1934).

TABLE IX. *Molybdenum—body-centered cubic.*

SAMPLE	a_0	$Sa_0 \cdot 10^5$	NO. OF LINES	RAD.
1	3.1409_0	3	5	Cu
1	3.1410_9	2	6	Cu
1	3.1410_3	2	6	Fe-Co
2	3.1410_8	6	6	Cu
2	3.1409_7	5	6	Cu
	Mean	$a_0 = 3.1410_3 \pm 0.0000_4$		

Sample No. 1. MoO_3 reduced with pure dry hydrogen at about 500°. Analysis of MoO_3: Mo—99.5; insoluble in NH_4OH—0.01; SO_4—0.01; Heavy metals as Pb—0.002; Cl—0.001; NH_3—0.002; PO_4—0.0005; NO_3—0.003.
Sample No. 2. Sample prepared by a second reduction. Starting material same as above. No further heat treatment—material was x-rayed as taken from reduction furnace.

TABLE X. *Tungsten—body-centered cubic.*

SAMPLE	a_0	$Sa_0 \cdot 10^5$	NO. OF LINES	RAD.
1	3.1583_7	4	7	Fe-Co
	Mean	$a_0 = 3.1583_7 \pm 0.0001_2$		

Sample No. 1. 99.95%—W. P. Sykes, General Electric Co., Euclid, O. Analysis: spectroscopic traces of Si, Mo, Fe, Cu. 68 hr.—980°. Air cooled.

TABLE XI. *Magnesium—hexagonal close packed.*

SAMPLE	a	$Sa \cdot 10^5$	c	$Sc \cdot 10^5$	NO. LINES	RAD.
1	3.2029_8	21	5.2001_0	18	8	Fe
1	3.2031_8	15	5.2001_2	13	8	Fe
1	3.2029_3	18	5.2003_3	16	8	Fe
2	3.2030_6	11	5.2001_2	9	8	Fe
3	3.2028_3	13	5.2003_9	11	8	Fe
4	3.2030_6	29	5.2002_9	25	8	Fe
	Mean:	$a = 3.2030_0 \pm 0.0001_6$,	$c = 5.2002_1 \pm 0.0001_4$,			
		$c/a = 1.62354 \pm 0.0001_2$.				

Sample No. 1. 99.987%. Aluminum Co. of America. Analysis: Cu—nil; Pb—nil; Fe, Al—0.004; Zn—trace; Si—0.009. Sample prepared from original rods. 140 min.—405°.
Sample No. 2. Another sample prepared as above.
Sample No. 3. Same material as sample No. 1, but first melted in a magnesia lined alundum crucible in a high frequency induction furnace in an atmosphere of tank hydrogen. 140 min.—405°.
Sample No. 4. Same material as sample No. 1, but first melted in an electrical resistance furnace in an atmosphere of pure dry hydrogen. The hydrogen was purified by passing through heated tubes containing copper and magnesium and then through bottles of solid NaOH and calcium chloride. 140 min.—405°.

TABLE XII. *Zinc—hexagonal close packed.*

SAMPLE	a	$Sa \cdot 10^5$	c	$Sc \cdot 10^5$	NO. LINES	RAD.
1	2.6597_4	17	4.9367_4	11	8	Fe-Co
1	2.6593_7	6	4.9367_8	8	10	Fe-Co
2	2.6594_9	8	4.9370_3	11	10	Fe-Co
3	2.6596_1	7	4.9368_4	11	7	Fe-Co
	Mean:	$a = 2.6594_8 \pm 0.0000_8$,	$c = 4.9368_0 \pm 0.0001_1$,			
		$c/a = 1.85631 \pm 0.0001_0$.				

