

CONTRIBUTIONS TO THE STUDY OF THE STRUCTURE OF MIXED CRYSTALS

PRELIMINARY REPORT

BY

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(WITH 2 TEXT FIGURES)

Mixed crystals form true solid solutions. Compared with liquid solutions there exist on several points complete analogies. However, there appears a new factor, bringing with it new complications, for contrary to the liquids the crystals have their atoms arranged at fixed positions in space.

Two substances may be able to form mixed crystals on the condition that the two crystal lattices have about the same spacings, and the two space groups are identical or replaceable. In proportion as these conditions are realized the formation of the mixed crystals takes place in more or less complete series.

There exist indeed some cases where one might assume that different arrangements of the peripheral electron orbits obstruct the formation of mixed crystals. But generally this formation is only contingent on the space lattices of the components.

Two salts, however, may often be able to form a compound in molecular ratios whereas they are otherwise mixable in a small degree or not at all. Such a double salt forms a singular point in the interruption exhibited by the series of the mixed crystals. As stated by SANDONNINI and AUREGGI¹ the system $AgCl$ $TlCl$ forms a double salt of the composition $2 AgCl, 3 TlCl$, but no mixed crystals are produced. The existence of this compound has been confirmed by our X-ray investigations.

A similar system is formed by $AgBr$ $TlBr$ which behaves in quite the same manner. A double salt of the composition

¹ Atti R. Accad. Lincei, [5] 20 588 (1911)

$2 AgBr, 3 TlBr$ has been stated, the crystal structure of which is analogous with that of $2 AgCl, 3 TlCl$, the spacings, however, are greater.

VEGARD¹, who for the first time carried out X-ray investigations on mixed crystals, has shown that KCl and KBr form mixed crystals, the lattice of which is homogenous and of the sodium chloride arrangement. This lattice is consequently of the same kind as those of the pure salts, the ions of chlorine and bromine may replace each other at random². G. TAMMANN³ considers the structure of mixed crystals as lattices where the ions of the components replace each other in a regular arrangement. Consequently there should appear new reflection planes in the crystal². E. C. BAIN⁴ has reported such new interference maxima in the case of the alloy molybdenum tungsten in equimolecular proportions. These additional interference lines have also been observed through X-ray analyses on some other alloys, but, according to M. v. LAUE⁵ these alloys ought to be considered as compounds.

At the proposal of Professor Dr. V. M. GOLDSCHMIDT we undertook the investigation of several systems of mixed crystals, especially $AgBr AgI$.

In the systems investigated by us we have been unable on the Debye-Hull diagrams to substantiate the additional lines, the presence of which might suggest a regular arrangement of the atoms in TAMMANN's sense. It should be mentioned, however, that such a regular arrangement may not be formed in a short time. Thus the new reflection lines observed by BAIN appeared only after careful annealing of the sample. Because of the diffusion in salts being assumed to take place more slowly than in metals⁶, it should be possible that an eventual regular arrangement would need more time to be formed. Nevertheless, the speed of the diffusion in salts has a considerable value, as shown by a

¹ Zeitschr. f. Physik 5, 17 (1921).

² M. v. LAUE, Ann. d. Physik 56, 497 (1918).

³ Zeitschr. anorg. Chemie 107, 1 (1919).

⁴ Chem. and Met. Eng. 26, 655; 28, 65 (1923).

⁵ Ann. d. Physik 78, 167 (1925).

⁶ Cfr. DESCH, Chem. News 106, 191 (1912).

simultaneous precipitation of $TlBr$ and TlI ¹. By heating the precipitates 16 h. at $110^{\circ}C$ there were produced homogenous mixed crystals (cfr. Table 1). On the contrary, fused and quenched homogenous mixed crystals of AgI with 25% $AgBr$ kept at an ordinary temperature during three months were found to be broken down into mixed crystals of two different species (cfr. table 2, last column). It has also been shown that the speed of the diffusion has different values for different substances.

