getragen für die Bedingung $(12{\cdot}0{\cdot}0) = 0$. Dies lieferte als mögliche Bereiche für $x(\mathrm{O_{III}})$ und $x(\mathrm{P_{II}})$:

$$0{,}202 < x(\mathrm{P_{II}}) < 0{,}216, \quad 0{,}286 < x(\mathrm{P_{II}}) < 0{,}298,$$

hierbei jeweils

$$0{,}285 < x(\mathrm{O_{III}}) < 0{,}298 \quad \text{oder} \quad 0{,}202 < x(\mathrm{O_{III}}) < 0{,}215.$$

Davon sind mit Raumerfüllungsbetrachtungen über den Bau des $\mathrm{P_4O_{12}}$-Ringes nur verträglich:

$$x(\mathrm{O_{III}}) \approx 0{,}28, \quad x(\mathrm{P_{II}}) \approx 0{,}2.$$

(4) Mit diesen vorläufig eingegrenzten $x$-Parametern wurden theoretische $\gamma$-Werte für die $h00$-Serie berechnet und mit den experimentall gefundenen (visuell geschätzte Intensitäten) relativen $\gamma$-Werten verglichen. Da sich gute Uebereinstimmung zeigte, konnten die erhaltenen relativen Intensitäten auf absolute Werte umgerechnet werden.

(5) Nunmehr wurden bei jeweils konstant gehaltenen $x(\mathrm{O_{IV}})$ für dessen verschiedene Werte von 0,114, 0,116, 0,118 usf. $x(\mathrm{O_{III}})$ als Funktion von $x(\mathrm{P_{II}})$ für die verschiedenen $\gamma$-Werte der $h00$-Serie berechnet. Die graphische Darstellung lieferte für jeden Reflex $h00$ eine Kurve im $x(\mathrm{O_{III}})$–$x(\mathrm{P_{II}})$-Diagramm. Für $x(\mathrm{O_{IV}}) = 0{,}116$ liefen alle diese Kurven durch ein kleines Feld, dem die Parameter

$$x(\mathrm{O_{III}}) = 0{,}279 \pm 0{,}003$$

und

$$x(\mathrm{P_{II}}) = 0{,}209 \pm 0{,}003$$

entsprachen. Gegen geringe Variation von $x(\mathrm{O_{IV}})$ war das Zustandekommen dieses kleinen Feldes sehr empfindlich, sodass $x(\mathrm{O_{IV}})$ auf

$$x(\mathrm{O_{IV}}) = 0{,}116 \pm 0{,}001$$

eingegrenzt werden konnte.

(6) Zur Kontrolle der ermittelten $x$-Parameter wurden die gefundenen $\gamma$-Werte mit den theoretisch berechneten für die Reflexe $h00$ verglichen:

| $h00$ | $\gamma_{\text{theoretisch}}$ | $\gamma_{\text{experimentell}}$ |
|---|---|---|
| 200 | 34,4 | 33 |
| 400 | 268,9 | 224 |
| 600 | 85,9 | 91 |
| 800 | 158,7 | 159 |
| 10.0.0 | 163,1 | 160 |
| 12.0.0 | 13,9 | 0 |
| 14.0.0 | 113,6 | 76 |

## Schrifttum

Andress, K. R. & Fischer, K. (1949). *Z. anorg. Chem.* **260**, 331.

MacGillavry, C. H. & Romers, C. (1949). *Nature, Lond.*, **164**, 960.

# Notes and News

*Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. Copy should be sent direct to the British Co-editor (R. C. Evans, Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England).*

## *International Tables:* X-ray wavelength values

The Editorial Commission of the *International Tables for X-ray Crystallography* have agreed that the X-ray emission and absorption edge wave-lengths to be used throughout the *Tables* shall be those given in *Tables de Constantes et Données Numériques*; *Longueurs d'Onde des Émissions X et des Discontinuités d'Absorption X*, by Y. Cauchois and H. Hulubei (Paris: Hermann, 1947). Since, however, the Cauchois–Hulubei tables are in X. units or in kX. units throughout, the conversion factor, ($\times 1{\cdot}00202 \times 10^{-3}$) or ($\times 1{\cdot}00202$) respectively, must be applied to express the given values in Ångström units.

The corrected values for some of the elements Ti–Au are given below and are compared, where possible, with those previously given by W. L. Bragg (*J. Sci. Instrum.* (1947), **24**, 27), and with the latest values kindly communicated by J. A. Bearden (now in the press).

