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The Experimental Determination of the Soundness of Crystals from X-ray and Density Measurements*

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A method is described which makes possible the detection of imperfections in crystals of elements, compounds and solid solutions by the determination of molecular weights from X-ray and density measurements. Precision determinations of density and lattice constants are necessary for the calculations.

It is shown that the elements Ag, Cu, Fe, Pb, Te and the compounds LiF, $Pb(NO_3)_2$ and calcite may be considered as having a normal structure, as the number of imperfect sites found does not exceed the possible error of determination of these imperfections. A normal structure is also shown by the tetragonal mixed crystals of the general formula (Zn, Cd, Co) $[Hg(CNS)_4]$ and by the α phase in solid solutions of the Ag–Zn system.

The problem

To determine whether a crystal is sound or whether it has vacant sites or interstitial atoms it is necessary to know the lattice constants and the density with high precision. It is well known from the publications of Barrett, Bunn, Buerger, Foote & Jette, Hume-Rothery, Laves, Owen and others how to distinguish the different types of imperfections in crystals. The method developed, however, is not unambiguous, e.g. concerning Avogadro's number, for which different values have been used by different investigators. A modification of the method which avoids such pitfalls may be proposed as follows.

The method

The idea of this method is to use the molecular (or atomic) weights determined by means of X-rays (M_X) and to compare them with the chemical data (M). The M_X can be calculated by the formula

$$M_X = k N_s v d/n, \qquad (1)$$

where v is the volume of the unit cell in kX³, d is the density, and n is the number of molecules per unit cell. The difference between this formula and other similar ones (for example, the one for the determination of density by X-rays) lies in two respects: (1) N_s represents the Avogadro number used by Siegbahn in his wave-length determinations ($N_s = 6{\cdot}0594 \times 10^{23}$), and (2) $k = 1{\cdot}0002$ is a factor representing the raising of the molecular weight of calcite from 100·075, as used in the time of Siegbahn's X-ray wave-length determinations, to 100·095, the most recent figure including the effect of mixed-crystal formation. The reason why Siegbahn's Avogadro number and the factor k must be used is shown in an article due to appear in the *Zeitschrift für Physik*. If it is desirable to use Ångström units, the Siegbahn Avogadro number must be replaced by

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$N_0 = 6{\cdot}02385 \times 10^{23}$, and the factor k in (1) must be omitted.*

If the molecular weight of a substance is found in this manner by means of X-rays, it is very simple to determine the kind of imperfections in the crystal by comparison with the chemical molecular weight. If, with D positive,

$$\left.\begin{array}{ll} M_X - M = -D, & \text{there are vacant sites,} \\ \text{and if } M_X - M = D, & \text{there are interstitial atoms} \\ & \text{in the crystal.} \end{array}\right\} \quad (2)$$

If, within the error limits, $M_X - M = 0$, the crystal is sound. The expression

$$(M_X - M)/M = I \quad (3)$$

gives the ratio of the numbers of imperfect sites to all sites. Of course, the absolute number of imperfect sites per mole can be also determined by multiplying D by Avogadro's number.

The uncertainty of an M_X-determination (ΔM) is at present

$$\Delta M = 3{\cdot}1 \times 10^{-4} M. \quad (4)\dagger$$

Therefore, only if the absolute value of D exceeds $3{\cdot}1 \times 10^{-4}$ can the presence of holes or interstitial atoms in the crystal lattice be considered as established. Otherwise the crystal may be provisionally regarded as normal.

Examples: some elements and compounds

The lattice constants of very many elements and chemical compounds are known with high precision, and, as some reliable density measurements can be found in the literature, it is possible to calculate M_X by this combined X-ray–density method using formula (1), and thence determine D. The results of the calculations are listed in Table 1.

From this table it seems that silver has vacant sites in its lattice, but as the value $-0{\cdot}02$ lies completely within the limits of error even if $\Delta M = 2{\cdot}1 \times 10^{-4} M$ we cannot be certain of this conclusion and may regard the lattice as sound or normal. The other elements of the first part of the table are in the same category. Calcite is close to the limit.

