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Tests for the Validity of the X-Ray Crystal Method for Determining N and e with Aluminum, Silver and Quartz

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The principal objections to the x-ray crystal method of determining N and e are that the presence of a mosaic effect or superstructure will not affect the lattice parameters as determined by x-ray diffraction but will affect the density, and further that the x-rays measure the lattice constant of only a very superficial layer which might not be characteristic of the interior of the crystal. The crystal structure of two polycrystalline metals, silver and aluminum, and one single crystal, powdered quartz, were precisely measured with the Seeman-Bohlin spectrograph. The crystallites were small enough so that the radiation penetrated them completely and the effect of distortion of the metal crystals on the density and crystal structure was investigated. The following values of N and e were found

	N	e
Silver	$6.0309 \pm 0.0024 \times 10^{23}$ mol g mol^{-1}	$4.7957 \pm 0.0019 \times 10^{-10}$ e. s. u.
Aluminum	6.0257 ± 0.0009	4.7998 ± 0.0007
Quartz (1)	6.0237 ± 0.0006	4.8014 ± 0.0005
(2)	6.0278 ± 0.0006	4.7982 ± 0.0005

where the two different values for quartz are for two different values of the molecular weight of silicon and the error is that due to internal consistency only. When the results of Tu are expressed in absolute units we find

	N	e
Calcite	$6.0235 \pm 0.0003 \times 10^{23}$ mol g mol^{-1}	$4.8016 \pm 0.0003 \times 10^{-10}$ e.s. u.
KCl	6.0215 ± 0.0005	4.8032 ± 0.0004
Rocksalt	6.0247 ± 0.0005	4.8006 ± 0.0004
Diamond	6.0256 ± 0.0003	4.7999 ± 0.0003

After examining these deviations from a consistent value of N and e and the effect of distortion on the metal crystals the authors believe that there is perhaps a small mosaic (or superstructure) effect that renders the value of N and e uncertain by 0.04 percent and that the best value of e is perhaps slightly lower than that obtained with macroscopic calcite, say $4.801 \pm 0.002 \times 10^{-10}$ e. s. u.

THE x-ray crystal method of determining Avogadro's number, N, and its associated constant, e, the charge of the electron, is open to two fundamental objections. Avogadro's number is given by $N = M/\rho f$, where M is the molecular weight of the crystal, ρ its density and f the volume associated with one molecule as determined from x-ray diffraction data. If either a more or less regular superstructure, random holes or imperfections in the crystal lattice exist their presence will not affect the lattice constants as measured by the x-rays for they measure only a periodic spacing, but the measured density, which is the average density, will not be the true density of the periodic sections of the lattice. The existence of a superstructure (or mosaic structure) has been proposed by Zwicky[1] to account for certain mechanical properties and habits of growth. He proposed that there are periodic variations in the grating space in the crystal along a direction normal to the planes. Their period would be of the order of 10^{-6} cm and the superposition of such a long period on the interplanar spacing of 10^{-8} cm would not affect the relative positions of the x-ray diffraction maxima and would have negligible effects on the intensity.

However, one would not expect the error introduced in the density by the presence of a superstructure or imperfections of the lattice to be the same for all crystals. Tu[2] measured the density and lattice parameters of calcite, rocksalt, potassium chloride and diamond crystals and found they gave a consistent value of N, the largest deviation being 3 parts in 10,000. If one uses the latest values of the molecular weights the agreement is not quite as good as this, as Table I shows. Bearden[3] claims that Tu has made some systematic error in his density measurements and also that he did not correct some observations for temperature even though he said he did. In view of these facts his results should be examined rather critically. Also, one would not expect, if there is a regular superstructure, that the secondary component would have exactly the same coefficient of thermal expansion as the normal component. A. H. Jay[4] measured

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* Now at the University of Pennsylvania.

[1] F. Zwicky, Phys. Rev. 40, 63 (1932).

[2] Y. C. Tu, Phys. Rev. 40, 662 (1932).

[3] J. A. Bearden, Phys. Rev. 54, 698 (1938).

[4] A. H. Jay, Zeits. f. Krist. 89, 282 (1934).

the thermal expansions of silver, quartz and bismuth by the x-ray powder method, precision methods being employed. The macroscopic thermal expansion was also measured by optical methods and the same values obtained indicating that the expansion of the atomic lattice does not differ from that of the crystal as a whole. Thus the presence of a large secondary component appears doubtful. However, it is one of the purposes of the present investigation to work with lattices known to be distorted and imperfect and to find how much these distortions affect the values of the lattice constants of the periodic part of the lattice and the average density of the crystal.

The second objection to the x-ray method is that because of the extinction of x-rays in passing through the crystal the lattice constant of an extremely thin superficial layer (5×10^{-5} cm for calcite in the first order with Mo$K\alpha$) is measured, and this may not be representative of the interior of the crystal. Allison and Armstrong[5] measured the wave-length of Mo$K\alpha_1$ in various orders of reflection from calcite (see Table II) and concluded that the lattice constant is uniform throughout the crystal. DuMond and Bollman[6] measured the density and lattice parameters of extremely fine powdered calcite, where the size of the individual crystals was of the order of the depth of half-penetration of the x-rays. They found that within experimental error the lattice constants and density were identical with those of macroscopic calcite.

