and because the deviations in $F_{\text{obs}}$ and $F_{\text{calc}}$ one wants to find may be partly obscured by incorrect 'refinement'.

### *The probable errors as functions of I and θ.*

We confine ourselves here to the first and the last of the above mentioned methods, and we designate the probable errors as estimated for the individual reflexions by $\delta$ and the values obtained by averaging $\delta$'s by $\sigma$.

It has been generally assumed that $\sigma$ can be considered as only a function of the magnitude of $F_{\text{obs}}$, though some authors have been aware of the influence of the Lorentz-polarization factor (*e.g.* Feil, 1961; Cruickshank *et al.*, 1960). Since maximum accuracy can be obtained with the least-squares method only when the weights assigned to the observations are correct (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1960), it was considered worth while to study this problem in some more detail.

From the formula $F_{\text{obs}} = \sqrt{I_{\text{obs}}/\text{Lp}}$ it follows that

$$\text{error in } F_{\text{obs}} = \frac{\text{error in } \sqrt{I_{\text{obs}}}}{\sqrt{\text{Lp}}},$$

and from this formula it is seen that the error in $F_{\text{obs}}$ may be expected to be a function of $I_{\text{obs}}$ and of $\theta$ (De Vries, 1963). It will be a function of $I_{\text{obs}}$ because the accuracy of the measurement is generally a function of the measured intensity. It will be a function of $\theta$ since

(*a*) the error in $F_{\text{obs}}$ is a function of the magnitude of the Lorentz-polarization factor;

(*b*) the error in $I_{\text{obs}}$ will be a function of $\theta$, *e.g.* through the $\alpha_1 - \alpha_2$ separation which increases with $\theta$.

Deviations in $F_{\text{calc}}$ due to approximations in the model will also be a function of $\theta$.

The correct way, therefore, to deal with the variation of $\sigma$ is not to regard it as a function of $F$ or as a function of $F$ and $\theta$, but as a function of $I$ and $\theta$.

### *The determination of φ(θ) and ψ(I).*

Since in most cases there will not be enough data to determine $\sigma$ directly as a function of two variables, we shall make the plausible assumption that the $I$-dependence of $\sigma$ is not influenced by $\theta$ or *vice versa*, in the formula:

$$\sigma = \varphi(\theta) \times \psi(\text{I}) .$$

This way it will be possible, after making an initial assumption about, say, $\varphi(\theta)$ (*e.g.* $\varphi(\theta) = 1/\sqrt{\text{Lp}}$; compare below), to use all $\delta$ values in each $I$ range to determine $\psi(I)$; this $\psi(I)$ is then used to obtain a better $\varphi(\theta)$, and so on. Thus the number of data over which averaging is performed each time will be large enough, and reliable estimates of $\varphi(\theta)$ and $\psi(I)$ can be obtained.

### *The interpretation of φ(θ) and ψ(I).*

Both $\varphi(\theta)$ and $\psi(I)$ have physical significance, so these functions may be of use not only for the calculation of weights but also as a check on the measurements and on the refinement.

From its definition it follows that $\psi(I)$ gives the variation of $\sigma$ with $I_{\text{obs}}$ when $\theta$ is constant, and since it does not seem likely that the error in $F_{\text{calc}}$ could be a function of $I$, this variation of $\sigma$ can always be attributed completely to the variation of the error in $F_{\text{obs}}$. So, a plot of $\psi(I)$ will give the variation of the error in $\sqrt{I_{\text{obs}}}$ with $I_{\text{obs}}$ (for constant $\theta$). For instance, for counter data the statistical counting error gives a constant contribution to $\psi(I)$, but, owing to the influence of errors in the measurement of the background scattering on the one hand and extinction, absorption and scaling errors on the other, one may expect an increase of $\psi(I)$ both for low and high values of $I$.

