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Incomplete Atomic Arrangement in Crystals

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γ -Fe₂O₃, γ -Al₂O₃ and the oxide obtained by the electrolytical oxydation of Al (γ' -Al₂O₃) are averaged structures with regard to the cations. Both the γ and γ' oxides have the same oxygen-lattice but there is a distinct difference in the degree of incomplete arrangement of the cations. γ' -Al₂O₃ and γ -Al₂O₃ (Fe₂O₃) are intermediate cases between the amorphous state and the completely arranged state.

CRYSTAL structures in which part of the atoms (ions) are distributed statistically (averaged structures) have been described for a few compounds. Thus, in Li₂O.Fe₂O₃, the Li and Fe ions are distributed at random over the cation positions of the simple NaCl-arrangement.¹ In a number of compounds with spinel structure, e.g. Mg₂GaO₄, the Ga-ions and half of the Mg-ions take equivalent positions, with an averaged distribution ("variate atom equipments").² An interesting type of averaged structure is shown by the high temperature modification of Ag₂HgI₄³ and related compounds, since here we deal with an averaged distribution of vacant positions and cations over a number of definite lattice positions.

Striking cases of a statistical atomic arrangement, partially differing from the types mentioned above, were found to exist with a number of oxides A₂O₃ and will be discussed in the present note. Crystallographical details, to be published in Zeits. Krist., will be omitted.

We examined the closely related compounds γ -Al₂O₃ and γ -Fe₂O₃, the instable cubic modifications of these oxides. From density relationships and considerations concerning ionic radii we believed both the structure proposed by Welo and Baudisch⁴ and the one given by Thewlis⁵ to be incorrect. γ -Fe₂O₃ and γ -Al₂O₃ were found to have a face-centered oxygen lattice; the unit cell contains 32 oxygen ions. The cations are distributed in a way statistically over

the 8+16 spinel positions in such a way that per unit cell on the average 21½ cations and 2½ vacant positions are distributed over the 24 definite positions.

Besides, we studied the structure of the Al₂O₃ obtained by the electrolytical oxidation of aluminium. This Al₂O₃ is closely related with γ -Al₂O₃ but in its x-radiograms some of the lines of γ -Al₂O₃ fail.⁶ We have called this oxide γ' -Al₂O₃. This γ' -Al₂O₃ has a face-centered arrangement of the oxygen ions too. The unit cell contains 4 oxygen ions and on the average 2½Al³⁺ ions. These cations are distributed in a way statistically over 12 positions, viz. 8 in which the Al³⁺ ion is surrounded by 4O²⁻-ions and 4 in which the coordination number is 6; the former positions contain about 30 percent, the latter about 70 percent of the cations.

Thus γ -Fe₂O₃, γ -Al₂O₃ and γ' -Al₂O₃ belong to the large class of compounds with a cubic close packed anion lattice, containing the smaller cations in the interstices between the anion spheres. Such a close packing contains, per unit cell of 4 anions, 8 tetrahedron holes (surrounded by 4 anions) and 4 octahedron holes. In Li₂O the tetrahedron holes are all occupied (CaF₂-type), in MgO, FeO, etc., and the Li₂O.Fe₂O₃ mentioned above, the octahedron holes are filled (NaCl-type), the unit cell containing in both cases 4 oxygen ions.

It is convenient to describe the structure of AgI, Ag₂HgI₄ (α and β) in a similar way. In these compounds too the unit cell contains 4I⁻-ions according to a face centered lattice. In AgI half of the tetrahedron interstices are occupied in such a way that the cubic symmetry is maintained. In Ag₂HgI₄ one of these positions

¹ E. Posnjak and T. F. W. Barth, Phys. Rev. **38**, 2234 (1931).

² T. F. W. Barth and E. Posnjak, Zeits. f. Krist. **A82**, 325 (1932); cf. also F. Machatschki, ibid. **82**, 348 (1932).

³ J. A. A. Ketelaar, Zeits. f. Krist. **A87**, 436 (1934); Zeits. f. physik. Chemie **B26**, 327 (1934).

⁴ L. A. Welo and O. Baudisch, Phil. Mag. (6) **50**, 399 (1925).

⁵ J. Thewlis, Phil. Mag., (7) **12**, 1089 (1931).