TABLE I. *Consistency in the value of N as calculated by Tu and as revised to conform with latest values of molecular weights.*

	Tu 1932		1939	
CRYSTAL	M	$\frac{N_{\text{Cal}}-N}{N_{\text{Cal}}}$	M	$\frac{N_{\text{Cal}}-N}{N_{\text{Cal}}}$
Calcite	100.075		100.090*	
NaCl	58.454	−0.033%	58.456†	−0.020%
KCl	74.557	0.012	74.553†	0.033
C (0.89k)	12.003	0.021	12.0115*	−0.033
C (1.78k)	12.003	0.015	12.0115*	−0.038

* Letter from R. T. Birge, September, 1939.

† Na = 22.998; Cl = 35.458. Landolt-Bornstein, *Physikalish-Chemische Tabellen*, 5th edition (J. Springer, 1935). K = 39.094 Baxter and McNevin, J. Am. Chem. Soc. **55**, 3185 (1933); K = 39.095 Hönigschmid and Sashtleben, Zeits. f. anorg. Chemie **213**, 365 (1933).

These experiments indicate the absence of any large superstructure or imperfections. The purpose of the present investigation is twofold. First, to make a precision determination of the density and lattice parameters of powdered quartz (a "perfect" crystal) by methods different from those employed by Tu[2] and Bearden.[7] Both measured their densities by immersion and their lattice parameters with a two crystal spectrometer. In the present research the densities were measured with a specific gravity bottle and the lattice parameters with a Seeman-Bohlin focusing spectrograph. Second, to make a precision determination of the density and lattice constants for two polycrystalline metals (silver and aluminum) and to see what effect distortion has on the density and lattice. Since the difference between a "perfect" crystal and a polycrystalline material is one of degree this will permit the estimation of the inherent accuracy of the x-ray crystal method of determining *e*.

TABLE II. *Allison and Armstrong's measurements of the wave-length of* Mo$K\alpha_1$ *in various orders of reflection from calcite.*

ORDER	HALF-DEPTH OF PENETRATION		λ	$\frac{\lambda n-\lambda_1}{\lambda_1}$
n	cm	No. of planes		
1	5×10^{-5}	1.6×10^{3}	0.707831	
3	4×10^{-4}	1.3×10^{4}	0.707902	0.01 %
4	6×10^{-4}	2×10^{4}	0.707850	0.003
5	1.2×10^{-3}	4×10^{4}	0.707840	0.001

Powder samples of aluminum and silver were prepared by filing or sawing and these samples along with some solid pieces which were as large as would enter through the neck of the specific gravity bottle were annealed together in a vacuum furnace. The powder sample of quartz was prepared by breaking up optically clear California quartz in a steel mortar by pounding with a heavy sledge hammer. The coarser grains were rejected by the fine screen through which the sample was sifted. The lattice parameters and density of these samples were measured. If we think of a sample of material as made up of many small perfect crystals or crystallites,

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[5] S. K. Allison and A. H. Armstrong, Phys. Rev. **26**, 701 (1925). (Corrected for the index of refraction.)

[6] J. W. M. DuMond and V. L. Bollman, Phys. Rev. **50**, 524 (1936).

[7] J. A. Bearden, Phys. Rev. **38**, 2089 (1931).

randomly situated relative to each other, then the resolving power of these units for x-rays will depend on their size, that is on the average number of perfectly periodically spaced planes that they contain. Thus from the width of the diffraction pattern (Debye-Scherrer rings) it is possible to measure the average length of the periodic sections of the lattice, i.e., the size of the crystallites. In the case of the metals the powder and large pieces were then distorted by mechanical working and the new density, grating constant and size of crystallite were determined. Actually the shape and dimensions of the unit cell were found to be unaffected by working, but the length of the regions of regular periodicity was found to decrease. The density was found to change slightly upon working, an increase for silver and a decrease for aluminum. On the basis of these measurements it is possible to estimate the effect of distortion on the value of N and e.

The Density Measurements

The weights used in the density determination were carefully calibrated and could be depended on to 0.1 mg. Double weighing was employed throughout and corrections were made for the buoyancy of the air. The specific gravity bottle was of conventional design and contained a thermometer. The bottle was weighed when empty, and then was filled with distilled water, which had been redistilled in an all Pyrex still and freshly boiled just before using, and weighed again. Fifteen measurements on the volume of the bottle at different temperatures were taken and the least-squares error in the calibration was 0.0003 percent. The temperature was adjusted by placing the bottle in a water bath and adjusting its temperature until the top of the distilled water was at the fiducial mark in the capillary of the specific gravity bottle and the temperature in the bottle the same as that of the water bath. The temperature was made uniform to 0.05°C. A weighed amount of sample was placed in the bottle, filled with water and weighed again. Then the volume of the sample could be calculated.