Thus mixtures of CuI AgI , containing 75 weight% CuI at $90^{\circ}C$ will form mixed crystals, the space lattices of which after heating at $400^{\circ}C$ increase. Consequently an additional admixture of AgI has taken place. Mixtures containing 25% CuI at $90^{\circ}C$ will form mixed crystals, the space lattices of which after heating at $400^{\circ}C$ decrease, depending on a further admixture of CuI . But a mixture containing 50% (45 mol%) AgI will form mixed crystals, the space lattices of which through the subsequent heating at $400^{\circ}C$ increase. In spite of an excess of cuprous iodide, the atoms of silver iodide did not manage to diffuse into the mixed crystals simultaneously with the atoms of cuprous iodide.

Consequently CuI is able to diffuse with greater velocity into the lattice of AgI than vice versa (cfr. table 3).

It will frequently occur, however, that two substances have a different arrangement of the atoms in space, but nevertheless are able to form mixed crystals. This phenomenon is then in most cases considered to be a case of *isodimorphism*. Isodimorphism is to be defined as the power of two different substances to crystallize in two different reciprocal isomorphous modifications. One of these modifications, however, is often unable at the temperature concerned, to exist independently of the other, and is then only known in isomorphous mixtures.

The conception of this may either be that one of the substances is forced to crystallize in the point group of the other (e. g. the said case of silver iodide, which, by means of an admixture of 25% silver bromide, is forced to crystallize in the sodium chloride arrangement), or it may be that the

¹ If the velocity of the diffusion depends on traces of moisture is questionable.

arrangement concerned is unstable at this temperature, an admixture of the other substance, however, rendering it more stable. (Thus the stabilisation of the cubic modification of thallos iodide may be managed by a small admixture of thallos bromide or chloride).

It is worth noticing that silver bromide is able to force 70% silver iodide into the sodium chloride grouping, whereas silver iodide can only force small quantities of silver bromide into the zinc sulfide arrangement.

In the system $AgI - AgBr$, thus, one of the components in different quantities may enter into the space lattice of the other component, and vice versa.

The system $TlI - TlCl$ behaves, however, in a somewhat different way, for thallos chloride does not enter into the lattice of the orthorhombic thallos iodide which is stable at an ordinary temperature, but the effect is that the cubic modification of the iodide is established.

When the system has a convenient composition two different crystal species are produced; viz. cubic crystals of TlI saturated with respect to $TlCl$, and cubic crystals of $TlCl$ saturated with respect to TlI .

Both for liquid and solid solutions the additivity of the molecular volumes has been maintained (provided no compounds are formed). It has thus been shown by RETGERS¹ that in a series of mixed crystals the molecular volume or volume of the unit cell is proportional to the molecular per cent.

If r represents the spacing of a (cubic) mixed crystal and a and b the spacings of the components; if further the mixed crystal contains x mol. per cent of a and $(1 - x)$ mol. per cent of b we have:

$$r^3 = a^3 x + b^3 (1 - x) \quad I$$

as a mathematical expression of RETGERS' law.

¹ Zeitschr. physik. Chemie 3, 497 (1889).

By application of the general lattice theory, however, it has been shown by GRIMM and HERZFELD¹ that the spacing of a mixed crystal has to be computed from the following equation:

$$r^n = a^n x + b^n (1 - x) \quad \text{II}$$

when r is defined through the minimal value of the potential energy (disappearance of the force).

VEGARD² has suggested the following equation as the result of his measurements:

$$r = ax + b(1 - x) \quad \text{III}$$

(The letters having the same meaning as above). I.e. the spacing of a mixed crystal is proportional to the molecular per cent. The exponent, n , of equation II is then by him put at $n = 1$. According to the lattice theory, however, one should expect to get n about 8 for the alkali halides³. As a matter of fact it has even been shown by GRIMM and HERZFELD (loc. cit.) that the measurements of VEGARD do not prove the correctness of equation II. Within the error of measurements his results are consistent with all values of the exponent, n , between 1 and 9.

Very accurate measurements of the spacings of mixed crystals of alkali halides by R. J. HAVIGHURST, E. MACH and F. C. BLAKE⁴ are, however, in agreement with n equal to 1 or 3 but not with $n = 8$.

If a mixed crystal is regarded as a building of ions of two components, and the different ions are able to replace one another in the lattice; if further the ions are regarded as rigid bodies, the volume effect which appears in the mixed crystal will be expressed by

$$n \approx 3.$$

According to the lattice theory, however, there exist repulsion forces, the influence of which effects a greater value of n .

