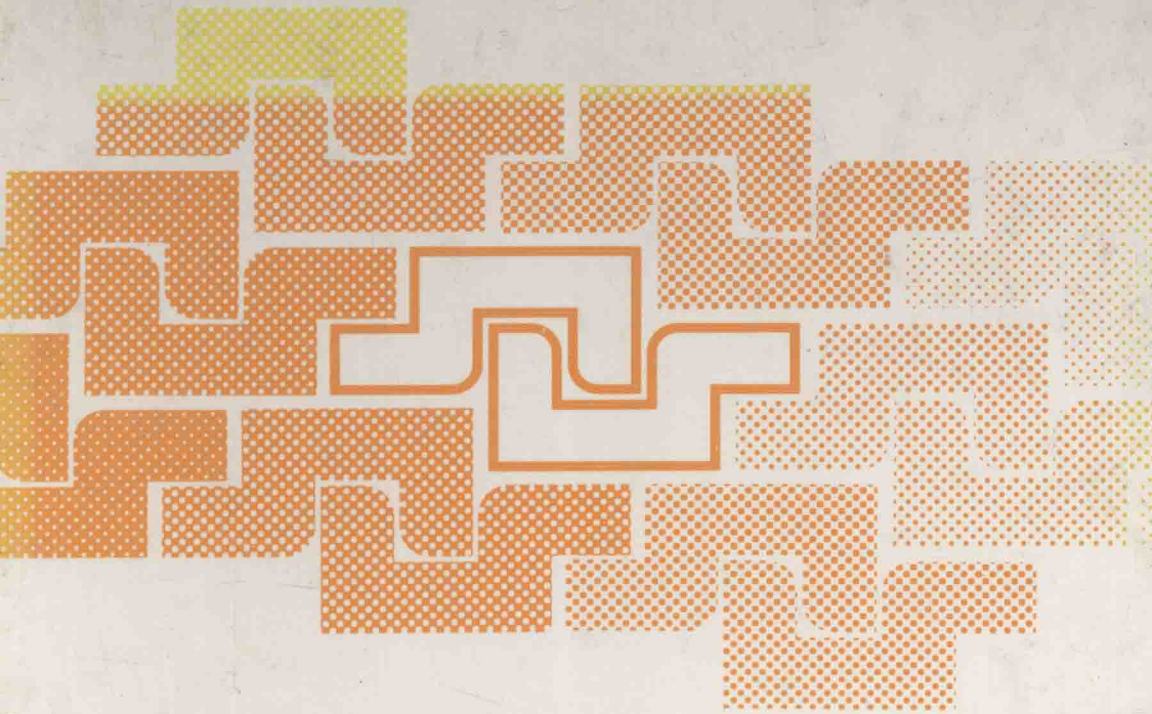

Structure-Property Relationships in Surface-Modified Ceramics

Edited by

Carl J. McHargue, Ram Kossowsky
and Wolfgang O. Hofer

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PREFACE

The use of ion beams for the modification of the structure and properties of the near-surface region of ceramics began in earnest in the early 1980s. Since the mechanical properties of such materials are dominated by surface flaws and the surface stress state, the use of surface modification techniques would appear to be an obvious application. As is often the case in research and development, most of the initial studies can be characterized as cataloging the response of various ceramic materials to a range of ion beam treatments. The systematic study of material and ion beam parameters is well underway and we are now designing experiments to provide specific information about the processing parameter - structure-property relationships.

This NATO-Advanced Study Institute was convened in order to assess our current state of knowledge in this field, to identify opportunities and needs for further research, and to identify the potential of such processes for technological application.

It became apparent that this class of inorganic compounds, loosely termed ceramics, presents many challenges to the understanding of ion-solid interactions, the relationships among ion-beam parameters, materials parameters, and the resulting structures, as well as relationships between structure and properties. In many instances, this understanding will represent a major extension of that learned from the study of metals and semiconductors.