The aluminum* was annealed for 4 hours at a temperature of 350°C in a vacuum furnace and allowed to cool in the furnace and the following value, representing nine observations on samples weighing from 8 to 10 g, of 2.69839 ± 0.00005 g cm^{-3} at 25.0°C obtained. The density was very reproducible for different samples. Some annealed aluminum was placed in an arbor press and compressed without sudden impact so the dimensions were changed by a factor of two. This should not change the lattice as much as hammering or severe working, but if there are any holes in the sample they should be closed and the density increased. The results of three measurements on a 14-g sample gave $\rho=2.69828\pm0.00004$ g cm^{-3} at 25.0°C. One may conclude from the fact that the density actually decreased a slight amount that there was no effect due to holes in the annealed sample. The sample was severely worked by hammering and the density redetermined with three measurements on a 12-gram sample and found to be 2.69801 ± 0.00006 g cm^{-3} at 25.0°C.

The silver was annealed in the same furnace for 24 hours at 600°C and allowed to cool in the furnace. The result of five determinations on a 40-g sample was $\rho=10.4868$ g cm^{-3} at 25.0°C. This sample was worked and then reannealed and the result of three determinations was $\rho=10.4873$ g cm^{-3} at 25.0°C. The average was $\rho=10.4870\pm0.0002$ g cm^{-3} at 25.0°C. The silver was then compressed without sudden impact in an arbor press and the density, representing six determinations on 29- and 40-g samples, found to be $\rho=10.4878\pm0.003$ g cm^{-3} at 25.0°C. One concludes from the fact that the density is reproducible upon annealing and that it increases only slightly when compressed that there are no large random holes in the sample. The silver was then severely worked by hammering and four determinations on a 40-g sample gave $\rho=10.4911\pm0.0006$ g cm^{-3} at 25.0°C.

When the quartz powder was being prepared some pieces as large as would conveniently enter the neck of the specific gravity bottle were saved and four determinations on a 12-g sample gave as the density $\rho=2.64822\pm0.00005$ g cm^{-3} at 25.0°C. In measuring the density of finely powdered quartz, the powder had a tendency to contain small air bubbles after the water was added, but these were almost completely re-

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* Obtained through the courtesy of William L. Fink of the Aluminum Company of America.

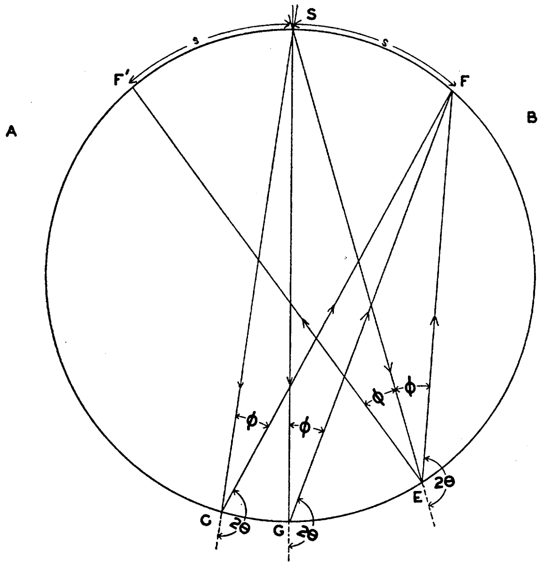

FIG. 1. The Seeman-Bohlin focusing spectrograph.

moved by boiling the water under vacuum (at room temperature). Some of the sample was almost colloidal in size and as it formed a suspension in the water a small amount of quartz (less than 0.2 mg) must be lost when the thermometer is inserted and displaces a small amount of water. The result of seven determinations on samples weighing from 10 to 16 grams is $\rho = 2.64810 \pm 0.00015$ g cm^{-3}. The density of powdered quartz seems to be identical with that of the macroscopic sample.

MEASUREMENT OF THE LATTICE CONSTANT

A Seeman-Bohlin focusing type of powder spectrograph was used because it gives strong lines with a relatively short exposure and if the wave-length of the x-rays is chosen so that the Bragg angle for some plane or planes is nearly 90° it is capable of very great accuracy for $\sin\theta$ varies slowly with θ in this region. Fig. 1 shows a diagram of the camera. The powder sample is placed along the arc *CGE* diametrically opposite the slit *S* through which the divergent and monochromatic x-rays enter. At every point there will be some crystals oriented in such a way as to obey the Bragg equation $\lambda = 2d\sin\theta$ and diffract the x-rays to *F*. The photographic film is placed along the arc *ASB*. That the camera is focusing is apparent when we consider that the arc *SF* subtends the same angle for every point along the arc *CGE*. There will be crystals oriented in such a way as to diffract the x-rays of wave-length λ to the point F' such that the arcs $F'S$ and *FS* are equal. The spectrograph gives a photograph which is symmetric with respect to the slit and by measuring $F'SF$ we can find $2s$ without knowing the position of the slit. If *D* is the camera diameter then

$$d = \lambda/2\sin\cdot\theta = \lambda/2\cos\phi/2 = \lambda/2\cos S/2D$$

and

$$\Delta d/d \backsimeq (S^2/4D^2)(\Delta S/S).$$

Then, as the largest value of $S^2/4D^2$ used was 0.1 we see that a one-percent change in *S* means a 0.1 percent change in *d*.