¹ Zeitschr. f. Physik 16, 79 (1923).

² Zeitschr. f. Physik 5, 17 (1921).

³ Cfr. M. BORN, Fortschr. d. Mathemat. Wissensch. 4, 2. Aufl. p. 735. For the repulsion potential $n' = n + 1$ of the alkali halides there were obtained values between 7 and 10.

⁴ Journ. Amer. Chem. Soc. 47, 29 (1925).

A consequence of this is that the molecular volume of the mixed crystal may disagree with RETGERS' law.

Fig. 1 shows the curve of the lattice constants of the mixed crystals of the system $TlI-TlBr$. As may be seen the course of the curve is in accordance with an exponent greater than three. On the film of TlI containing 10% $TlBr$, a few faint lines from the orthorhombic TlI were observed. On the other films, however, it was impossible to detect any additional lines.

The reason why in most cases the disagreement with RETGERS' law is very insignificant is easily understood. The

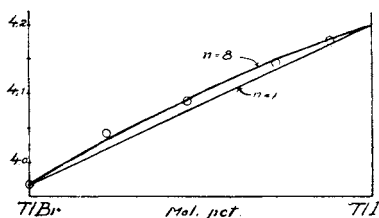


Fig. 1

Lattice constants of the mixed crystals of the system $TlBr-TlI$.

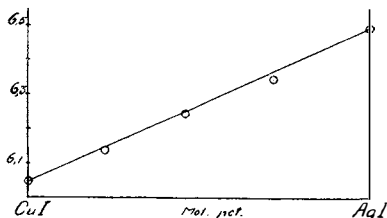


Fig. 2

Lattice constants of the mixed crystals of the system $CuI-AgI$.

condition of formation of mixed crystals was the slight difference between the molecular volumes of the two components, and then the curves of the spacings of the mixed crystals, computed from different values of n , will differ very slightly from each other, compared with the probable amount of experimental error. Therefore the effects of an eventual expansion lie within the error of measurements.

According to K. FAJANS¹ an increasing deformation of the anion affects the colour of a salt. Consequently it is possible to prove a slight deformation of the ions in mixed crystals through observation of the colours.

Thus the mixed crystals of $AgI-CuI$ have a light yellow colour, whereas the pure components are faint yellowish green and white respectively. The curve of the spacings of the mixed crystals accords best with $n=1$ according to VEGARD'S additivity law (Fig. 2). All the mixed crystals of $AgI-AgBr$ have more

¹ Naturw. 11, 165, (1923).

intense colours than the pure components. (This may, however be due to a stronger colour of *AgI* in the sodium chloride arrangement).

The mixed crystals of *TlBr* - *TlI* have colours which shade from light yellow to dark red, but the crystals rich in thallos iodide are darker than might be expected if there had been a gradual shading of the colours.

It is possible to observe the formation of mixed crystals even by the precipitation, for if a solution of *KI* and *KBr* at an ordinary temperature is precipitated with *AgNO₃*, the precipitate has a strong yellow colour, and it was proved by X-ray investigation to consist of mixed crystals. This holds also true in products, of simultaneous precipitation of *AgI* and *CuI*. The precipitate consists of mixed crystals and has a stronger colour than pure silver iodide. By precipitation of *TlI* - *TlBr* mixtures there are formed orange to red precipitates. The precipitate from *1TlI, 3TlBr* (in weight), dried at 20° C, gives homogenous mixed crystals. Precipitates from equal quantities of the two compounds consist, however, also of the orthorhombic modification of *TlI*. But by a short heating at 110° C, only homogenous mixed crystals were obtained.

Precipitates of *3TlI, 1TlBr*, heated 16 h at 110° C consist of crystals with a homogenous lattice of the caesium chloride type. It should nevertheless be possible that traces of the orthorhombic modification of the iodide was present, on account of which a sample was fused and quenched. The spacings of these crystals had actually increased, but very little. (Cfr. table 1.)

Precipitates of *AgI* - *CuI*, in all ratios, heated at 90° C, consist of homogenous mixed crystals of the zinc sulfide arrangement. No traces of lines from the hexagonal modification of silver iodide were observed. (Cfr. table 3.)