Sample No. 1. Spectroscopic. N. J. Zinc Co. Analysis: Pb—0.0004; Fe—extremely faint; Cd—absent; Hg—extremely faint; Cu—extremely low; Mn—absent. 24 hr.—285°.
Sample No. 2. 99.936%. Eimer & Amend. Analysis: As—0.00005; Pb—0.05; Fe—0.01; Cd—0.001; sulfate (SO_4)—0.0019; chloride (Cl)—0.001. 36 hr.—285°.
Sample No. 3. 99.982%. Merck. Analysis: As—0.000025; Pb—0.010; substances oxidized by $KMnO_4$, such as Fe—0.0056; compds. of S & P =0.0000. 24 hr.—285°.

nitrogen and perhaps boron and oxygen; these elements are seldom reported in the analyses.

The powders, prepared by grinding or filing, were sealed in glass or quartz tubes and gently heated during evacuation with a mercury diffusion pump, the evacuation system was provided with a condensation trap to prevent mercury or oil vapor reaching the metal.

The annealing data on the powders are given with the analysis and source of the material.

TABLE XIII. *Cadmium—hexagonal close packed.*

SAMPLE	a	$Sa \cdot 10^5$	c	$Sc \cdot 10^5$	NO. LINES	RAD.
1	2.97298	10	5.60681	33	10	Fe-Co
2	2.97324	8	5.60707	26	10	Fe-Co
	Mean:	$a = 2.9731_1 \pm 0.0001_4$,	$c = 5.6069_4 \pm 0.0004_8$,			
		$c/a = 1.88588 \pm 0.0002_4$.				

Sample No. 1. Spectroscopic purity—N. J. Zinc Co. Analysis: Cu—extremely low; Mn—extremely faint; Fe—very faint; Zn, Pb, Hg—absent. 72 hr.—245°.
Sample No. 2. Baker—99.94%. Analysis on label: Zn—0.057; Pb—0.000; Fe—0.000; Cu—0.000. 72 hr.—245°.

TABLE XIV. *Antimony—hexagonal rhombohedral.*

SAMPLE	a	$Sa \cdot 10^5$	c	$Sc \cdot 10^5$	NO. LINES	RAD.
1	4.2995_7	9	11.2515_9	18	14	Fe
Mean	Hexagonal axes: $a = 4.2995_7 \pm 0.0002_0$, $c = 11.2515_9 \pm 0.0004_6$,					
	$c/a = 2.6169_1 \pm 0.0002_1$.					
	Rhombohedral axes: $a_{rh} = 4.4976_2 \pm 0.0001_8$, $\alpha = 0.99671_1$ $\pm 0.00009_2$ radians, $\alpha = 57°\ 6'\ 27'' \pm 19''$.					

Sample No. 1. Kahlbaum "Zur analyse." No analysis. 18 hr.—475°.

TABLE XV. *Bismuth—hexagonal-rhombohedral.*

SAMPLE	a	$Sa \cdot 10^5$	c	$Sc \cdot 10^5$	NO. LINES	RAD.
1	4.53722	29	11.83708	105	9	Fe
2	4.53732	9	11.83883	35	12	Fe
3	4.53722	16	11.83800	65	12	Fe
Mean	Hexagonal axes: $a = 4.5372_6 \pm 0.0002_0$, $c = 11.8381 \pm 0.0008$,					
	$c/a = 2.6091 \pm 0.0003$.					
	Rhombohedral axes (calculated from the above means): $a_{rh} = 4.7364 \pm 0.0003$, $\alpha = .99898 \pm 0.00011$ radians, $\alpha = 57°$ $14'\ 13'' \pm 23''$.					

All samples were Merck's bismuth, minimum purity 99.95%. Impurities as reported on the label are: Sb—0.00; Fe—0.008; Sn—0.003; As—0.000; Pb—0.010; S—0.01; Cu—0.005; Ag—0.010.
1. 5 hr.—200°.
2. very finely ground, 5 hr.—200°.
3. 24 hr.—165°.

TABLE XVI. *Tin—tetragonal.*

SAMPLE	a	$Sa \cdot 10^5$	c	$Sc \cdot 10^5$	NO. LINES	RAD.
1	5.8195_0	14	3.1750_0	5	8	Fe
	Mean:	$a = 5.8195_0 \pm 0.0003_0$,	$c = 3.1750_0 \pm 0.0001_2$,			
		$c/a = .54557_9 \pm 0.00005_7$.				