*K emission lines in Ångström units*

(C.–H. = Cauchois–Hulubei value.)

| | $K\alpha_1$ C.–H. | Difference* | | $K\alpha_2$ C.–H. | Difference* | | $K\beta_1$ C.–H. | Difference* | |
|---|---|---|---|---|---|---|---|---|---|
| | | $X$ | $Y$ | | $X$ | $Y$ | | $X$ | $Y$ |
| Ti | 2·74841 | — | 0 | 2·75207 | — | −2 | ($\beta_1\beta_3$) 2·51381 | — | 0 |
| Va | 2·50348 | — | −1 | 2·50729 | — | 0 | ($\beta_1$) 2·28434 | — | −2 |
| Cr | 2·28962 | 0 | 0 | 2·29351 | +1 | 0 | 2·08480 | −1 | −1 |
| Mn | 2·10175 | −1 | 0 | 2·10569 | +1 | 0 | 1·91015 | +1 | −1 |
| Fe | 1·93597 | 0 | −1 | 1·93991 | 0 | −1 | 1·75653 | +1 | 0 |
| Co | 1·78892 | −2 | −1 | 1·79278 | +1 | 0 | 1·62075 | −2 | 0 |
| Ni | 1·65784 | −1 | −2 | 1·66169 | −1 | 0 | 1·50010 | −2 | −1 |
| Cu | 1·54051 | −1 | 0 | 1·54433 | +1 | 0 | 1·39217 | 0 | +1 |
| Zn | 1·43511 | −1 | 0 | 1·43894 | 0 | +1 | 1·29522 | −2 | 0 |
| Ga | 1·34003 | — | 0 | 1·34394 | — | 0 | 1·20784 | — | +1 |
| Ge | 1·25401 | — | 0 | 1·25797 | — | −1 | 1·12890 | — | 0 |
| Mo | 0·70926 | 0 | 0 | 0·71354 | 0 | — | 0·63225 | 0 | — |
| Rh | 0·61325 | +1 | +1 | 0·61761 | +1 | — | 0·54559 | 0 | — |
| Pd | 0·58542 | +3 | −1 | 0·58980 | +2 | — | 0·52052 | 0 | — |
| Ag | 0·55936 | +5 | +2 | 0·56378 | +3 | — | 0·49701 | 0 | — |
| W | 0·208992 | — | — | 0·213813 | — | — | 0·184363 | — | — |
| Pt | 0·185504 | — | — | 0·190372 | — | — | 0·163664 | — | — |
| Au | 0·180185 | — | — | 0·185064 | — | — | 0·158971 | — | — |

* $X$ = Bragg value − Cauchois–Hulubei value.
$Y$ = Bearden value − Cauchois–Hulubei value.

The differences are small and are significant only in the case of the shorter wave-lengths, which are not generally used in precision crystal measurements. The maximum difference between the Cauchois–Hulubei and the latest $K\alpha$ Bearden values is 0·00002 for Ni and Ag. Bearden estimates his possible experimental error as ± 0·00001, so that the maximum significant discrepancy is 1 in 50,000 for Ag radiation, and 1 in 160,000 for Ni. Where differences of this order are significant, it is probable that the Bearden values are the most accurate and should be used (with a clear statement to that effect). For general crystallographic purposes, however, the use of the more complete Cauchois–Hulubei tables is advised. It should be remembered that there is an uncertainty of about ± 0·00003 in the conversion factor, and a resulting uncertainty of ± 0·004 % in the *absolute* values of the wave-lengths. The uncertainty in the absorption-edge wave-lengths is greater (nearly 0·1 % in some cases) but this is not of importance in most crystal measurements.

*K absorption-edge wave-lengths in Ångström units*

(C.–H. = Cauchois–Hulubei value.)

| | C.–H. | Difference* | | C.–H. | Difference* |
|---|---|---|---|---|---|
| Ti | 2·4973 | — | Ga | 1·1957 | — |
| Va | 2·2690 | — | Ge | 1·1165 | — |
| Cr | 2·0701 | 0 | Mo | 0·6198 | −01 |
| Mn | 1·8964 | −10 | Rh | 0·5338 | +03 |
| Fe | 1·7433 | −04 | Pd | 0·5092 | −02 |
| Co | 1·6081 | −09 | Ag | 0·4858 | −03 |
| Ni | 1·4880 | −11 | W | 0·17837 | — |
| Cu | 1·3804 | −02 | Pt | 0·15817 | — |
| Zn | 1·2833 | −02 | Au | 0·15344 | — |

* Bragg value − Cauchois–Hulubei value.

The values of the wave-lengths used should always be stated in any publication where precision is of importance.