The interpretation of $\varphi(\theta)$ depends upon the method used to determine the $\delta$'s, since also the errors in $F_{\text{calc}}$ vary with $\theta$. Restricting ourselves for the moment to the influence of errors in $F_{\text{obs}}$, we get (for $I_{\text{obs}}$ = constant):

$$\begin{aligned} \text{error in } F_{\text{obs}} &= c \times \varphi(\theta) \\ \text{error in } I_{\text{obs}} &= 2c \times \text{Lp} \times F_{\text{obs}} \times \varphi(\theta) \\ &= 2c \times \sqrt{\text{Lp}} \times \sqrt{I_{\text{obs}}} \times \varphi(\theta) \\ &= c' \times \sqrt{\text{Lp}} \times \varphi(\theta) . \end{aligned}$$

Thus we find the following interpretation for $\varphi(\theta)$: a plot of $\sqrt{\text{Lp}} \times \varphi(\theta)$ gives the variation of the error in the intensity measurement with the Bragg angle (for constant $I_{\text{obs}}$). A variation of this kind may be caused for instance by the $\alpha_1 - \alpha_2$ separation, the varying breadth of the diffracted beam, slight misalignment of the crystal or absorption effects.

The $\theta$-dependence of various errors in $F_{\text{calc}}$ will be discussed in another article.

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## The Mo K$\alpha_1$/Cu K$\alpha_1$ wavelength ratio.

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The commonly used values of the wavelength of X-radiation were determined by Siegbahn (1931) and are based on the cleavage spacing of calcite. Cohen & DuMond (1963), in redetermining the value of Avogadro's number, have analyzed 16 X-ray lattice constant determinations. They found that the value of [illegible] determined from measurements made with copper radiation is 76 ± 25 ppm larger than the value determined with molybdenum radiation, when the Siegbahn wavelength values are used. This suggests that the ratio of the wavelengths, Mo $K\alpha_1$/Cu $K\alpha_1$, needs to be revised.

This ratio has been redetermined by the precise lattice constant method of W. L. Bond. The instrument used is the one described by Bond (1960) except that for the detection of molybdenum radiation the two Geiger tubes were replaced by scintillation counters and the dimensions of the collimator slits were increased to 0·010 inch wide × 2 mm high to give more intensity.

The specimen used was cut from a single crystal of super-pure germanium prepared by the Czochralski technique by E. Kolb of Bell Telephone Laboratories, and having a resistivity of 46·0–51·0 $\Omega$ cm. Cu $K\alpha_1$ radiation was used to measure the 444 reflection ($\theta = 70{\cdot}6^\circ$) and Mo $K\alpha_1$ was used to measure the 999 reflection ($\theta = 77{\cdot}7^\circ$). Corrections were made for polarization, refraction, and axial divergence of the beam. The temperature was held to ±0·1 °C and corrected to 25 °C using the expansion coefficient $6{\cdot}1 \times 10^{-6}$ deg$^{-1}$. Each $\theta$ value used in the calculations is the average of four determinations of the peak of the X-ray profile. The standard deviation was computed from the variation in measured $\theta$.

Assuming $\lambda$Cu $K\alpha_1 = 1{\cdot}537395$ kX, the lattice constant of germanium computed from the measured 444 reflection angle is $a = 5{\cdot}646141 \pm 0{\cdot}000037$ kX. This value was used with the measured 999 reflection angle to compute $\lambda$Mo $K\alpha_1 = 0{\cdot}707840 \pm 0{\cdot}000005$ kX. Details of this computation appear in Table 1. Thus the ratio is

$$\lambda(\mathrm{Mo})/\lambda(\mathrm{Cu}) = 0{\cdot}707840/1{\cdot}537395 = 0{\cdot}460415 \pm 0{\cdot}000005 .$$

This result is in good agreement with the ratio recently redetermined by Bearden, Henins, Marzolf, Sauder & Thomsen (1964). In a lengthy program of measurements using a two-crystal spectrometer, they have obtained the ratio

$$\lambda(\mathrm{Mo})/\lambda(\mathrm{Cu}) = 0{\cdot}707831/1{\cdot}537370 = 0{\cdot}460417 \pm 0{\cdot}000002 .$$

However, the change in wavelength ratio is in the wrong direction to harmonize the two sets of lattice constant data studied by Cohen & DuMond. Since an increase in the wavelength value of 1 ppm decreases the value of $\mathcal{N}$ by 3 ppm, based on my wavelength ratio, the two values of Avogadro's number would now differ by 126 ppm.

