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DEFECT INTERACTIONS AND ORDER-DISORDER IN TRANSITION METAL OXIDES

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Résumé. — Nous discutons la structure de défaut des oxydes MnO, FeO, CoO et NiO en utilisant les résultats des calculs énergétiques. Nos résultats montrent que les modèles simples qui ne prennent pas en considération l'agrégation des lacunes ne sont pas valables. Des larges aggrégats de lacunes peuvent se former ; ils sont stabilisés par la formation d'interstitiels d'ions métalliques. Les paramètres du champ de ligand jouent un rôle important, puisqu'ils contrôlent la charge de l'interstitiel ce qui, détermine finalement le mode d'agrégation des lacunes et il en résulte des différences notables entre les structures des défauts des différents oxydes. Notre étude attire l'attention sur les conséquences de l'association des lacunes sur les propriétés de transport et thermodynamiques de ces oxydes.

Abstract. — The defect structure of the four oxides, MnO, FeO, CoO and NiO, is discussed using the results of calculations of defect energetics. Our results show that simple models, neglecting vacancy aggregation, are invalid. Large vacancy clusters may form ; they are stabilised by the accompanying formation of cation interstitials. Ligand field factors play an important role, as they control the interstitial charge ; this, in turn, determines the mode of vacancy aggregation and results in considerable differences between the defect structures of the different oxides. The discussion draws attention to the consequences of the association of vacancies for transport and thermodynamic properties of these oxides.

1. **Introduction.** — Defect aggregation in the cation deficient transition metal oxides has until recently been discussed using simple models. Extensive accounts of disorder in the rock salt structured oxides are given by, for example Kofstad [1], who treats defect interactions using the concept of *vacancy ionisation.* In such models, defect aggregation is restricted to the formation of vacancy-hole complexes containing no more than one vacancy. The models, however, give apparently successful analyses of the thermodynamic and transport data available for the divalent binary oxides.

There is, nevertheless, clear evidence that these simple models are inadequate. Their deficiencies are strikingly illustrated by the results of diffraction studies — both X ray [2] and neutron [3] — on the most grossly cation deficient phase, i.e. $Fe_{1-x}O$. The experiments showed that this non-stoichiometric oxide contained metal *interstitials* in addition to vacancies ; X-ray and electron microscopy studies [15] also found evidence for *vacancy aggregation,* at least in quenched $Fe_{1-x}O$. Catlow and Fender [4] have proposed a complex scheme of vacancy clustering for $Fe_{1-x}O$. They suggest that large vacancy aggregates may be stabilised by cation interstitial formation ; and a number of different modes of aggregation are proposed. The models lead to a satisfactory account of the experimental data.

Powerful computer simulation techniques assisted the formulation of the new cluster models. These methods yield reliable estimates of defect formation and interaction energies. The same techniques are therefore used in the present study to extend our account of vacancy aggregation to include the remaining three insulating divalent oxides, i.e. MnO, CoO and NiO. We show that the simple models are generally inadequate. Moreover, our arguments predict major differences between the defect structure of the three oxides. We also consider briefly how the replacement of the simpler treatments, which ignored vacancy aggregation, by our more sophisticated models modifies the interpretation of transport and thermodynamic data.

2. **Calculations.** — For detailed descriptions of the computational methods we refer to the extensive accounts available elsewhere [5, 6]. The calculations used the HADES program which simulates explicitly the specified defect configuration and a surrounding region of lattice while employing a continuum description of the remoter regions of the crystal. The simulation uses lattice and defect potentials based on the ionic model, with simple analytical pair interactions to represent short range terms ; ionic polarisation is described by the shell model [7]. The potentials for the four oxides investigated in this study, are of a

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standard form, and details are presented in other papers [4, 8]. Several studies have shown that, for ionic crystals, these methods and potentials give values of defect formation and interaction energies in good agreement with experimental data [9, 10].