KATHLEEN LONSDALE
*Chairman of Editorial Commission*

## *Acta Crystallographica*

1. Attention is drawn to the revised notices printed on the wrapper of this issue.
2. Readers are reminded that current subscriptions expire on the appearance of Part 6 to be published on 10 November 1950. To ensure continuity of supply orders for Volume 4, with remittance, should be placed through the usual channels as soon as possible and in any case in time to reach the publishers in London not later than 31 December 1950.

## Computers and the Phase Problem in X-ray Crystal Analysis

A conference on the above subject was organized by Prof. Ray Pepinsky at the Pennsylvania State College 6–8 April 1950 at the invitation of that College and sponsored by the Office of Naval Research and the Rockefeller Foundation. Some fifty specialists in this field attended, among them six British and three Dutch who had come for that purpose; further European experts who happened to be in the U.S.A. were also present. The meeting during the Easter recess of this delightful University afforded a unique chance for reviewing all the computational procedures of applying Fourier methods to crystal analysis, starting with the various analogue arrangements, following up with punched-card methods, and culminating in Ray Pepinsky's electronic synthesizer X-RAC which was most impressively demonstrated. Even the adherents to simple and cheap devices readily acknowledged the enormous possibilities offered by a machine in which 820 complex Fourier coefficients could each be set in amplitude and phase by the simple operation of turning two dials and two switches, and the complete picture of contour lines of the two-dimensional synthesis obtained instantly on the screen of the oscilloscope. Apart from the gain in time, this method revolutionizes our approach to the entire problem by making it easy to experiment on the effect of alteration of phase or on the influence of a limited group of Fourier terms on the result. By changing the magnification given by the oscilloscope it is possible to present either one or more crystal cells, or parts of one, e.g. for the detailed study of a group within a molecule. Coordinate systems can be superimposed on the projection, and photographic recording as well as visual observation is possible. It is also possible to extinguish all but one contour line which can be set at any level, or to allow only those within any range to show.

While this machine has the convenience of presenting an instantaneous survey accurate to about 1 % of the recorded value, the digital computers, which are an extension of the Beevers–Lipson strip method, give greater accuracy of computation. How far this is a desirable feature in view of the limited accuracy of the $|F|$ values and of the termination effects was discussed repeatedly. The financial implications of the various methods were also reviewed. It was stressed that the cost of crystal analysis by Fourier methods should not be underestimated; a figure of about $40 per workday seemed to emerge from the discussion which assumed continuous operation of punched-card machines (including the pay of one operator), or about $50 per workday for X-RAC. This figure would be reduced by the part-time use of machines engaged for other work, by space being available without cost, etc. J. M. Robertson stressed the importance of having computing centres, so as not to distract the research workers from their main line to a technical side line.

For trial-and-error analysis, where the computed structure factors from a model have to be compared with the observed intensities, the use of optical 'fly's eye' methods was warmly recommended by all those who have had experience with it. H. Lipson stressed the advantage of obtaining the continuous transform of a single basis and sampling this at a later stage at points corresponding to the nodal points of the reciprocal lattice.

One of the main difficulties of converting the experimental $|F|^2$ information directly by optical means into a diagram of the density function $\rho(x)$ of the crystal, according to the method first described by W. L. Bragg, lies in the fact that even for centrosymmetrical crystals the phases with which some of the waves corresponding to individual $F$ values are made to interfere, have to be negative. M. J. Buerger described his 'microscope' in which the phase reversal (or, more generally, change) is obtained by setting small inclined mica flakes of uniform thickness in the optical path of each of these waves. The resulting picture of a projection of marcasite showed a clear resolution of the atoms.

For a rational method of crystal analysis the central problem is that of supplementing the $|F_h|$ values by their phase factors $\exp(i\phi_h)$, or, provided the crystal has a centre of symmetry, by the ± signs. If this problem were answered, the determination of the mass distribution in the crystal would be reduced to a merely computational operation. Recent years have seen much progress, the first general advance beyond the method of heavy atoms being given by Harker & Kasper's inequalities. After this breach the approach has been widened by MacGillavry, Karle & Hauptmann and Goedkoop, as reported at the conference. In order to obtain phase-determining relations, point atoms are assumed in the crystal; to this sharpening of the atomic peaks there corresponds in Fourier space the reduction of the observed $F$ values by an assumed atomic factor common to all atoms; furthermore a 'unitary structure amplitude' $U_h$ or $|\hat{F}_h|$ is introduced by dividing $F_h$ by $F_{000}$. The first source of relation between the $U_h$ is the limited number ($N$) of atoms in the cell. Banerjee showed in 1933 that as a consequence there exist linear equations between any $N+1$ successive $U_h$ values on any lattice row passing through the origin of the reciprocal lattice. Goedkoop generalized this equation to det $U_{H-K}=0$, where the vectorial orders $H$ and $K$ form any two different or identical sets of $N+1$ lattice vectors in the reciprocal lattice. By a proper choice of these sets the $U$ values appearing in this relation can be adapted to the ones known from observation; this makes his relations more supple than the original ones of Banerjee. As is the case for the latter, symmetry reduces the number of orders involved (Avrami).