M. U. Cohen[8] has discussed the errors introduced by vertical divergence of the beam, slit width, thickness of the powder sample, shrinkage of the film and errors in the measurement of the camera radius and has shown that for cubic crystals $\Delta d/d \backsimeq K\phi\tan\phi/2$ and suggests plotting *d* against $\phi\tan\frac{1}{2}\phi$ which when extrapolated to $\phi = 0$ would give the correct value of the lattice constant. Two and three parameter crystals can be treated similarly. In the present investigation each of the errors was corrected for separately, and the consistency of the values of *d* obtained was used as a criterion for the validity of the corrections. The shrinkage of the photographic film was corrected by making two fine marks on the photographic film just before developing and then measuring the distance between the marks after developing and assuming the shrinkage to be uniform. The following correction was added to the measured value of *s*.

$$\Delta s = \frac{s}{D}\left(1 + \frac{s^2}{3D^2}\right)\left(\frac{f}{2} - t + \frac{h^2}{4D}\right),$$

where *f* is the thickness of the photographic film (double emulsion), $2h$ is the vertical height of the illuminated sample and *t* is the thickness of the powder sample. Because of the thermal expansion of the lattice a change of one degree centigrade introduces an error of about 0.002 percent in *d*. The temperature of the camera was held constant within half a degree during the ex-

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[8] M. U. Cohen, Rev. Sci. Inst. **6**, 68 (1935).

posure. The camera dimensions were not affected by temperature by an appreciable amount. If the crystallites were less than 1000A on a side the diffraction patterns of the components of the $K\alpha$ doublets would begin to overlap because of the finite resolving power of the crystal grating and the apparent maxima would be shifted in position. Corrections were made for this when necessary.

X-ray diffraction pictures were taken with carefully annealed samples of the metals and the lines were made up of distinct spots from which it was estimated that the size of the crystallites was about 2000A. When the sample was distorted by mechanical working the spots disappeared and the lines became continuous and broadened. With $\mathrm{Cu}K\alpha$ radiation upon aluminum and silver samples which are face-centered cubic crystals diffraction occurs with θ almost 90° from the (511) and (333) planes. If the lattice is strictly cubic the interplanar distance for (511) and (333) planes (and all permutations of the indices) is the same. If there is any change of shape of the unit cell the interplanar distances for the (333), $(3\bar{3}3)$, $(33\bar{3})$ and $(\bar{3}33)$ sets of indices might all be different and these four planes would give rise to four separate diffraction patterns. If the distortion is small the patterns will overlap and give the appearance of a single but broader line. In the same way, with distortion of the unit cell, the permutations of the (511) indices will give rise to as many as twelve nonequivalent interplanar distances. If a cubic crystal has undergone a small distortion where $a_1=a+\Delta a_1$, $a_2=a+\Delta a_2$, $a_3=a+\Delta a_3$, $\alpha_1=\pi/2-\epsilon_1$, $\alpha_2=\pi/2-\epsilon_2$ and $\alpha_3=\pi/2-\epsilon_3$ ($a_1a_2a_3$ are the axial lengths and $\alpha_1\alpha_2\alpha_3$ the interaxial angles in a general lattice) then it can be shown that

$$d\backsimeq\frac{a}{(h_1{}^2+h_2{}^2+h_3{}^2)^{\frac{1}{2}}}+\frac{h_1{}^2\Delta a_1+h_2{}^2\Delta a_2+h_3{}^2\Delta a_3}{h_1{}^2+h_2{}^2+h_3{}^2}+\frac{h_1h_2\epsilon_3+h_2h_3\epsilon_1+h_3h_1\epsilon_2}{h_1{}^2+h_2{}^2+h_3{}^2}.$$

We see that for the (511) and the (333) planes the first term is the same. For any change in the axial lengths the second term always has the same sign for both positive and negative values of the h's. However, the third term is sometimes positive and sometimes negative and its average value is zero. Thus when we find that our diffraction patterns are broadened when the samples are distorted by working it may be caused by either the finite resolving power of the shorter crystal grating or by the fact that we have formed several planes with nearly the same interplanar distance. However, if the position of the central maximum is unchanged upon working we can say definitely that there is no change in the axial lengths for $h_1{}^2\Delta a_1+h_2{}^2\Delta a_2+h_3{}^2\Delta a_3$ cannot vanish for (333), (511), (151) and (115) simultaneously except $\Delta a_1=\Delta a_2=\Delta a_3=0$. This assumes all the crystallites are distorted in the same way. Furthermore, since a face-centered lattice is a close-packed configuration it is difficult to see how the interaxial angles could be changed without altering the lengths of the sides. In the calculation of N it is only the volume of the unit cell we use. Since the volume of the unit cell is $V=a_1a_2a_3[1-\cos^2\alpha_1-\cos^2\alpha_2-\cos^2\alpha_3+2\cos\alpha_1\cos\alpha_2\cos\alpha_3]^{\frac{1}{2}}$ then when the unit cell is distorted as above the volume becomes, considering only first-order terms $V=a^3+a^2(\Delta a_1+\Delta a_2+\Delta a_3)$. This second term on the right is proportional to the average values of $h_1{}^2\Delta a_1+h_2{}^2\Delta a_2+h_3{}^2\Delta a_3$ when we consider all permutations of the Miller indices. Therefore, if the latter term is zero (average value of the interplanar distance unchanged), then the distortion

TABLE III.