This method of lattice constant determination eliminates many of the errors present in powder methods, and corrections can be accurately computed for those remaining (Bond, 1960). The refraction correction applied here differs slightly from the classical one used by Bond, in which $\delta$ is unity minus the index of refraction of the crystal for the wavelength used, and

$$\delta = ne^2\lambda^2/2\pi mc^2 .$$

$n$, the number of electrons per cm$^3$, must be modified by a dispersion correction to allow for interaction of these electrons. This dispersion correction was taken from data of Dauben & Templeton published in *International Tables for X-ray Crystallography* (1962). $\delta$ calculated with this correction is $14{\cdot}4 \times 10^{-6}$ for germanium with copper radiation. The classical equation gives $15{\cdot}0 \times 10^{-6}$. For molybdenum radiation the value of $\delta$ used above is $3{\cdot}2 \times 10^{-6}$.

Bearden (1932) has used a prism method for measuring $\delta$ in quartz. His prism was prepared by wringing two optically flat plates together and polishing one mutual edge until the line of demarcation disappeared. This produced a sharp corner when the plates were separated. Our germanium prism was prepared in a similar way. It is more difficult to produce a flat surface and a sharp edge on germanium than on quartz because germanium is much softer and cleaves easily. The refracted and reflected lines on the X-ray film are, therefore, broader, decreasing the precision. Analysis of four films yielded a value of $\delta = (13{\cdot}1 \pm 1{\cdot}2) \times 10^{-6}$ for copper radiation.

Another method sometimes considered for determining the refraction correction is that of measuring several orders of reflection and finding $\delta$ from the slope of a plot of $a$ *vs.* cosec$^2$ $\theta$. Data from the 333, 777 and 999 reflections from germanium gave $\delta = 3{\cdot}95 \times 10^{-6}$ for Mo radiation, and measurement of the 111, 333 and 444 reflections gave $\delta = 7{\cdot}52 \times 10^{-6}$ for Cu radiation. Analysis of the Bragg equation corrected for refraction (James, 1948):

$$m\lambda = 2d(1 - \delta/\sin^2 \theta_m) \sin \theta_m$$

reveals that an error as small as a few seconds in measuring $\theta$ produces an uncertainty in $\delta$ of the same order of magnitude as $\delta$ itself. Therefore, it is impossible with out present facilities to determine $\delta$ by this method.

A second possible error will occur if there is a difference in the peak position of an X-ray line depending on whether it is excited by a small or a large excess voltage above the critical value. Van den Berg (1957) has reported such a shift in the Cu $L\alpha$ and Ni $L\alpha$ lines. Comparison was made of values of the lattice constant of germanium computed from the 999 reflection of Mo radiation with voltages of 25,