The second source of relations is the positiveness of the density in the crystal. This leads Harker & Kasper and later Karle & Hauptmann to their inequalities. By their present contributions Karle & Hauptmann show how both equalities and inequalities can be obtained from the same form of determinant, according to whether its order is greater or smaller than the number, $N$, of atoms in the basis.

Altogether this new development of the theory of structure analysis has at present a rather forbidding mathematical aspect; it is, however, quite likely that this will mellow by more intensive discussion.

It is well known that according to the general scheme of Fourier transformation the Fourier series formed with the observable $|F|^2$ values (Patterson) represents the convolution or 'fold' of the density $\rho(x)$ of the crystal with $\rho(-x)$. The transition from $|F|^2$ to $F$ in Fourier space finds its geometrical counterpart in crystal space in the 'unfolding' of the Patterson diagram. In attempting this process it is important to clear the way by recognizing the effects caused in the Patterson diagram by the presence of symmetry elements in the crystal, or even in single groups of atoms of the basis (e.g. the symmetry $3/m$ of a $CO_3$ group). A. L. Patterson showed how such symmetry elements could be brought out on the fold by a suitable superposition of the fold on itself.

Altogether the impression left by this meeting is that the advance in the systematic tackling of the problems of structure determination has been very rapid along the three lines of computational aids, of algebraic approach and of understanding the relations contained in the theory of Fourier transformation. The X-RAC stands in a class by itself as, apart from its proficiency as a computing device, it permits, as it were, mathematical experimentation on two-dimensional Fourier series on a hitherto unknown scale.

P. P. EWALD

## Book Reviews

*Works intended for notice in this column should be sent direct to the Editor (P. P. Ewald, Polytechnic Institute of Brooklyn, 99 Livingston Street, Brooklyn 2, N.Y., U.S.A.). As far as practicable books will be reviewed in a country different from that of publication.*

### Einführung in die Mineralogie (Kristallographie und Petrologie),

By CARL W. CORRENS. Pp. 414, with 405 figs. Berlin: Springer. 1949. Price DM. 38·00; bound DM. 41·60.

We are accustomed to seeing books entitled 'Introduction' turning out to be nothing but ordinary text-books at a rather elementary level. The traditional type of a mineralogical text-book, initiated by Wallerius in 1749, consisted of a bare description of mineral species arranged in some sort of order.

To this original skeleton there were added by successive stages an introductory chapter, including the structure of crystals as well as the general physical and chemical properties of minerals, and a chapter dealing with the genesis of minerals in their natural setting—involving petrogenesis. The emphasis, however, was still overwhelmingly on the descriptive sections. The progress made during the last fifty years in the field of crystallography on the one hand, and in the field of petrogenesis on the other, has prompted Prof. Correns to discard the old type of mineralogy text-book and to produce a book which is completely novel both in its scope and in the arrangement of material, a book in which the purely descriptive part is reduced in the main to tables and occupies a bare 73 out of a total of 414 pages. This new type of 'Introduction to mineralogy' represents a very daring and radical attempt to get away from the traditional scheme and to outline the 'shape of things to come' in the field of mineralogy teaching.

The plan and structure of this book are based on two fundamental ideas: that minerals, with trifling exceptions, are crystalline substances, and that minerals are constituents of rocks. Thus the book is divided into (1) crystallography (150 pp.), (2) petrology (130 pp.), and (3) an appendix containing various tables, bibliography and indexes (129 pp.). This logical foundation scheme is not obtrusive. The novice will find no difficulty in following the text, while the specialist will find the factual material well and clearly arranged.

The first part is rather boldly entitled 'Crystallography'. It is true that it deals with crystals, but an English reader may think that the term 'crystallography' in the present case covers a very wide field. In a logical fashion this part is subdivided into (*a*) geometrical crystallography (*Kristallmathematik*), which includes crystal morphology, indices, projections, space lattices, point groups and space groups; (*b*) crystal chemistry (*Kristallchemie*), which in-