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ORDERING IN FLUORITE-RELATED OXIDE SYSTEMS

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Résumé. — La mise en ordre dans les phases fluorine non stoechiométriques (MO_{2-x}) peut entraîner la mise en ordre complète ou partielle des lacunes anioniques. La mise en ordre anionique complète a pour résultat la formation de surstructures apparentées à la fluorine qui peuvent présenter aussi des degrés différents de mise en ordre cationique. La mise en ordre anionique partielle provoque une diffraction diffuse d’électrons ; cette diffusion peut être interprétée dans un modèle de micro-domaines ordonnés cohérents, ou bien en termes d’occupations de site corrélées dans une matrice statistique homogène.

Abstract. — Ordering in the defect fluorite MO_{2-x} phases may involve either complete or partial ordering of the anion vacancies. Complete anion ordering results in the formation of fluorite-related superstructures which may exhibit varying degrees of cation ordering also. Partial anion ordering results in diffuse electron diffraction effects, which may be interpreted in terms of coherent ordered microdomains, or in terms of correlated site occupancies in a statistically homogeneous matrix.

1. Introduction. — The fluorite structure, CaF_{2} type, Fm3m, consisting of a face-centred cubic array of cations with anions in all of the tetrahedral holes is adopted by the oxides MO_{2} of large-radius tetravalent metals. A grossly non-stoichiometric phase MO_{2-x}, 0 < x < 0.4, of fluorite structure may be produced in many oxide systems by substitution of the tetravalent cations by those of lower valence, either by reduction, e.g. PrO_{2-x}, or by solid solution, e.g. Ca_{2}Zr_{1-x}O_{2-x} [1, 2].

In these defect fluorite materials, the cation sublattice is totally occupied in essence, while the anion deficiency is accommodated as vacant lattice sites. This structure accounts for a characteristic property: Anion movement (diffusion, conductivity) is rapid even at relatively low temperatures, whereas cation movements are slow and occur at high temperature. These materials thus differ in structure from the oxides of the smaller-radius metals, where the anion substructure is close-packed, and any deviations from stoichiometry are absorbed in the cation array.

2. Ordering in the defect fluorite phase. — States of disorder, partial or complete order of cation type or of anion vacancies, or both, can be imagined to occur in the defect fluorite phase, giving rise to new structures. Not all of these have been observed in actual systems, however.

2.1 Structures involving complete vacancy ordering. — Fluorite-related superstructure phases of narrow homogeneity range often appear at relatively low temperature within a defect fluorite phase field. Numerous examples, some of which belong to a series M_{x}O_{2n-2}, are known. The structures of a few of these, e.g. In_{2}O_{3} [3], UY_{6}O_{12} [4] and Zr_{2}Yb_{6}O_{12} [5] of M_{2}O_{12} type, the pyrochlore Cd_{2}Nb_{2}O_{7} [6] and the mineral calcirite, CaZr_{2}TiO_{5} [7] have been determined from single crystal data. In general, however, only powder data are available, from which some structures, e.g. Zr_{2}Sc_{2}O_{13} [8] Pr_{2}O_{12} [9] and numerous pyrochlores have been determined. The structures of Ca_{2}Hf_{2}O_{16} [10], Ca_{6}Hf_{2}O_{19} and Ca_{4}Hf_{9}O_{44} [11], some ternary M_{2}O_{12} compounds [12] and Mn_{2}O_{7} compounds (unpublished) were determined from powder data supplemented by the unambiguous subcell-supercell relationships and symmetry information afforded by single crystal electron diffraction patterns obtained with an electron microscope.

In the known superstructures, all anion vacancies occur in pairs separated by a 1/2 < 111 > fluorite lattice vector with a cation in between, so that with anion relaxation, this cation becomes octahedrally coordinated by O. The cation-vacancy pair complex may be isolated, as in M_{2}O_{12}, or linked into zig-zag chains (pyrochlore), helical chains (Ca_{6}Hf_{12}O_{44}) or clusters (CaHf_{2}O_{8}). The linking is such that no vacancy approaches another closer than the 1/2 < 111 > fluorite separation, with the exception of the C-type rare-earth oxide structure (25% vacancies) where 1/2 < 110 > separations occur.

Cation ordering is linked to the vacancy ordering in that it is the smallest available cation that is octahedrally coordinated. The remainder are either 8-fold
is stable to temperatures well above those at which anion mobility is appreciable in the disordered phase of this composition (retained metastably by rapid cooling from above 1 500 °C).

2.1.3 The pyrochlore structure, Fd3m, has a unit cell that is derivable from an array of $2 \times 2 \times 2$ fluorite cells by ordering of cations and omission of one eighth of the anions in an ordered way. Oxide pyrochlores have the formula $A_2B_2O_7$: The A cation is in 8-fold coordination by O, B is in 6-fold coordination, and one seventh of the anions are crystallographically distinct. Usually the radius ratio of the cations lies in the range 1.2-1.6, and there are restrictions on the individual radii as well [17, 18]. Several types of disorder have been reported to occur in pyrochlores.

a) Isomorphous replacement of cations is very common. Either or both of the A and B sites may be occupied randomly by different cation species under relaxed radius restrictions, provided that the distinction between large A and smaller B cations is preserved, and the sum of A and B valencies is 7.

b) Some phases of formula $A_2B_2O_7$ have been reported to be pyrochlores, implying random population of A and B cations at the B site. The published evidence for this is not conclusive, and our own studies of such materials show that they have fluoride-related structures quite distinct from pyrochlore.

c) Some pyrochlores, e.g. $Gd_2Zr_2O_7$ exhibit a reversible order-disorder transition to the defect fluorite phase at elevated temperatures: As may be expected from the low cation mobilities, the high-temperature form may be retained on quenching. For $B = Zr, A = rare earth,$ the disordering temperature increases with increasing radius of A until melting intervenes in the case of $A = Nd, La$ [19].