The Institute was divided into four main areas. The first group of lectures dealt with the fundamentals of ion-solid interactions and the defect structure of compounds. Chemical and thermodynamic factors appear to be significantly more important than for simple metallic systems. The second group of lectures concerned the experimentally observed microstructural features and phase structures that develop during ion-beam processing of ceramics. The properties of ion-implanted and ion-beam-mixed ceramics were treated in Part III, and included discussions on mechanical, tribological, chemical, electrical, and optical properties. The final section was concerned with thin films and coatings prepared by ion-beam-assisted processes.

The Institute was held at Il Ciocco International Tourist and Conference Center, Castelvecchio Pascoli, (Tuscany) Italy during the period of August 28 to September 9, 1988. The setting and facilities were ideal for such a learning experience. The hotel possesses the proper blend of isolation that enhances group identification and interaction with the amenities of a first-class hotel and easy access to the cultural and historical attractions of Tuscany. The organizers are particularly grateful to Mr. Bruno Giannasi who served as our contact with the hotel staff and was instrumental in making possible our productive and successful meeting. The conference secretary was Ms. Lou M. Pyatt who also deserves much of the credit for our success and for the timely preparation of these proceedings.

The major support for the Institute was provided by the Scientific Affairs Division of NATO. Significant additional support was given by

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The home institutions of the directors provided much direct and indirect support for the planning and organization of the Institute. Their assistance, cooperation, and leniency are gratefully acknowledged.

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PROPERTIES OF CERAMICS AND THEIR STUDY BY COMPUTER SIMULATION METHODS

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1. INTRODUCTION

The defect physics and chemistry of non-metallic solids show a large degree of diversity and complexity. Defects can be created by several mechanisms and a wide range of defect species are possible particularly in the structurally more complex materials. In this chapter we will first eview the basic nature of defects in insulating solids. We will then escribe the techniques that are available for simulating defects and efect-dependent phenomena in these materials. The field of defect simulaions in insulators has enjoyed considerable success over the last ten ears. Static and dynamical methods have been used, and the techniques have een applied with success to both bulk and surface defects. This success uggests that the methodology should be extended to the complex problems osed by ion beam implanted ceramics. Complex defect reactions occur in nsulators, following radiation change as illustrated by our discussion ater in the article, of irradiation damage in NaCl. Even greater complexity can be expected for oxide ceramic materials.

2. DEFECTS AND DEFORMATION IN INSULATORS

2.1. Types of defects

It is useful to classify defects in ceramics into four principle categories.

(A) Point defects in which the defect is located at a single site or small group of sites in the crystal. These comprise vacancies, i.e. atoms missing from the regular lattice sites; interstitials, i.e. atoms present in sites that are unoccupied in the perfect lattice; substitutionals, that is foreign atoms present at perfect lattice sites; and clusters, i.e. aggregates comprising several of the above. A simple example of the latter is given in Fig. 1, which shows a complex of a divalent dopant ion and a cation vacancy in NaCl.

(B) Extended defects, which have an indefinite extent in one or two dimensions. The commonest example is provided by dislocations which occur in all crystalline materials. These defects whose nature is amply discussed in several texts are "conservative defects," i.e. their formation does not change the over-all chemical composition of the solid. In contrast, "non-conservative" extended defects known as shear planes form in certain non-stoichiometric oxides, e.g. TiO_{2-x} and WO_{3-x}. A diagramatic illustration of such defects for the case of WO_3 is shown in Fig. 2, which shows a section through the ReO_3 structure a distorted version of which is adopted by WO_3. On reduction to form WO_{3-x} we might envisage that oxygen would be lost with the formation of vacancies. If we imagine the latter being aligned to form a vacancy disk as shown in Fig. 2(a), then by a subsequent process of shear in which the bottom half of the crystal is displaced as shown, the vacancies

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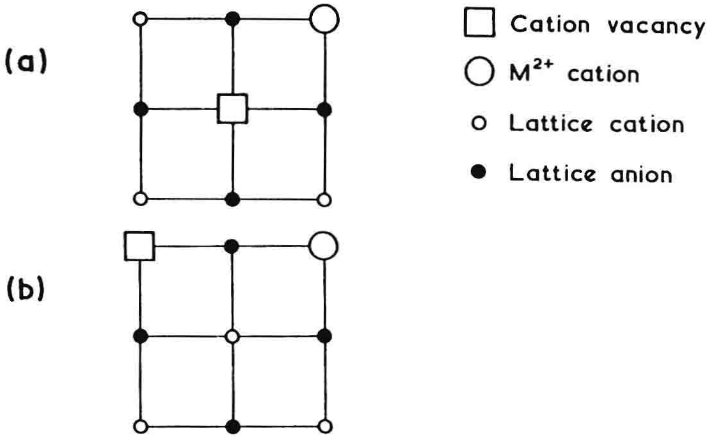