Sample No. 1. 99.995%. Baker. Analysis: As—0.0000; Zn—0.000; Pb—0.003; Cu—0.000; Fe—0.002. 117 hr.—151°.

TABLE XVII.

METAL			DENSITY 25°C	
			X-RAY	I.C.T. VOL. II
	a_0	*Cubic*		
Al	$4.0413_9 \pm 0.0000_8$		2.695	2.702　2.698
Ni	$3.5168_4 \pm .0000_5$		8.900	$8.90 \pm .05$
Ag	$4.0778_7 \pm .0000_8$		10.494	10.489　10.483(1)
Au	$4.0704_2 \pm .0000_6$		19.287	19.264
Si	$5.4198_2 \pm .0003_4$		2.325	2.4
Fe	2.8604_6 (see text)		7.868	7.90
Mo	$3.1410_3 \pm .0000_6$		10.217	10.2*
W	$3.1583_7 \pm .0001_2$		19.261	19.3*

Hexagonal

METAL	a	c	X-RAY	DENSITY I.C.T. VOL. II
Mg	$3.2030_0 \pm 0.0001_8$	$5.2002_1 \pm 0.0001_4$	1.736	1.738(2)
Zn	$2.6594_9 \pm .0000_8$	$4.9368_8 \pm .0001_1$	7.130	7.135
Cd	$2.9731_1 \pm .0001_4$	$5.6069_4 \pm .0004_5$	8.637	8.644
Sb	$4.2995_7 \pm .0002_0$	$11.2516 \pm .0004$	6.688	6.71　6.69
Bi	$4.5372_8 \pm .0002_0$	$11.8381 \pm .0008$	9.798	9.80

Tetragonal

Sn	$5.8195_0 \pm 0.0003_5$	$3.1750_0 \pm 0.0001_4^t$	7.281	7.30

Rhombohedral

METAL	a_{rh}	radians		
Sb	$4.4976_2 \pm 0.0001_8$	0.99671 ± 0.00009		57° 6′ 27″ ± 19″
Bi	$4.7364 \pm .0003$	$.99898 \pm .00011$		57° 14′ 13″ ± 23″

* No temperature given.
(1) Density determined in this laboratory = 10.492 at 25°C.
(2)　　　″　　　″　　″　　″　　　=.1.733　″　　″

The wave-lengths used in calculating these lattice constants were those given by M. Siegbahn.[17] Attention is called to the excellent agreement (cf. Table XVII) between densities calculated from x-ray measurements using these wave-lengths and the value of 6.0644×10^{23} for Avogadro's number.[18] Wave-lengths determined by means of ruled gratings and refraction phenomena[19] are on the average 0.25 percent higher than the crystal wave-lengths, and therefore the calculated (x-ray) densities would be nearly 0.75 percent lower than those given in Table XVII, unless Avogadro's number is changed in proportion.

It may be observed that the fiduciary limits range from ± 2 to 7 parts per 100,000 and that from the way in which the fiduciary limits have been computed the chance that the correct value

of the lattice constant falls within the respective limits is 19 out of 20.

The measurements on fourteen metallic elements are tabulated in Table XVII in text, together with densities calculated from the x-ray data and densities obtained by direct measurement. All measurements were corrected for refraction and temperature (to 25°). The limits given are the fiduciary limits for $P = 0.05$.

In conclusion, we wish to thank the various firms and individuals who have supplied pure materials and carried out analyses to assist in this work. We are indebted to Mr. Wm. Hurwitz for making a large proportion of the calculations included in this paper and for valuable suggestions as to the use of fiduciary limits. We are also indebted to the Federal Emergency Relief Administration for making available a number of student assistants who carried out the laborious routine of the photometric measurements of the x-ray films.

[17] M. Siegbahn, reference 9, p. 183, Table 46.
[18] R. T. Birge, Rev. Mod. Phys. 1, 58 (1929).
[19] Cf. J. A. Bearden, Phys. Rev. 47, 883 (1935).