	SIEGBAHN UNITS	ABSOLUTE ANGSTROMS
$\mathrm{Cu}K\alpha_2$*	1.541232	1.544361
$\mathrm{Cu}K\alpha_1$	1.537395	1.540516
$\mathrm{Cr}K\alpha_2$†	2.28891	2.29356
$\mathrm{Cr}K\alpha_1$	2.28503	2.28967
$\mathrm{Mo}K\alpha_1$‡	0.707831	0.709268

* I. Wennerlöf, Ark. Mat. Astro. o. Fys. (A) **22**, No. 8 (1930).
† S. Eriksson, Zeits. f. Physik **48**, 360 (1928).
‡ A. Larsson, Phil. Mag. (7) **3**, 1136 (1927).

TABLE IV.

RADIATION AND PLANES	TYPE	LATTICE LENGTH	% CHANGE IN A
$\mathrm{Cu}K\alpha$ (511) (333)	Powder	530A	0.001
$\mathrm{Cr}K\alpha$ (222)	Powder	740	−0.014
$\mathrm{Cu}K\alpha$ (511) (333)	Foil	1200	−0.007
$\mathrm{Cu}K\alpha$ (511) (333)	Foil	490	0.002
$\mathrm{Cr}K\alpha$ (222)	Foil	740	−0.007

TABLE V.

RADIATION AND PLANE	NUMBER OF PHOTOS	TYPE	a
Cr$K\alpha$ (222)	3	Powder	4.08595×10^{-8} cm
Cu$K\alpha$ (511) (333)	3	Powder	4.08616
Cr$K\alpha$ (222)	4	Foil	4.08599
Cu$K\alpha$ (511) (333)	3	Foil	4.08569
			Av. 4.08595 ± 0.00004

we have pictured changes the volume of the unit cell by second-order terms only. As the largest first-order change in some interplanar distance required to explain the observed width of line is 0.2 percent, any second-order effects are negligible.

The wave-lengths used in the calculations are given in Table III. The absolute wave-length† is taken as 1.00203 ± 0.00006 times the conventional Siegbahn value.

The result of powder photographs of annealed aluminum for Cu$K\alpha$ reflected from the (511) (333) planes (three photographs) and Cr$K\alpha$ from the (222) planes when corrected for the index of refraction* is $a=4.90932\pm0.00002\times10^{-8}$ cm at 25.0°C. The probable error is based on the inner consistency only and assumes the wave-length to be known exactly. The estimated length of lattice was 2000A. Both powder and foil samples were severely worked by hammering and the results given in Table IV were obtained.

One may conclude that when aluminum is worked by hammering smaller diffracting units having the same unit cell as the diffracting units in the carefully annealed sample are formed. In all cases the microphotometer traces were symmetrical and they did not have a flat top which one would expect if the width were due to several planes with nearly the same interplanar distances. Since a difference of 0.2 percent in some interplanar distances which were identical before distortion would be required to explain the observed width and in every case but one the maximum was shifted by less than a 0.007 percent change in the average interplanar distance one concludes that the distortion occurs mainly in the layers separating the diffracting units. Powder photographs were taken of aluminum evaporated on mica with the film being of the order of a wave-length of light thick. The lines were extremely weak and difficult to measure but the result of three photographs was $a=4.0492\pm0.0012\times10^{-8}$ cm. It is interesting to note that in order to take a successful photograph it was necessary to take the x-ray picture immediately after the evaporation was completed, otherwise no lines were obtained. When a second exposure was tried one day later with the same sample used in a successful photograph the diffraction lines were no longer present. The aluminum crystallites had presumedly taken up some preferred orientation on the clean freshly-cleaved mica surface.

The results of the powder photograph of annealed silver corrected for the index of refraction and at 25.0°C are given in Table V. The estimated lattice for both the foil and powder is 2000A. The samples were severely worked and the lattice constant redetermined with the following results:

RADIATION AND PLANES	TYPE	LATTICE LENGTH	% CHANGE IN A
Cu$K\alpha$ (511) (333)	Powder	280A	−0.004
	Foil	230	−0.011
	Foil	185	−0.006

and the evidence is that the unit cell is not distorted by working.