FIGURE 1. Dopant-defect paris in divalent cation doped rock salt structured halides: (a) n.n. pair (b) n.n.n. pair.

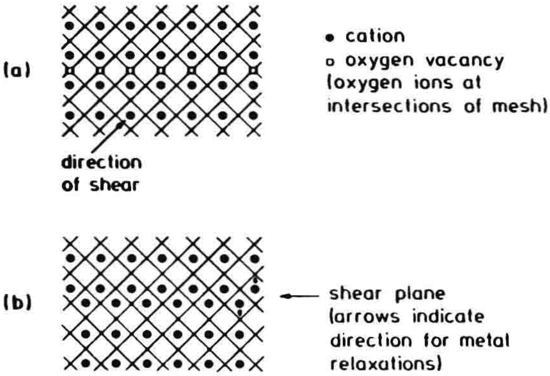

FIGURE 2. Schematic illustration of shear-plane formation in ReO_3 structured oxides.

maybe eliminated with the creation of a planar fault on the cation sublattice. The formation of such defects clearly changes the oxygen to metal ratio.

(C) Surfaces and surface defects. A broad definition would include surfaces as a "defect" in that they are a discontinuity of the bulk crystal. More relevant, however, is the fact that well defined surface defects are now discussed in the ceramic literature; in particular, surface vacancy and impurity states are thought to be of importance.

(D) Nuclei of precipitates. A new phase precipitated into a host crystal cannot, of course, strictly be included in the classification of defect species. But there is a "fuzzy" division between nuclei of new phases (which may be defect aggregates) and precipitates, and for this reason we have included such species in our classification.

2.2. Defect creation mechanisms

The following types of mechanism are important in ceramic materials.

(A) Thermal Creation of Instrinsic Disorder, by which we mean the creation by thermally induced excitation of the disorder which is invariably present even in hypothetically pure materials at temperatures above absolute zero. Different types of intrinsic disorder reaction are possible and the defect concentrations are highly temperature dependent.

Themal generation of defects is best understood using the concept of defect reactions: the first, known as the Frenkel disorder reaction, involves the generation of interstitials by the displacement of ions from normal lattice sites to interstitial positions in the crystal structure. The Frenkel disorder reaction can therefore be written as:

$$I_L \rightarrow V_L + I_I \ ,$$

where I_L indicates an ion occupying a normal site; I_I is the interstitial species and V_L is the vacancy at the regular lattice position that is created by displacement of the ion I. The advantage of this way of describing the thermal generation of defects is that it can readily be shown that defect reactions are governed by the same chemical thermodynamic considerations as more conventional chemical reactions. Thus assuming that Frenkel disorder dominates, the equilibrium activities of vacancies and interstitials (written as a_V and a_I) are given by:

$$a_V a_I = k_F = \exp\,(-g_F/kT) \ , \tag{1}$$

where k_F is the Frenkel disorder constant, and g_F is the free energy of formation of the Frenkel pair. The activity of perfect lattice ions may be taken as unity. Activities may of course be related to concentrations (x_V and x_I) via activity coefficients, i.e.

$$a_V = f_V x_V \ ; \ a_I = f_I x_I \ . \tag{2}$$

At very high dilutions it may be acceptable to take the activity coefficients as unity. Due, however, to the fact that defects are charged species and have therefore long-range Coulomb interactions, this is in general not an acceptable approximation; and the calculation of defect activity coefficients has been an important area of the theory of defects in solids.