We draw attention to only one specific feature of the present calculations, which concerns the distribution of holes around the vacancy aggregates. (In our calculations we treat holes as small polarons, localised on the cation sublattice, i.e. Fe^{3+} cations.) We attempted to maximise vacancy-hole interaction energies, by investigating for each cluster a variery of possible hole configurations. Our choice of configurations was, however, constrained by the requirement that the defect configuration should have some symmetry; otherwise the size of the explicitly simulated region will be insufficient for an accurate result. (For further discussion of this point see references [4] and [5].) The symmetry constraint also prevented the use of electroneutral defect configurations for the majority of calculations. Instead calculations were performed for charged defect aggregates, but with more symmetrical hole distributions. To estimate the energy of the corresponding electroneutral defect, we add (or subtract) the sum of the energies of the number of holes necessary to achieve electro-neutrality. This procedure is again discussed in greater detail by Catlow and Fender [4].

3. **Results.** — We examined a wide range of cluster structures for the four oxides, although our choice is restricted in the case of larger aggregates by the symmetry constraints discussed above. Results for those clusters for which strong binding was found are reported in table I. They comprise the following defects :

A) Simple aggregates of holes and one vacancy.

B) A tetrahedral aggregate of four vacancies and one interstitial — the 4 : 1 cluster shown in figure 1 — for which we considered both divalent and trivalent interstitials.

C) Extended vacancy-interstitial aggregates in which a common *edge* is shared between tetrahedral vacancy clusters of the type discussed above. Many of the calculations, in both this and the following category of defect are expensive in computer time. These were performed therefore only for those interstitial charges that are favoured by ligand field factors, as discussed below. Such calculations are also omitted for NiO, as deviations from stoichiometry in this crystal are small, and the formation of large defect clusters is therefore unlikely.

D) Extended vacancy-interstitial aggregates based on *corner* sharing between tetrahedral vacancy units. Two types of cluster are considered : the 13 : 4 cluster (see figure 4) in which a common corner is shared by 4 vacancy tetrahedra, and the 16 : 5 cluster (figure 5) where a central tetrahedral cluster shares each corner with a further 4 : 1 cluster.

TABLE I

Cluster Binding Energies

Defect	Q(*)	Binding Energy per Vacancy (eV) MnO	FeO(**)	CoO	NiO
—	—	—	—	—	—
Aggregate of one vacancy + one hole	—	0.53	0.63	0.49	0.51
Aggregate of one vacancy + two holes	—	0.71	0.90	0.69	0.78
4 : 1 cluster (fig. 1)	2	1.65	1.75	1.65	1.74
	3	1.77	1.98	1.76	1.83
6 : 2 — (— 2)	2	1.64	—	1.62	1.70
	3	2.06	2.42	2.05	2.14
8 : 3 — (— 3)	2	1.84	—	1.70	1.76
	3	—	2.52	—	—
13 : 4 — (— 4)	2	0.06	—	0.42	—
	3		2.10	—	—
16 : 5 — (— 5)	2	1.94	—	1.82	—
	3	—	2.38		—

(*) Q = Interstitial charge (where relevant).

For larger clusters calculations only performed for interstitial charge suggested on the basis of ligand field arguments — see text.

(**) The majority of these results are taken from Catlow and Fender [4]. There are small differences between the types of potential used in this work, and those employed for the remaining oxides, but these may have only a minor effect on the calculated binding energies.

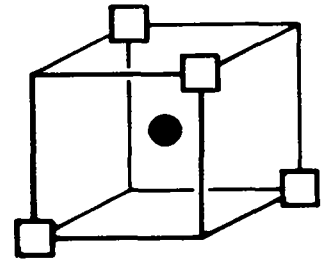

FIG. 1. — 4 : 1 cluster.

The results of the calculations reported in table I are given as the cluster binding energy per *net* vacancy (for further discussion of this procedure see reference [4]). Vacancy aggregation occurs if this energy is large enough to outweigh the unfavourable loss of configurational entropy that results from cluster formation.