Precipitates of *AgI* - *AgBr*, heated at 110° C, also consist of mixed crystals at 50% *AgI*. Precipitates from 75% *AgI* consist, at 110° C, mostly of crystals with the sodium chloride arrangement, but there also occur in a lesser degree crystals of the zinc sulfide arrangement, the spacings of which were somewhat smaller than in pure silver iodide. (Table 2.) Through fusing and rapidly cooling of this precipitate there were formed

homogenous mixed crystals of the sodium chloride grouping, which, however, were unstable.

Through fusing and rapidly cooling of precipitates with 5.0%—10.0% silver bromide there was formed a mixture of cubic crystals of the zinc sulfide grouping and hexagonal crystals of the zinc oxide grouping. But these crystals were unstable, for through heating of the fused mixtures containing 10–20% *AgBr* at 150° C there were produced mixed crystals of *AgBr*, rich in *AgI*, crystallizing in the sodium chloride arrangement. An almost identical mixture of crystals was also directly obtained through precipitation and subsequent heating at 110° C (cfr. table 2, col. 2). It is worth noticing that *AgBr* enters in the zinc oxide modification as well as in the zinc sulfide modification of *AgI*, as seen from the spacings of the zinc oxide lattice which are smaller than those of the lattice of pure *AgI*. Thus the system *AgI–AgBr* is *isotrimorphous*. It should further be noticed that *AgI* has a greater tendency to enter into the sodium chloride lattice of *AgBr* than vice versa¹.

Added during correction:

We have succeeded in producing a powder photograph of the high temperature modification of *TlI*. The caesium chloride arrangement has been found, the length of the edge of the unit cube being $a_0 = 4.18 \text{ \AA}$ at 20° C, in good agreement with the extrapolated value (table 1).

Table 1. Mixed Crystals of *TlBr* and *TlI*.

Weight per cent		Lattice Constants in Ångström Units					
		Precipitated and Dried at 20° C		Precipitated and Heated 16h. at 110° C		Fused and Quenched	
<i>TlBr</i>	<i>TlI</i>	Bodycentered Cubic	Orthorhombic	Bodycentered Cubic	Orthorhombic	Bodycentered Cubic	Orthorhombic
100	—	3.968		3.968			
75	25	4.042	—	4.042	—		
50	50	4.079	±	4.091	—		
25	75	?	±	4.139	?	4.146	
10	90					4.181	?
—	100					[4.20] ²	±

¹ R. B. WILSEY (Journ. Franklin Inst. 200, 739, 1925) has also studied mixed crystals of *AgI–AgBr* by means of X-rays.

² Extrapolated.

Table 2. Mixed Crystals of *AgBr* and *AgI*.

Weight per cent		Lattice Constants in Ångström Units					
		Precipitated and Dried 16 h. at 110°C		Fused and Cooled rapidly		Fused, Tempered 150 h. at 150°C	
<i>AgBr</i>	<i>AgI</i>	Simple Cubic	Diamond Cubic	Simple Cubic	Diamond Cubic	Simple Cubic	Diamond Cubic
100	—	5.755	—	—	—	—	—
75	25	5.829	—	—	—	—	—
50	50	5.896	?	5.859	?	—	—
25	75	5.867	6.433	6.026	—	5.938 ¹	6.43 ¹
20	80	5.883	6.446	5.946	(6.37)	5.887 ²	6.458 ²
15	85	5.899	6.448	—	—	6.071	6.468
10	90	5.912	6.455	—	6.424	?	6.460
5	95	5.946	6.483	—	6.467	—	—
—	100	—	6.491	—	6.491	—	6.491

Table 3. Mixed Crystals of *CuI* and *AgI*.

Weight per cent		Lattice Constants in Ångström Units		
		Precipitated and Heated 16 h. at 90°C	Precipitated and Heated 16 h. at 400°C	Fused and Cooled rapidly
<i>CuI</i>	<i>AgI</i>	Diamond Cubic	Diamond Cubic	Diamond Cubic
100	—	6.047	—	—
75	25	6.107	6.134	—
50	50	6.191	6.244	6.246
25	75	6.376	6.345	—
—	100	6.491	—	—

¹ Fused and kept at ordinary temperature for three months.

² Tempered but for 50 h. at 150°C.

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