The second type of defect reaction, known as Schottky disorder involves generation of vacancies by displacement of lattice ions to the surface of the crystal. For ionic materials Schottky disorder requires the formation of vacancies in stoichiometry ratios. Thus in 1:1 crystals, e.g. NaCl, equal concentrations of defects must be created; while in 2:1 crystals, e.g. CaF_2, cation and anion vacancies are created in the ratio 1:2. The Schottky disorder reaction for 1:1 ionic crystals may be written as:

$$I_L^+ + I_L^- \rightarrow V_L^+ + V_L^- \ , \tag{3}$$

where the superscripts, + and -, indicate defects created at cation and anion sites respectively. Again, we may apply standard chemical thermodynamics to this equilibrium, giving for the vacancy activities, a_V^+ and a_V^-:

$$a_V + a_L- = K_S = \exp\,(-g_S/kT) \ , \tag{4}$$

where KS is the Schottky disorder equilibrium constant and g_S is the free energy of formation of the Schottky pair.

Since g_F and g_S are always finite (although possibly large), both Frenkel and Schottky reactions are always operative in a crystal. In practice, however, one type of disorder appears to dominate in a given crystal (although an unlikely coincidence in some material in the values of g_F and g_S cannot be ruled out). Crystals may be classified therefore according to whether the intrinsic disorder is of the Frenkel or Schottky type. Such a classification for the commoner materials is presented in Table 1.

TABLE 1
Dominant Intrinsic Disorder of Ionic Crystals

Compounds	Crystal structure	Dominant Intrinsic Disorder Reaction
NaCl (+ all isostructural alkali halides)	Rock-salt	Schottky
AgCl, AgBr	Rock-salt	Cation Frenkel
MgO (+ alkaline earth oxides)	Rock-salt	Schottky
MnO (+ other divalent transition metal oxides)	Rock-salt	Schottky
CaF_2 (+ other isostructural halides)	Fluorite	Anion Frenkel
UO_2 (+ other isostructural oxides)	Fluorite	Anion Frenkel
TiO_2 (+ isostructural oxides)	Rutile	(Schottky)
ZnO	Zinc-blende	(Cation Frenkel)
Al_2O_3 (+ isostructural oxides)	Cordundum	(Schottky)

Note: reaction types given in brackets indicate that some uncertainty may still be associated with the nature of the predominant disorder.

(B) Chemical induction of defects. All real materials contain impurities, either accidentally present or deliberately introduced as dopants. If the dopant is an "aliovalent" species, i.e. with a different valence from the host lattice ions, then whether it is a substitutional (which is most commonly the case) or an interstitial, it must be "charge compensated" to retain electroneutrality. A simple example is given by the case of aluminium in magnesium oxide. Al^{3+} is invariably present even in high purity MgO; it substitutes for Mg^{2+} which disturbs the charge balance of the crystal. The Al substitutional, which may be denoted as $Al^{\bullet}$ (using the notation of Kroger and Vink) has an effective charge (i.e. charge relative to that of the same site in the perfect latice) of +1. It must be compensated by defects with an effective negative charge; and since the intrinsic disorder of the material is of the Schottky type, vacancies are created with one doubly charged cation vacancy (V_{Mg}) for every two Al^{3+} impurities.

A second example is given by Nb^{5+} doping of UO_2. The niobium substitutional $Nb_U^{\bullet}$ again must be compensated by defects with an effective negative charge. As UO_2 is a Frenkel disordered material, oxygen interstitials ($O_I^{''}$) are created. The case of UO_2 also illustrates well how variable cation valence, which gives rise to non-stoichiometry in oxide has very similar consequences, as regards defect structures, to aliovalent doping. Thus oxidation of U^{4+} to U^{5+}, creating a quasi defect U_U leads to oxygen anion interestitial compensation. Indeed, non-stoichiometry is a very common cause of defect creation in oxides.

(C) Mechanical Creation of Defects. It is well known that mechanical deformation of materials may lead to defect creation, and indeed dislocations are commonly induced by mechanical treatment. Such processes may be important in ceramic materials as well as in metals.

(D) Radiation Damage. Radiation may induce defects via a variety of mechanisms. Implantation of course directly introduces impurities into materials. However, radiation creates lattice defects by "knock-on" or displacement processes which occur during the radiation induced cascade; in addition defects may be induced by photolysis where the primary act of the radiation is the creation of electron-hole pairs, which via secondary processes lead to defect generation. Examples for the case of NaCl will be presented in Section 3.