d) The pyrochlore structure may be described alternatively in terms of a three-dimensional framework of corner-linked BO$_6$ octahedra, of overall composition BO$_3$, with the A cations and the remaining O located in large tunnel-like interstices. Although it has been asserted that the A cations and extra O are essential to the structure [20], there have been subsequent reports of grossly defective pyrochlores [21, 22], particularly in systems involving Ta and Nb, with formulae such as $A_2B_2O_6$ (seven O totally absent) and $AB_2O_6$ (seven O and half the A cations absent). It seems possible that a distinction should be drawn between these $A^2B^+$ $B^3+$ pyrochlores for which the BO$_3$ framework description seems more appropriate, and the $A^3B^4$ type, whose properties are more in keeping with those of the generality of fluoride-related superstructures considered here.

2.2 STRUCTURES INVOLVING PARTIAL ANION VACANCY ORDERING. — 2.2.1 Structures with fully ordered cations and partially ordered anion vacancies are rare, since usually the two effects are linked. However, an example is Na$_3$U$_2$O$_7$, which has a
distinct fluorite-related structure in which anions are distributed on two sets of sites, one of which contains a random population of vacancies [23].

2.2.2 Partially ordered cations and anion vacancies may occur whenever an ordered fluorite-related phase exhibits a range of composition, as in the case of some pyrochlores such as $\text{Gd}_2\text{Zr}_2\text{O}_7$. A detailed study of density, lattice parameter and X-ray diffraction intensities supported by electron diffraction would be needed to determine the nature of the disorder in non-stoichiometric pyrochlores. No such study appears to have been made.

2.2.3 The defect fluorite phase may contain a relatively high concentration of vacancies, so that vacancy interaction and ordering effects may be expected to occur. Non-linear variation of anionic conductivity with vacancy concentration has been attributed to such order [24]. Since the stabilised zirconias of industry are in this class, an understanding of the ordering could be of value in predicting and controlling such properties as conductivity, precipitation phenomena and destabilisation.

The most direct evidence for partial ordering comes from diffraction studies. Diffuse reflections are obtained in addition to the sharp Bragg reflections from the fluorite structure. This diffuse intensity appears in single crystal X-ray photographs, but may be seen more readily in electron diffraction. For a variety of defect fluorite phases at about 10% vacancy concentration, the diffuse patterns, though complex, are remarkably similar and differ mainly in scale. Such scattering could arise from statistically homogeneous medium-range ordering of cations or anion vacancies, or from fully-ordered microdomains coherent with the fluorite matrix with the superlattice reflections broadened by particle size effects.

The lime-zirconia and lime-hafnia systems have been studied in some detail in our laboratory, and the observed electron diffraction patterns have been satisfactorily matched by those calculated for domains of monoclinic $\varphi_1$, $\text{Ca}(\text{Zr}, \text{Hf})_2\text{O}_9$, about 30 Å in diameter in all possible orientations coherent with the fluorite matrix [25]. In this case, the appearance of appropriately scaled mottled contrast in dark-field micrographs imaged with the diffuse reflections supports the heterogeneous model. Also, on annealing, these microdomains grow until individual crystals of $\varphi_1$ can be identified.

However, there are some difficulties. The diffuse scattering is virtually unchanged for $\text{ZrO}_2(\text{HfO}_2)$ specimens containing from 10 to 20 mole % CaO, which, according to the above model, requires marked cation segregation to be present in those compositions far removed from that of $\varphi_1$. Since the diffuse intensity is apparent in samples quenched from the melt, and since cation diffusion is very slow at the ordering temperature of $\varphi_1$, this implies the formation of segregated microdomains well above the ordering temperature. The segregation and ordering of the more mobile anion vacancies alone is scarcely credible in this system because of the strong anion-cation correlations imposed by both size and ionic charge.

The diffuse scattering observed from yttria-zirconia samples of similar vacancy concentration is less well explained by the microdomain model. The scale of the diffuse features is inconsistent with $\varphi_1$-type ordering. The only ordered phase known to occur in this system is $\text{Zr}_2\text{Y}_4\text{O}_{12}$ [13]. Microdomains of this phase give quite different diffuse patterns, which in fact may be observed for specimens of vacancy concentration near 13%. At higher concentrations (~15%), diffuse scatter due to domains of $\text{Y}_2\text{O}_3$ (C-type) structure occurs.

In principle, a set of order parameters can be derived from the diffuse intensity [26, 27], but this approach is descriptive rather than explanatory, and becomes very cumbersome when correlations over 10 Å or more are considered. Alternatively, a few short-range restrictions (i.e. interaction energies) may be specified, and varied, from which extended sets of order parameters can be calculated by methods developed by Dr. A. Verhagen in our laboratory. Initially, anion vacancies alone, at 10% concentration, were considered, with three or four restrictions derived from the known ordered structures, e.g. vacancy separations less than 1/2 <111> are prohibited, while the 1/2 <111> separation is energetically favourable. Electron diffraction patterns have been calculated which match the observed patterns qualitatively provided that no less than 25 order parameters are included.

At this stage, the model is somewhat naive, and ignores cation ordering completely, although this possibly is valid for Y and Zr with similar scattering factors. However, the initial success justifies elaboration of this approach and its application to other physical properties.

3. Conclusion. — Electron microscopy and diffraction has proved to be a powerful aid to the study of ordering in fluorite systems. Nevertheless, further structural studies are required to achieve an understanding of the principles underlying superstructure formation in these systems, and to provide an adequate description of the defect fluorite phase itself.

References