The effective length of perfect lattice was determined by means of the following formula:

$$B=0.90\lambda\left[\Lambda\cos\theta\left\{1-\left(\frac{\pi\Lambda\cos\theta}{\lambda}\right)^2\left(\frac{\beta^2}{9}+\frac{\delta^2}{4}\right)\right\}\right]^{-1}$$

where B is the half-breadth of the diffraction pattern (defined as the area under the microphotometer trace of the diffraction line divided by the maximum height) expressed in radians, Λ is the length of the lattice, θ the Bragg angle, 2β (radians) the width of the camera slit subtended at the sample and $\delta=(h^2/2D^2)\tan 2\theta$ is the ver-

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† Footnote (*) to Table I.

* The Siegbahn index of refraction correction for the well-known case of Bragg reflection consists of two parts, that due to the change of wave-length in the crystal and that caused by the refraction (bending) of the x-rays at the surface of the crystal. Actually only the former was corrected for. Since in a powder sample the planes through which the radiation enters are randomly orientated with respect to the Bragg planes a complete calculation of its effect is difficult. However, it is believed that this second correction for $\theta>75°$ is less than one part in 100,000.

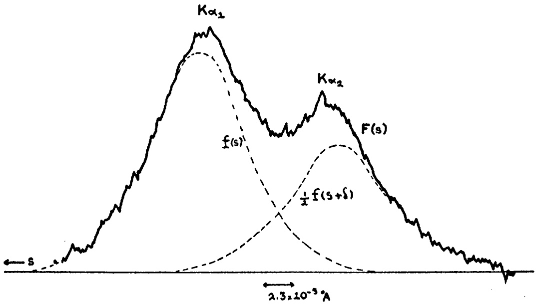

FIG. 2. Microphotometer trace of Ag sample for Cu$K\alpha$ from the (511) (333) planes. $\Lambda = 280$A.

tical divergence of the beam. The term in the brackets corrects for the effect of the broadening of the diffraction pattern by the vertical divergence of the beam and the finite slit width. It is a good approximation (within 5 percent) if $\{(\pi\Lambda\cos\theta)/\lambda\}\ (\beta+\delta/2)<1.5$. The formula for B is based on the following assumptions. (1) The crystals are all cubes with $2N+1$ particles on a side. (2) The crystals are oriented at random. (3) The crystals are undistorted and act independently. (4) The radiation is monochromatic. (5) Absorption and extinction in a crystallite are negligible. Various investigators have given formulas for various shaped crystals and found that the line breadth is not particularly sensitive to shape. If each of our cubes does not have $2N+1$ particles on a side but obeys a distribution function $f(N)$ then our formula gives

$$\Lambda = 2a \frac{\int_0^\infty N^4 f(N)dN}{\int_0^\infty N^3 f(N)dN}.$$

Actually the shape of the diffraction pattern depends only on the depth of the lattice perpendicular to the Bragg plane and the dimensions parallel to the Bragg plane affect only the total intensity. A typical microphotometer trace is shown in Fig. 2. The overlapping doublets were decomposed by the method given by DuMond.[9]

Six photographs using two different samples of quartz were taken with Cu$K\alpha$ radiation. The lines were indexed from similar photographs taken by Bradley and Jay.[10] Six planes and ten different lines were used. When lines from two different planes overlapped no attempt to resolve them was made and they were omitted from the calculation (Table VI). When we solve for a and c (quartz has a hexagonal unit cell) by least squares, correct for the index of refraction, change to absolute units and correct to 25.0°C we find

Lattice Constants of Quartz at 25.0°C
$a = 4.91267 \pm 0.00009 \times 10^{-8}$ cm
$c = 5.40459 \pm 0.00011$.

MOLECULAR WEIGHTS OF THE SAMPLES

The molecular weight of pure aluminum was taken as 26.9844. This is Aston's[11] mass spectroscopic value corrected to $C_{12} = 12.00388$ (physical scale) and changed to the chemical scale. The aluminum was analyzed for impurities and with the assumption that the foreign atoms fit into the aluminum lattice without distorting it, the effective molecular weight found to be 26.989+0.001. In the case of silver the molecular weight is taken as 107.880 and when this is corrected for the impurities in the sample the effective molecular weight found to be 107.858.

Unfortunately there is no universal agreement about the molecular weight of silicon. The value accepted by the International Committee on Atomic Weights is based on the determination of Baxter, Weatherill and Scripture[12] who compared $SiCl_4$ and $SiBr_4$ with Ag and found the molecular weight of silicon to be 28.063 ± 0.003. However, more recently Hönigschmid and Steinheil[13] by comparing $SiCl_4$ with Ag found the

TABLE VI. *Interplanar distances for quartz at* 26.0°C.

PLANE AND WAVE-LENGTH	θ	INTERPLANAR DISTANCE
(216) Cu$K\alpha_2$	79.287°	0.78429A (Siegbahn)
(216) Cu$K\alpha_1$	78.563	0.78427
(234) Cu$K\alpha_2$	77.509	0.78961
(234) Cu$K\alpha_1$	76.765	0.78967
(421) Cu$K\alpha_2$	76.159	0.79366
(315) Cu$K\alpha_1$	75.113	0.79539
(420) Cu$K\alpha_2$	73.843	0.80230
(420) Cu$K\alpha_1$	73.330	0.80242
(331) Cu$K\alpha_2$	72.510	0.80797
(502) Cu$K\alpha_1$	71.636	0.80994

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[9] J. W. M. DuMond, Rev. Mod. Phys. **5**, 1 (1933).