2.3. Defect aggregation

In all types of solid, defect interaction and aggregation processes become important at higher defect concentrations. This is, however, specially the case in ionic materials owing to the strong Coulomb interactions between defects. Defect clustering may be included within the mass-action formation discussed above. For example, the formation of the cluster shown in Fig. 1 may be described in terms of the defect reaction:

$$D_L = V_L \rightarrow C \ ,$$

where D_L indicates a dopant ion occupying a regular lattice site and C the cluster. The consequent mass action equation is given by:

$$\frac{a_c}{a_d a_v} = K_c = \exp\,(-g_c/kT) \ ,$$

where a_c and a_d are the activities of the cluster and dopant ion respectively and g_c is the free energy of cluster formation.

Highly complex modes of defect aggregation occur in many heavily doped and non-stoichiometric ionic materials. An example is shown in Fig. 3 for the case of $Fe_{1-x}O$, a grossly non stoichiometric compound in which cation vacancies are created to compensate the oxidation of lattice cations from Fe^{2+} to Fe^{3+}. It is now well established (see for example Chapter 16 of reference 2) that in these heavily defective oxides vacancies are stabilized by a mode of aggregation that involves the creation of additional cation interstitials as shown in Fig. 3.

2.4. Consequences and effects of defects

We have noted that defects radically alter the properties of solids. The properties influenced include mechanical, electrical, spectroscopic, and diffusional behavior. Many accounts of these phenomena are given elsewhere (1-3). Thus, we will concentrate on one aspect, viz the influence of defect structure on atomic transport in solids.

Atomic transport is manifested by the bulk properties of conductivity and diffusion and is nearly always effected by defects. Interstitial atoms may jump through the lattice, and lattice atoms may jump into vacant sites (hence effecting vacancy transport). As discussed below, these processes may be described using absolute rate theory. Given knowledge of the frequencies of these activated jumps,we may write the diffusion coefficient D, as:

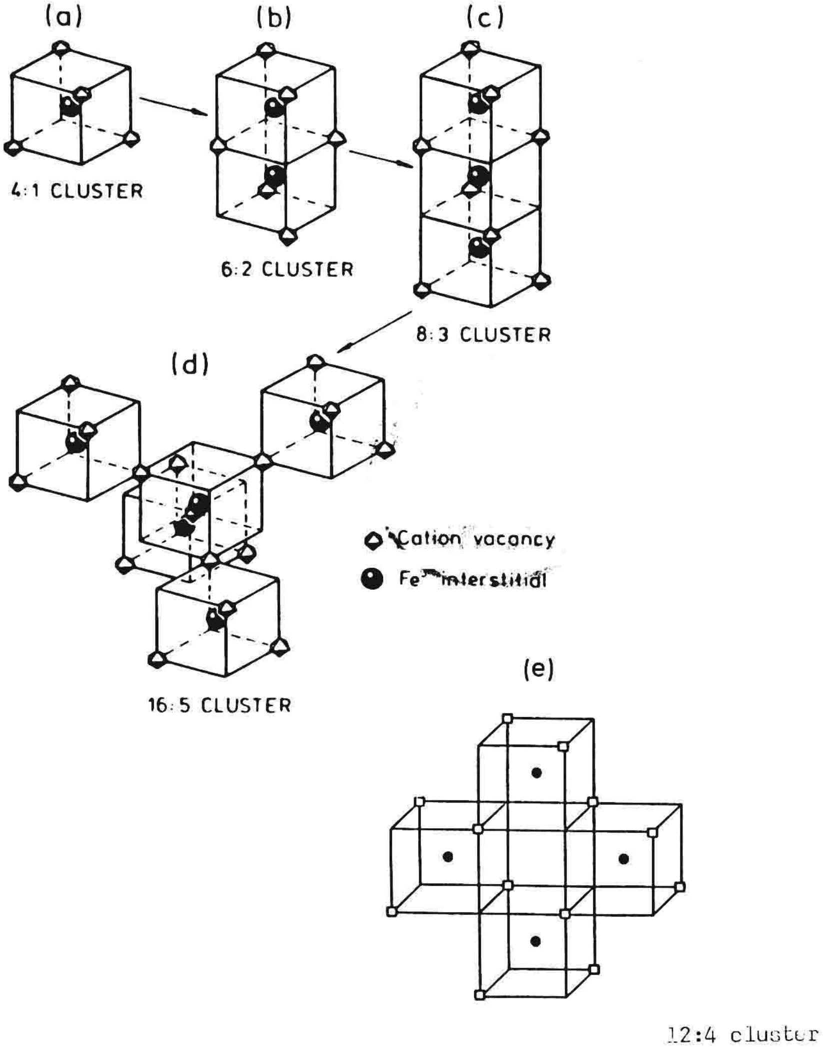

FIGURE 3. Vacancy-interstitial cluster models in $Fe_{1-x}O$.

$$D = 1/6\ x\upsilon r^2\ , \tag{5}$$

where x is the defect concentration and r is the distance of the defect jump. If, as argued below, υ shows Arrhenius behavior, then since x is either fixed by the level of impurities (or of mechanical and irradiation damage), D itself will show Arrhenius behavior. Similar behavior will be shown by the electrical conductivity if it is effected by the same atomic transport mechanisms, which now transport charge rather than mass. In these circumstances the conductivity (σ) and diffusion coefficient (D) are related by the Nernst-Einstein relationship:

$$\frac{\sigma}{D} = \frac{ne^2}{fkT} , \tag{6}$$

where n is the number density of mobile ions, e is the electron charge, and f is a numerical factor (the correlation coefficient) which is close to unity and which depends on the migration mechanism.

The prediction of Arrhenius behavior is borne out experimentally. Figure 4 shows an Arrhenius plot for conductivity in KCl. Two linear regions are observed: that at higher temperature corresponds to normal intrinsic generation of defects; whereas at low temperatures the defect population is dominated by impurities. In ceramic materials, the low temperature, extrinsic region commonly dominates except at the highest temperatures, close to the melting point.

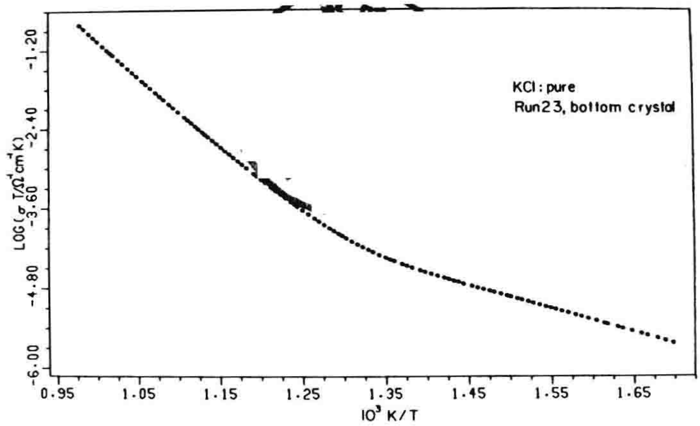

FIGURE 4. Arrhenius plot of conductivity for KCl (see Chapter by Jacobs in reference 2).

2.5. Defect structure of ceramics: summary

It should be clear from the above discussions that the defect properties of ceramics show complex features that are not encountered in parallel studies of metals. The variety of atom types leads to a corresponding variety in defect species. Low levels of impurities can lead to an enormous enhancement in defect concentrations and on defect dependent properties, e.g. diffusion. Defect aggregation is observed at all but the lowest defect concentrations. Because of this complexity, guidance from reliable theoretical techniques has played and continues to play a vital role in the development of this field. The remainder of this chapter will review the present state of theoretical studies of defects in ceramics.

3. DEFECT CALCULATIONS: TECHNIQUES

The methodology of defect calculations in ceramics has been extensively reviewed in recent years by the present author and others (1,4-6). For this reason the account here will concentrate on key features of the techniques; the reader is referred to references (1-6) for details. We shall concentrate on simulation techniques, i.e. methods which are based on models of the interatomic potentials describing the forces between the atoms or ions