Table 1. *Difference between the atomic or molecular weights determined by means of X-rays, and those determined by chemical methods*

Element or compound	M_X	M	D	ΔM from (4)
Ag	107·86	107·88	−0·02	±0·033
Cu	63·540	63·54	±0·000	0·019
Fe	55·858	55·85	+0·008	0·017
Pb	207·17	207·21	−0·04	0·064
Te	127·62	127·61	+0·01	0·039
LiF	25·939	25·940	−0·001	0·080
$Pb(NO_3)_2$	331·282	331·226	+0·056	0·103
Calcite	100·065	100·095	−0·03	0·031
Al	26·988	26·97	+0·018	±0·008
Mg	24·330	24·32	+0·01	0·008
Se	78·889	78·96	−0·071	0·025
NaCl	58·425	58·454	−0·029	0·018

In all other cases D exceeds the error limits and there must be imperfections in the crystals, e.g. Al has interstitial atoms, NaCl vacant sites. Further careful work before making final conclusions will show whether the figures of the lower part of Table 1 are true or not.

In a similar way (without using Avogadro's constant) Hutchison & Johnston (1940, 1941), Johnston & Hutchison (1942), C. A. Hutchison (1942) and D. A. Hutchison (1945), who made the first very accurate atomic-weight determinations by means of X-rays, came to a similar conclusion, that the substances LiF, KCl, calcite, diamond and even NaCl must have a normal structure.

The complex compounds (Zn, Cd, Co) [Hg(CNS)$_4$]

By the above method it can be proved that even some substitutional mixed-crystal systems have a normal structure. In the blue tetragonal complex compound $Co[Hg(CNS)_4]$, the cation Co^{2+} can be replaced partly or completely, e.g. by Zn^{2+}; mixed crystals of the formula (Zn, Co) $[Hg(CNS)_4]$ result. It is also easy to obtain crystals with the composition, for example, (Zn, Cd, Co) $[Hg(CNS)_4]$, where the sum of the 3 Me^{2+} makes together one g.-ion. Even the quantitative composition of such compounds may be indicated as follows: ($\frac{1}{2}$Zn, $\frac{1}{6}$Cd, $\frac{1}{3}$Co) $[Hg(CNS)_4]$. The distribution of these ions throughout the crystal is random, while the $[Hg(CNS)_4]^{2-}$ retain their positions (Straumanis & Stahl, 1943, 1944; Stahl & Straumanis, 1943, 1947). The chemical analysis of the compound gives the possibility of calculating the molecular weight, which can be compared with the weight determined by means of X-rays (see Table 2).

Table 2. *Molecular weights of mixed crystals of the general formula* (Cd, Co, Zn) $[Hg(CNS)_4]$

Composition of the cation in parts by weight			Mean			ΔM
Cd	Co	Zn	M_X	M	D	from (6)
1	0·02	0	543·85	543·37	+0·41	±0·46
1	0·5	0	518·59	519·23	−0·64	0·44
1	1	0	510·15	510·26	−0·11	0·43
30·72	7·715	28·95	510·32	510·31	+0·01	0·43

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* The new Avogadro's number follows from

$$N_0 = kN_s/(1{\cdot}00203)^3 = 1{\cdot}0002\, N_s/(1{\cdot}00203)^3 = 6{\cdot}02385 \times 10^{23}$$

(using the conversion factor 1·00202, N_0 is

$$(6{\cdot}02403 \pm 0{\cdot}00030) \times 10^{23}).$$

This number is close to the Avogadro's number

$$N = (6{\cdot}0235 \pm 0{\cdot}0004) \times 10^{23},$$

based on the chemical scale of atomic weights, recently calculated by DuMond & Cohen (1948).

† The relative error is calculated from (1) by the expression

$$\Delta M/M = 3\Delta a/a + \Delta k/k + \Delta d/d,$$

supposing that $\Delta a/a = 2 \times 10^{-5}$ ($v = a^3$), $\Delta k/k = 5 \times 10^{-5}$ and $\Delta d/d = 2 \times 10^{-4}$. N_s and n are constants. In cases when the accuracy of density determination is higher (e.g. in the upper part of Table 1, where $\Delta d/d = 10^{-4}$) the relative error is $2{\cdot}1 \times 10^{-4}$.