Table 1. *Summary of data used to compute wavelengths*

| | Cu $K\alpha_1$ | Mo $K\alpha_1$ | Co $K\alpha_1$ | Fe $K\alpha_1$ |
|---|---|---|---|---|
| *hkl* | 444 | 999 | 333 | 333 |
| $\theta_1$ | 70° 36′ 27″ | 77° 43′ 54″ | 55° 14′ 16″ | 62° 45′ 18″ |
| $\theta_2$ | 70° 36′ 29″ | 77° 43′ 47″ | 55° 14′ 12″ | 62° 45′ 19″ |
| $\theta_3$ | 70° 36′ 21″ | 77° 43′ 47″ | 55° 14′ 18″ | 62° 45′ 20″ |
| $\theta_4$ | 70° 36′ 29″ | 77° 43′ 51″ | 55° 14′ 18″ | 62° 45′ 17″ |
| $\theta_{\mathrm{mean}}$ | 70° 36′ 26·5″ ± 3·8″ | 77° 43′ 49·8″ ± 3·4″ | 55° 14′ 16·0″ ± 1·8″ | 62° 45′ 18·5″ ± 1·3″ |
| Lp correction | 0·2″ | 0·9″ | 0·05″ | 0·1″ |
| **a* (Kx) | 5·646014 | 5·646141 | 5·646141 | 5·646141 |
| $\delta$ | $14{\cdot}4 \times 10^{-6}$ | $3{\cdot}2 \times 10^{-6}$ | $20{\cdot}4 \times 10^{-6}$ | $23{\cdot}8 \times 10^{-6}$ |
| Refraction correction | 0·000091 | 0·000019 | 0·000171 | 0·000170 |
| Axial divergence | 0·000023 | 0·000092 | 0·000023 | 0·000023 |
| Temperature | 24·63° | 24·75° | 24·95° | 24·9° |
| Temperature correction | 0·000013 | 0·000009 | 0·000002 | 0·000003 |
| *a* (corr.) | 5·646141 | 5·646021 | 5·645945 | 5·645945 |
| $\lambda$ (kX) | | 0·707840 | 1·78528 | 1·93204 |
| Standard deviation | ±0·000037 | ±0·000005 | ±0·00002 | ±0·00001 |

**a* is the calculated value in the case of Cu $K\alpha_1$, assumed in the three other cases.

35, and 50 kV. The variation observed was less than the standard deviation of the measurements. For the 444 reflection with Cu radiation at 20, 35 and 50 kV, there was no difference in the values of $a$, the difference in measured $\theta_{444}$ being only 1·0 sec.

In the same way, and using the same germanium crystal, determination was made of the ratio of the Co $K\alpha_1$ wavelength and of the Fe $K\alpha_1$ wavelength to Cu $K\alpha_1$. $\lambda$ Co $K\alpha_1$ was computed from the 333 reflection for which $\theta = 55\cdot2°$. $\lambda$ Fe $K\alpha_1$ was measured from the 333 reflection at $\theta = 62\cdot7°$. A summary of the calculation and corrections is given in Table 1. The calculated wavelengths and wavelength ratios are shown in Table 2 where they are compared with the values of Siegbahn.

Table 2. *Calculated wavelengths and ratios*

| | Cooper | Siegbahn |
|---|---|---|
| Cu $K\alpha_1$ | 1·537395 kX (assumed) | 1·537395 kX |
| Mo $K\alpha_1$ | $0\cdot707840 \pm 0\cdot000005$ | 0·707831 |
| Co $K\alpha_1$ | $1\cdot78528 \pm 0\cdot00002$ | 1·78529 |
| Fe $K\alpha_1$ | $1\cdot93204 \pm 0\cdot00001$ | 1·932076 |
| $\lambda$(Mo)/$\lambda$(Cu) | 0·460415 | 0·460409 |
| $\lambda$(Co)/$\lambda$(Cu) | 1·16124 | 1·16124 |
| $\lambda$(Fe)/$\lambda$(Cu) | 1·25670 | 1·25672 |

The Co/Cu ratio is identical with Siegbahn's, while the Fe/Cu ratio differs by 16 ppm, and the Mo/Cu ratio differs by 13 ppm.

I am indebted to W. L. Bond and to J. W. M. DuMond for helpful advice and discussion.

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## New intermediate phases in transition metal systems. II.

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This report is a continuation of a former abstracted communication (Giessen & Grant, 1964) on intermediate phases encountered in the course of an examination of binary transition metal systems containing a refractory metal component. Detailed descriptions of this work have been published, or submitted for publication (Giessen, Ibach & Grant, 1964; Ritter, Giessen & Grant, 1964; Giessen, Kane & Grant, 1965). Since, additional binary and ternary systems have been investigated and 18 new ordered phases have been found. Detailed descriptions of this work will again be published elsewhere.