⁶ W. G. Burgers, A. Claassen and J. Zernike, Zeits. f. Physik **74**, 593 (1932).

is vacant; however, the three remaining positions can be occupied in different ways. In β - Ag_2HgI_4 (low temperature modification) the cations take three definite positions, which leads to a tetragonal (pseudocubic) symmetry;⁷ in α - Ag_2HgI_4 the three cations are distributed statistically over the 4AgI positions, and the symmetry is again a cubic one.

Now in γ - Al_2O_3 , γ - Fe_2O_3 and γ' - Al_2O_3 the cations are distributed over both tetrahedron and octahedron holes.

γ - Fe_2O_3 and γ - Al_2O_3 can be derived from the spinel structure; this structure involves a larger cell, containing 32 oxygen ions per unit. In normal spinels the cations are distributed according to a regular arrangement over 8 tetrahedron holes and 16 octahedron holes. (The unit cell contains 64 tetrahedron positions and 32 octahedron positions.) In the γ -oxides a number of these 24 positions are vacant (preferably octahedron positions), on the average $2\frac{1}{2}$ per unit cell. The averaged structures of the γ -oxides and of α - Ag_2HgI_4 are therefore of a similar type. There is a partial arrangement of the cations since only part of the available interstices are used. A number of cations and vacant places are distributed at random over these definite positions.

However, a distinct difference between the γ -oxides and α - Ag_2HgI_4 exists. The latter compound has a transition point: at 50° the averaged structure is converted to the regular arrangement of β - Ag_2HgI_4 (low temperature modification). This transition indicates that the cations in α - Ag_2HgI_4 must have a large mobility, and move more or less freely in the lattice. The α -modification has actually a high electrolytical conductivity⁸ and is a cation conductor. Accordingly there is an intimate connection between this conductivity and the averaged structure: the cations (especially the Ag^+ ions) jump frequently from one AgI-position to another, leaving each of them on the average $\frac{1}{4}$ of the time vacant. One could say that the Ag^+ ions, though partially arranged according to AgI-positions, are in a kind of *fluid state* in these lattices. If the temperature is lowered to the transition point,

the Ag^+ -ions "crystallize" and take definite positions.

γ - Fe_2O_3 has no appreciable electrolytical conductivity in its existence region.⁸ The probability of a jump from one spinel position to another is obviously negligible. The case is therefore different from that of α - Ag_2HgI_4 . The incomplete arrangement of the cations is not caused by their thermal agitation but by the impossibility or improbability of a simple arrangement in the cubic close packed O^{2-} -lattice. It is comparable with a partially *amorphous state* of these cations.

In γ' - Al_2O_3 the Al-ions are distributed quite statistically over all interstices of the lattice; the only restriction is that averaged 70 percent of the Al-ions have chosen an Al^6 position (octahedron hole), 30 percent an Al^4 position. The arrangement of the cations is still more incomplete than in the γ -oxides, and the partial (spinel) arrangement of the latter fails. Only small deviations from the statistical distribution are present, i.e., the cations are practically entirely in an amorphous state.⁹ In this respect, γ' - Al_2O_3 is actually one of the most striking averaged structures so far found.

γ' and γ - Al_2O_3 can be considered as intermediate cases between the amorphous and the totally arranged state. In γ' - Al_2O_3 only the anions are arranged regularly. The second step from the amorphous to the completely arranged state can be realized by a careful heating of γ' - Al_2O_3 (900°C). Then γ - Al_2O_3 is formed, and a partial arrangement of the cations occurs in the way described which leads to a spinel arrangement with a larger unit cell. A *complete* arrangement of the cations is finally realized when γ - Al_2O_3 is heated above 1000° . Then α - Al_2O_3 is formed, i.e., the cubic close packed oxygen lattice is transformed into a hexagonal close packing. A simple complete arrangement of cations and anions in a ratio 2 : 3 is, for geometrical reasons, obtained easily in the latter class of symmetry: α - Al_2O_3 has a rhombohedral cell with 4Al^{3+} and 6O^{2-} , in which the cations occupy $2/3$ of the octahedron holes.

⁸ H. Sachse, Zeits. f. Physik **70**, 539 (1931).

⁹ An example of a "wholly fluid" state of the cations is probably α -AgI. However, the structure given recently by L. W. Strock, Zeits. f. physik. Chemie **B25**, 441 (1934), seems to be not quite clear.

⁷ J. A. Ketelaar, Zeits. f. Krist. **80**, 190 (1931).