As the lines of the rotating-crystal diagrams were not too distinct, the error must be higher than indicated by the expression (4), and formula (6) must be used. From the figures of Table 2 it can be concluded that generally in the mixed-crystal system under consideration no holes and no interstitial atoms can be proved, although in some cases there may be imperfections in the crystals (second line of Table 2).

The silver–zinc system

The mixed-crystal α phase of the system Ag–Zn has been investigated by Stockdale (1940). He made very careful density determinations of a series of Ag–Zn alloys. In a later paper Lipson, Petch & Stockdale (1941) determined the lattice constants of the same alloys in order to find the X-ray densities and to get some information about the imperfections in these metallic mixed crystals. They found that in the alloys near 3, 17 and 29 atomic % of Zn all sites of the lattice are filled or, alternatively, there are some interstitial atoms. From the standpoint developed here it is possible (by means of M_X and M) to distinguish between these two cases, but the accuracy obtainable with the figures of the three authors must be determined. From a footnote at the end of their paper it follows that the accuracy of lattice-constant determination was about 10^{-4} or even 2×10^{-4}. Instead of (4) we get then

$$\Delta M = 5{\cdot}5 \times 10^{-4} M, \tag{5}$$

or

$$\Delta M = 8{\cdot}5 \times 10^{-4} M. \tag{6}$$

But as the accuracy of density determination was remarkably high ($\Delta d/d = 5 \times 10^{-5}$), we finally get

$$\Delta M = 4 \times 10^{-4} M \quad \text{or} \quad 7 \times 10^{-4} M. \tag{7}$$

Therefore the accuracy of determination is at about 16 or 28 imperfect sites per 10,000 face-centered unit cells.

The results of the calculations, using the expressions (1), (2) and (3), are summarized in Table 3. The I column of the table shows the imperfections in the Ag–Zn mixed crystal phase. Indeed, near 3, 17 and 29 atomic % Zn (30 and 31 % also) there seem to be some interstitial atoms in the alloys. But it is impossible to be certain of this statement because the number of imperfections found falls within the error limits given by expression (7), that is, 16 or 28 imperfections on 10,000 unit cells. Thus these alloys must be regarded as sound, as was already supposed by Stockdale in 1940.

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Table 3. M_X, M, D, D/M and I (*imperfect sites per* 10,000 *unit cells*) *of the* Ag–Zn *mixed crystals, computed from the figures of Lipson, Petch & Stockdale*

Zn (atom %)	M_X	M	D	D/M	I
0	107·83	107·88	−0·05	−0·00046	−18
1	107·41	107·46	−0·05	−0·00046	−18
2	106·99	107·03	−0·04	−0·00037	−15
3	106·64	106·61	+0·03	+0·00028	+11
5	105·75	105·76	−0·01	−0·00009	− 4
7	104·87	104·91	−0·04	−0·00038	−15
9	104·01	104·06	−0·05	−0·00046	−18
11	103·17	103·20	−0·03	−0·00029	−12
13	102·34	102·36	−0·02	−0·00019	− 8
15	101·51	101·51	±0·00	±0	± 0
17	100·67	100·66	+0·01	+0·00009	+ 4
19	99·77	99·81	−0·04	−0·00040	−16
21	98·95	98·96	−0·01	−0·00010	− 4
23	98·105	98·11	−0·006	−0·00006	− 2
25	97·255	97·26	−0·005	−0·00005	− 2
27	96·41	96·41	±0·000	±0	± 0
29	95·605	95·56	+0·045	+0·00047	+19
30	95·14	95·13	+0·01	+0·00010	+ 4
31	94·715	94·71	−0·005	+0·00005	+ 2
33	93·856	93·86	−0·004	−0·00004	− 2
35	92·99	93·01	−0·025	−0·00027	−11