4. **Discussion.** 4.1 INITIAL DEFECT AGGREGATION. — The results in table I clearly show that discussions of the defect structure of divalent transition metal oxides, which omit vacancy aggregation are inadequate. The vacancy binding energy for the 4 : 1 and larger complexes is far greater than calculated for the simple vacancy-hole clusters. Indeed the magnitude of the calculated binding energy for the vacancy aggregates suggests that these defect structures will dominate at all but very high temperatures and low defect concentrations. The point is given greater emphasis by calculations of the equilibrium concen-

TABLE II

Relative Concentration of Different Defect Species in MnO

Deviation (*) from stoichiometric composition	Percentage of Vacancies in Clusters: Isolated vacancy	Singly ionised vacancy	Unionised vacancy	4 : 1	Larger Aggregates
—	—	—	—	—	—
10^{-6}	100.0	0.0	0.0	0.0	0.0
10^{-5}	100.0	0.0	0.0	0.00	0.00
10^{-4}	95	4.97	0.0	0.0	0.0
10^{-3}	58.2	21.5	0.1	19.5	0.7
10^{-2}	8.3	4.7	0.0	76.8	10.2
10^{-1}	1.0	0.8	0.0	76.4	21.8

trations of the various clusters as a function of x, the deviation from stoichiometry in the oxides $M_{1-x}O$. In these calculations we used a mass action treatment of the defect-cluster equilibria, using equilibrium constants obtained from our calculated binding energies. Greater details which include a discussion of the defect entropy term, are presented elsewhere [11]. The results for MnO, which are typical of those for the other oxides, are given in table II. They show that the simple vacancy-hole clusters — singly ionised or unionised vacancies in the terminology of Kofstad [1] — are of importance in only a very limited range of vacancy concentrations. They are moreover never dominant, since when the vacancy concentration becomes sufficiently large for clustering to occur, the more strongly bound vacancy aggregates begin to form immediately. This confirms that an adequate treatment of defect aggregation at any defect concentration in these oxides must include the complex defect structures discussed in this paper.

Our calculations also showed that extensive vacancy aggregation may only occur when accompanied by interstitial formation. Vacancy aggregates in which no interstitials are present show no greater binding than the simple vacancy-hole complexes. The stabilisation is essentially Coulombic in origin (see Catlow and Fender [4]). Thus in the simplest vacancy aggregate, the 4 : 1 cluster, the tetrahedral aggregate is stabilised by the attractive interactions with the central cation interstitial.

The dominant factor in determining defect aggregation in these systems appears therefore to be Coulombic interactions between defects. But ligand field factors are, we believe, also important; their role is to determine the cation charge in the interstitial site. This is suggested by the results in table I, where we find only a small change ($\sim$ 0.2 eV) in the binding energy of the 4 : 1 cluster on replacing a divalent by a trivalent interstitial. The changes in ligand field energies on transferring a cation from a lattice (octahedral) site to an interstitial (tetrahedral) site will, however, be considerably larger ($\sim$ 0.5-1 eV). Thus the latter factors will control the interstitial charge. For the larger clusters, we find bigger differences between the binding energies for different interstitial charges. In the following section, however, we will assume that the interstitial charge does not vary with the extent of defect aggregation — an assumption which leads to a satisfactory explanation of a number of experimental observations. Ligand field factors will favour the transfer of the divalent ions to interstitial sites in MnO, CoO and trivalent ions in the case of FeO and NiO. Our calculations on certain of the larger clusters below are therefore performed only for the interstitial charge favoured by the ligand field term.

4.2 EXTENDED DEFECT FORMATION. — 4.2.1 *Edge Shared Clusters.* — The simplest extended aggregate is the 6 : 2 cluster (figure 2) — an edge shared complex of two 4 : 1 defects. This complex, unlike corresponding small corner shared aggregates, is considerably more strongly bound than the 4 : 1 defect *but only when trivalent ions are present in the interstitial site.* A large increase in binding energy is not obtained for divalent interstitials, as will be noted from the results in table I.

Further edge shared aggregation is apparently possible for trivalent interstitial-vacancy aggregates.

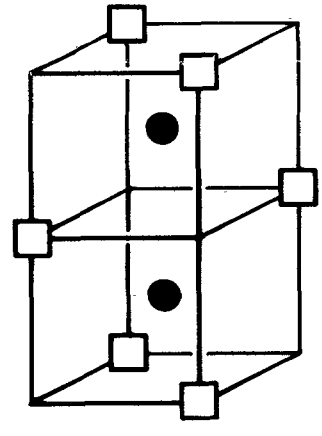

FIG. 2. — 6 : 2 cluster.