The structures were all derived from powder patterns taken with an XRD 5 diffractometer or with a 114·6 mm camera and Cu $K\alpha$ radiation; this was made possible by the fact that the complex close-packed structures are related, and that their powder patterns show typical coincid-

Table 1. *New binary and ternary transition metal phases*

| Compositional designation | Crystal system | Structure type | Layer structure symbol | $a_0$ | $b_0$ | $c_0$ |
|---|---|---|---|---|---|---|
| MoIr | Orthorhombic | $B19-$AuCd | AB(2) | 2·752 Å | 4·804 Å | 4·429 Å |
| WIr | Orthorhombic | $B19-$AuCd | AB(2) | 2·760 | 4·811 | 4·452 |
| $\alpha-$VIr | Orthorhombic | $\alpha-$VIr | — | 5·791 | 6·756 | 2·796 |
| $(V_{0\cdot96}Ir_{0\cdot04})Ir:(\beta-VIr)$ | Tetragonal | $L1_0-$AuCu | AB(3) | 3·887 | | 3·651 |
| $TaNi_2$ | Tetragonal | $MoSi_2$ | — | 3·154 | | 7·905 |
| $MoIr_3$ | Hexagonal | $DO_{19}-MgCd_3$ | $AB_3$(2) sh 0 | 5·487 | | 4·385 |
| $WRh_3$ | Hexagonal | $DO_{19}-MgCd_3$ | $AB_3$(2) sh 0 | 5·453 | | 4·350 |
| $\beta-TaNi_3$ | Monoclinic | $\beta-NbPt_3$* | $AB_3$(12) sh $\frac{1}{2}$ | 5·11 | 4·54<br>$\alpha = 90°38'$ | $25\cdot5_0$ |
| $Ta(Pd_{0\cdot92}Rh_{0\cdot08})_3$ | Orthorhombic | $\beta-NbPd_3$† | $AB_3$(6) sh $\frac{1}{2}$‡ | 5·492 | 4·829 | 13·54 |
| $Ta(Pd_{0\cdot72}Rh_{0\cdot28})_3$ | Rhombohedral | $\beta-Ta(Pd, Rh)_3$<br>(ordered Sm) | $AB_3$(9) sh 0 | 5·517 | | 20·26 |
| $Ta(Pd_{0\cdot88}Ru_{0\cdot12})_3$ | Rhombohedral | $\beta-Ta(Pd, Rh)_3$ | $AB_3$(9) sh 0 | 5·531 | | $20\cdot25_2$ |
| $Ta(Pd_{0\cdot67}Rh_{0\cdot33})_3$ | Hexagonal | $\gamma-Ta(Pd, Rh)_3$ | $AB_3$(10) sh 0 | $5\cdot52_0$ | | $22\cdot4_3$ |
| $Ta(Pd_{0\cdot5}Rh_{0\cdot5})_3$ | Hexagonal | $PuAl_3(VCo_3)$ | $AB_3$(6) sh 0 | 5·530 | | $13\cdot49_3$ |
| $Ta(Pd_{0\cdot75}Ru_{0\cdot25})_3$ | Hexagonal | $PuAl_3(VCo_3)$ | $AB_3$(6) sh 0 | 5·509 | | 13·44 |
| $Ta(Pd_{0\cdot725}Rh_{0\cdot225})_3$(H.T.) | Hexagonal | $DO_{24}-TiNi_3$ | $AB_3$(4) sh 0 | 5·517 | | 8·978 |
| $Ta(Pd_{0\cdot78}Ru_{0\cdot22})_3$(H.T.) | Hexagonal | $DO_{24}-TiNi_3$ | $AB_3$(4) sh 0 | 5·525 | | 9·027 |
| $Ta(Pd_{0\cdot5}Ru_{0\cdot5})_3$ | Cubic | $L1_2-AuCu_3$ | $AB_3$(3) sh 0 | 3·893 | | |
| $(Ta_{0\cdot5}Al_{0\cdot5})Ni_3$ | Hexagonal | $DO_{24}-TiNi_3$ | $AB_3$(4) sh 0 | 5·112 | | 8·340 |

* Giessen, Kane & Grant (1965).
† Giessen & Grant (1964).
‡ Shift density not certain.