[10] A. J. Bradley and A. H. Jay, Proc. Phys. Soc. **45**, 507 (1933).

[11] F. W. Aston, Proc. Roy. Soc. **A163**, 391 (1937).

[12] Baxter, Weatherill and Scripture, Proc. Am. Acad. **58**, 245 (1923).

[13] O. Hönigschmid and W. Steinheil, Zeits. f. anorg. Chemie **141**, 101 (1924).

molecular weight to be 28.105±0.003 and Weatherill and Brundage[14] using the same method found 28.103±0.003 as the molecular weight. Because of the large differences between these observers it is unsatisfactory to average their values so we shall carry through the calculation of N and e for quartz using two different values for its molecular weight, 60.063±0.003 and 60.104±0.003. The mass-spectroscopic determination of the molecular weight of silicon gives 28.125 (chemical scale) but this must be regarded as quite inaccurate for the calculation is based on some preliminary values of the relative abundances of the isotopes as measured by McKellar[15] using the band spectrum of SiN.

Depth of Half-Penetration

For Cu$K\alpha$ radiation reflected from the (333) and (511) planes the depth of half-penetration is for

Al 1.4×10^{-4} cm or 1.8×10^{4} planes
Ag 5.8×10^{-5} cm or 7.3×10^{3}.

For Cr$K\alpha$ radiation reflected from the (222) plane the depth of half-penetration is for

Al 6.1×10^{-5} cm or 5.2×10^{3} planes
Ag 1.6×10^{-5} cm or 1.4×10^{3}.

and as the largest diffracting units were about 2000A the radiation penetrated the sample completely.

For quartz with Cu$K\alpha$ radiation the depth of half-penetration varies from plane to plane but is on the average about 1.3×10^{-4} cm or 1.6×10^{4} planes. The largest particles that could get through the screen were 5×10^{-3} cm, but when a sample of the powder was viewed under a microscope the average size appeared to be about 5×10^{-4} cm. As the radiation could penetrate from either side this is equivalent to an effective thickness of 2.5×10^{-4} cm so the x-ray information is fairly representative of all the sample used.

Calculation of N and e

The value of Q* used is $2.89224\pm0.00031\times10^{14}$ e. s. u. g mol^{-1}. The first probable error represents the errors in the molecular weight, the internal consistency of the lattice constant measurements and the density measurements. The second probable error takes into consideration also the uncertainty in the ruled grating measurements, and the uncertainty in Q. All the values of N and e should agree within the first probable error. For silver and aluminum the value of the density of the annealed sample is used but the probable error is increased to include the values for the worked samples.

For Al
$\rho=$ 2.69839±0.00038 g cm^{-3} at 25.0°C
$M=$ 26.989±0.001 g g mol^{-1}
$a=$ $4.04932\pm0.00002\times10^{-8}$ cm at 25.0°C
$N=$ $6.0257\pm0.0009\pm0.0014\times10^{23}$ mol g mol^{-1}
$e=$ $4.7998\pm0.0007\pm0.0012\times10^{-10}$ e. s. u.

For Ag
$\rho=$ 10.4870±0.0041 g cm^{-3} at 25.0°C
$M=$ 107.858±0.002 g g mol^{-1}
$a=$ $4.0859\pm0.0004\times10^{-8}$ cm at 25.0°C
$N=$ $6.0309\pm0.0024\pm0.0026\times10^{23}$ mol g mol^{-1}
$e=$ $4.7957\pm0.0019\pm0.0021\times10^{-10}$ e. s. u.

For Quartz
$\rho=$ 2.64810±0.00015 g cm^{-3} at 25.0°C
$a=$ $4.91267\pm0.00009\times10^{-8}$ cm at 25.0°C
$c=$ $5.40459\pm0.00011\times10^{-8}$ cm at 25.0°C
$M=$ 60.063±0.003 g g mol^{-1}
$N=$ $6.0237\pm0.0006\pm0.0011\times10^{23}$ mol g mol^{-1}
$e=$ $4.8014\pm0.0005\pm0.0010\times10^{-10}$ e. s. u.
or if
$M=$ 60.104±0.003 g g mol^{-1}
$N=$ $6.0278\pm0.0006\pm0.0011\times10^{23}$ mol g mol^{-1}
$e=$ $4.7982\pm0.0005\pm0.0010\times10^{-10}$ e. s. u.

Tu[2] did not make a direct determination of N and e but was only interested in their consistency in terms of arbitrary units. Using 0.709268×10^{-8} cm as the wave-length of Mo$K\alpha_1$* and the latest values of the molecular weights we shall calculate, from his data on values of the Bragg angle and his densities, the values of N and e.