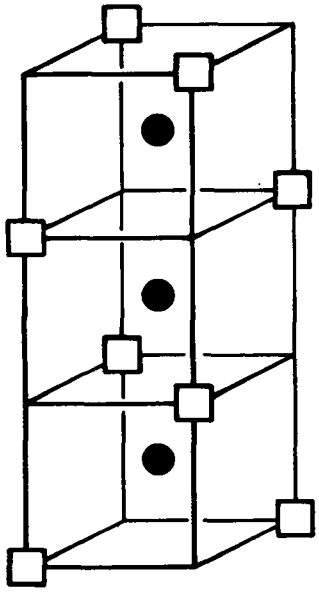

FIG. 3. — 8 : 3 cluster.

Formation of the 8 : 3 cluster (figure 3) results in an increased vacancy binding energy for FeO where we have trivalent interstitials ; but again, no significant increase in binding energy is calculated when divalent cations are present in the interstitial site. Trivalent ions are necessary in edge shared aggregates, as large vacancy interstitial attractive terms are needed to stabilise the vacancy cluster. For divalent ions, the interstitial charge is insufficient to give increased binding for the compact edge shared aggregates.

4.2.2 *Corner Shared Clusters.* — The extent of edge shared aggregation is limited even for clusters containing trivalent interstitials. We could not find an edge shared structure for which we could calculate a binding energy significantly larger than that obtained for the 8 : 3 cluster. Some caution is, however, necessary here, as the reliability of our calculations may be reduced, as discussed above, owing to the size and low symmetry of the clusters. Nevertheless further extensive aggregation probably involves the formation of the large *corner* shared complexes (figures 4 and 5). For the former structure — the 13 : 4 cluster, originally discussed by Koch and Cohen [2] — an increase in binding energy is obtained for trivalent but not for divalent interstitials. The latter aggregate — the 16 : 5 cluster — however, shows, with divalent interstitials, an appreciable increase in binding energies, over those obtained for the 4 : 1 cluster ; moreover, for the trivalent interstitial, the binding energy is greater than that calculated for the Koch-Cohen structure. We believe therefore that the 16 : 5 cluster is the more important of the corner shared aggregates. And as this cluster is an element in the spinel structure adopted by the ordered M_3O_4 phases, this result is clearly of relevance to the relationship between the disordered $M_{1-x}O$ structures and the corresponding ordered spinel phase.

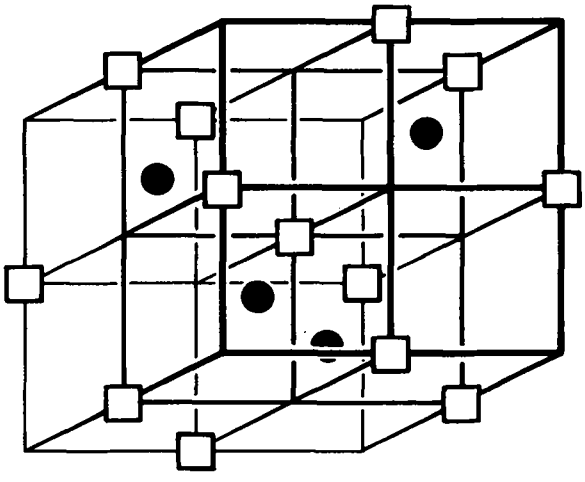

FIG. 4. — Koch-Cohen cluster (13 : 4 cluster).

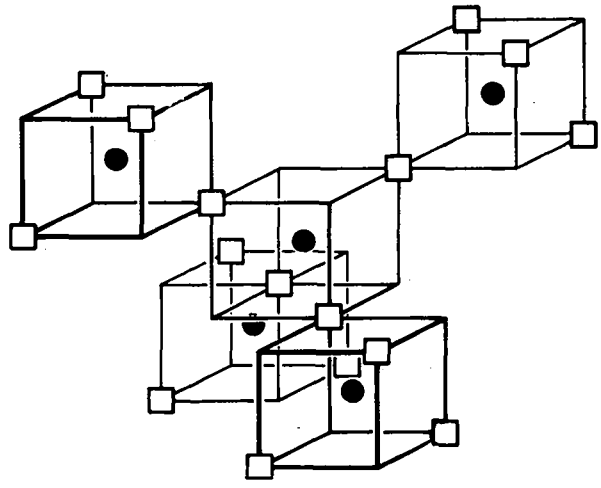

FIG. 5. — 16 : 5 spinel-like aggregate.