For Calcite
$\rho=$ 2.71003±0.00005 g cm^{-3} at 18°C
$d=$ 3.03557±0.00001 at 18°C (cleavage)
$\Phi(\beta)=$ 1.09602±0.00001 at 18°C
$M=$ 100.090±0.005 g g mol^{-1}
$N=$ $6.0235\pm0.0003\pm0.0011\times10^{23}$ mol g mol^{-1}
$e=$ $4.8016\pm0.0003\pm0.0010\times10^{-10}$ e. s. u.

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[14] P. F. Weatherill and P. S. Brundage, J. Am. Chem. Soc. **54**, 3932 (1932).

[15] A. McKellar, Phys. Rev. **45**, 761 (1934).

* See footnote (*) to Table I.

* See footnote (‡) to Table III.

For KCl
$\rho = 1.98930 \pm 0.00014$ g cm^{-3} at 18°C
$d = 3.14541 \pm 0.00004 \times 10^{-8}$ cm at 18°C
$M = 74.553 \pm 0.0003$ g g mol^{-1}
$N = 6.0215 \pm 0.0005 \pm 0.0011 \times 10^{23}$ mol g mol^{-1}
$e = 4.8032 \pm 0.0004 \pm 0.0010 \times 10^{-10}$ e. s. u.

For Rocksalt
$d = 2.81962 \pm 0.00003 \times 10^{-8}$ cm at 18°C
$\rho = 2.16418 \pm 0.00014$ g cm^{-3} at 18°C
$M = 58.456 \pm 0.002$ g g mol^{-1}
$N = 6.0247 \pm 0.00050 \pm 0.0011 \times 10^{23}$ mol g mol^{-1}
$e = 4.8006 \pm 0.0004 \pm 0.0010 \times 10^{-10}$ e. s. u.

For C (0.89k)
$\rho = 3.5141 \pm 0.0001$ g cm^{-3} at 18°C
$d = 3.56692 \pm 0.00002 \times 10^{-8}$ cm at 18°C
$M = 12.0115 \pm 0.0005$ g g mol^{-1}
$N = 6.0255 \pm 0.0003 \pm 0.0011 \times 10^{23}$ mol g mol^{-1}
$e = 4.8000 \pm 0.0003 \pm 0.0010 \times 10^{-10}$ e. s. u.

For C (1.78k)
$\rho = 3.5142 \pm 0.0001$ g cm^{-3} at 18°C
$d = 3.56683 \pm 0.00002 \times 10^{-8}$ cm at 18°C
$N = 6.0258 \pm 0.0003 \pm 0.0011 \times 10^{23}$ mol g mol^{-1}
$e = 4.7998 \pm 0.0003 \pm 0.0010 \times 10^{-10}$ e. s. u.

Birge* after investigating the values for the density and lattice constants for calcite as given by different observers gives

$$N = 6.0227 \pm 0.0014 \times 10^{23} \text{ mol g mol}^{-1}$$
$$e = 4.8022 \pm 0.0010 \times 10^{-10} \text{ e. s. u.}$$

It is not surprising that the polycrystalline samples fall out of range of the single crystal values, for we do not really know how the small crystallites pack together to affect the average density. The fact that density of aluminum decreases on working and that of silver increases is interesting. One explanation is that there are small empty holes between the crystallites whose effect on the density is practically reproducible for different samples and that upon mechanical working some of the crystalline material is converted into an amorphous phase so that either of two things may happen (depending on the material). (1) Case of silver. Amorphous detritus (for both silver and aluminum probably less dense than the crystalline form because these metals expand on melting) partially or totally fills the holes with an accompanying decrease in macroscopic volume thus increasing the observed density of the sample. (2) Case of aluminum. The conversion of the crystalline form into the amorphous form not only fills any holes if such exist but also occurs for a sufficient fraction of the total material actually to decrease the observed density in spite of the partially compensating effect of filling the holes. It is also quite possible that the tenacity of the bonds between the little crystals of aluminum is rather poor and that cold working opens up internal holes like crushing a block of cement. However, the fact that the density and lattice constants change so little upon distortion and the values of N and e turn out to be in the range of those of single crystals is reassuring; there can be no large effect due to the inhomogeneity of the crystals (mosaic effect). But the different single crystals give values of N and e which differ by more than the experimental error, the e values being all somewhat lower than those obtained with macroscopic calcite. It is easy to be mislead by least squares errors but the present authors believe that there is perhaps a small mosaic effect that renders the value of e by the x-ray crystal method with large crystals invalid by 0.04 percent and that the best value of e may be slightly lower than we thought, say $4.801 \pm 0.002 \times 10^{-10}$ e. s. u. This value is the author's personal estimate. Actually the average value of e using our results and those of Tu[2] (weighing the metals as one-half and using the mean of the two values obtained for quartz) is $4.8005 \pm 0.0004 \times 10^{-10}$ e. s. u. However, as the individual values differ by many times the experimental error the least squares probable error means nothing for the spread in values is not due to statistical fluctuation but to something fundamental in the method.

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* Footnote (*) to Table I.