4.2.3 *General Scheme of Vacancy Aggregation.* — Our calculations thus suggest two alternative modes of extended defect formation. First when trivalent interstitials are present 4 : 1 clusters grow to form initially, 6 : 2 and larger edge shared structures, and subsequently to form large corner shared structures which are essentially nuclei of the ordered spinel structure ; hence the formation of 16 : 5 and related clusters will probably lead to spinel precipitation. When divalent interstitials are present, the edge shared structures are not stable ; aggregation will occur directly to the spinel like aggregates, with consequent spinel nucleation.

Thus in crystals containing divalent interstitials, extended defect formation cannot occur without nucleation of the ordered spinel phase ; but for trivalent interstitials, smaller extended defects unrelated to the spinel structure may form. In the latter, extensive deviations from stoichiometry will consequently be possible, as large vacancy concentrations can be

stabilised in clusters without phase precipitation; in the former, we predict a narrower composition range for the disordered phase, as vacancy stabilisation requires the nucleation of the spinel phase.

How do these arguments accord with experimental observation ? Of the four oxides only $Fe_{1-x}O$ exists as a grossly non-stoichiometric phase. In this compound we argue that the interstitial trivalent ion favours extensive vacancy aggregation without the formation of spinel-like nuclei; thus over a wide composition range the disordered $Fe_{1-x}O$ structure is stable relative to the spinel, rock salt two phase oxide system. In contrast for MnO and CoO, the composition ranges are much less broad at comparable temperatures. This difference may, in part, be associated with less favourable heats of oxidation. But the absence of large stable clusters, other than spinel nuclei, must be a contributing factor. The behaviour of NiO is different from the other three oxides. A well characterised spinel phase is not known. The narrowness of the non-stoichiometric phase in this case can be rationalised simply in terms of the large partial heat of oxidation of NiO — an argument which is *not* sufficient for any of the other oxides where stable spinel phases are formed.

In summary therefore, while our earlier models showed how models based on vacancy aggregation could rationalise the details of the diffraction studies on $Fe_{1-x}O$, the work in this paper has now demonstrated how the models may be extended to account for the difference between $Fe_{1-x}O$ and the other non-stoichiometric oxides.

4.3 THERMODYNAMIC AND TRANSPORT PROPERTIES. — Defect aggregation of the type discussed above presents problems for the analysis of the thermodynamic data, since the experimental results have been treated with apparent success using the much simpler models described by Kofstad [1]. We believe, however, that such analyses are inadequate. They are based mainly on measurements of the slopes of the plot of the logarithm of the equilibrium oxygen partial pressure versus the logarithm of the deviation from stoichiometry, x. These slopes, it is argued, can be related directly to the number of defect species created for each oxygen molecule reacting with the crystal. We have shown elsewhere [11] that such arguments are valid only when the partial heat of oxidation does not vary with composition — a condition which does not hold when clustering occurs. Our more complete treatment [11] successfully accounts for the main features of the experimental data, for which, however, we find no possibility of a simple interpretation in terms of numbers of defect species formed on oxidation.

There can, similarly, be no simple analysis of the transport data, as is shown by the complex dependence composition of the measured cation diffusion coefficient in $Fe_{1-x}O$ [12]. We also expect that the strong binding of vacancies in the larger aggregates will prevent the operation of simple migration mechanisms effected by isolated vacancies. Instead cation transport will occur by a concerted migration of the whole cluster [14]. We have shown that such mechanisms are indeed possible; and they are discussed in greater detail in a separate study [13].

5. **Conclusions.** — Our discussion in this paper has clearly shown that defect interactions in the divalent transition metal oxides are dominated by vacancy aggregation, and not simply by vacancy-hole pairing. Treatments of the defective phases which ignore this feature are evidently quite inadequate, except for the very near stoichiometric regions of the phase. Theories of the structure, transport and thermodynamic properties of the phase must clearly therefore be modified to include this dominant factor in their defect structure.

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