

**TREATISE ON
SOLID STATE CHEMISTRY**

**Volume 2
Defects in Solids**

TREATISE ON SOLID STATE CHEMISTRY

Volume 2 Defects in Solids

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**TREATISE ON
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**Volume 2
Defects in Solids**

TREATISE ON SOLID STATE CHEMISTRY

- Volume 1 • The Chemical Structure of Solids**
- Volume 2 • Defects in Solids**
- Volume 3 • Crystalline and Noncrystalline Solids**
- Volume 4 • Reactivity of Solids**
- Volume 5 • Changes of State**
- Volume 6 • Surfaces**

Foreword

The last quarter-century has been marked by the extremely rapid growth of the solid-state sciences. They include what is now the largest subfield of physics, and the materials engineering sciences have likewise flourished. And, playing an active role throughout this vast area of science and engineering have been very large numbers of chemists. Yet, even though the role of chemistry in the solid-state sciences has been a vital one and the solid-state sciences have, in turn, made enormous contributions to chemical thought, solid-state chemistry has not been recognized by the general body of chemists as a major subfield of chemistry. Solid-state chemistry is not even well defined as to content. Some, for example, would have it include only the quantum chemistry of solids and would reject thermodynamics and phase equilibria; this is nonsense. Solid-state chemistry has many facets, and one of the purposes of this *Treatise* is to help define the field.

Perhaps the most general characteristic of solid-state chemistry, and one which helps differentiate it from solid-state physics, is its focus on the chemical composition and atomic configuration of real solids and on the relationship of composition and structure to the chemical and physical properties of the solid. Real solids are usually extremely complex and exhibit almost infinite variety in their compositional and structural features.

Chemistry has never hesitated about the role of applied science, and solid-state chemistry is no exception. Hence, we have chosen to include in the field not only basic science but also the more fundamental aspects of the materials engineering sciences.

The central theme of the *Treatise* is the exposition of unifying principles in the chemistry, physical chemistry, and chemical physics of solids. Examples are provided only to illustrate these principles. It has, throughout, a chemical viewpoint; there is, perforce, substantial overlap with some areas of solid-

Foreword

state physics and metallurgy but a uniquely chemical perspective underlies the whole. Each chapter seeks to be as definitive as possible in its particular segment of the field.

The *Treatise* is intended for advanced workers in the field. The scope of the work is such that all solid-state chemists, as well as solid-state scientists and engineers in allied disciplines, should find in it much that is new to them in areas outside their own specializations; they should also find that the treatment of their own particular areas of interest offers enlightening perspectives.

Certain standard subjects, such as crystal structures, have been omitted because they are so well covered in many readily available standard references and are a part of the background of all solid-state scientists. Certain limited redundancies are intended, partly because they occur in different volumes of the series, but mainly because some subjects need to be examined from different viewpoints and in different contexts. The first three volumes deal with the structure of solids and its relation to properties. Volumes 4 and 5 cover broad areas of chemical dynamics in bulk solids. Volume 6 treats both structure and chemical dynamics of surfaces.

N.B.H.

Preface to Volume 2

Volume 1 of this Treatise was concerned with the chemical structure of solids. This volume treats disorder in solids in relationship to physical properties. Many of these properties stem from simple defects in crystals, i.e., isolated impurity atoms and the point defects, vacancies, and interstitials. In the case of mechanical properties, dislocations (line defects) are dominant. Control of defects in solids thus provides the key to control of properties in many practical solids. This volume examines this relationship in detail.

N. B. H.

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Electronic Structure and Spectra of Impurities in the More Ionic Crystals

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1. Introduction

The physics and chemistry of the solid state nearly always involve impurities or defects in crystals. It is impossible to get rid of them entirely, so they are present whether we want them or not. But a large class of phenomena and devices depend on impurity or defect behavior, so the control and understanding of these objects is very important.

This chapter is concerned mainly with the electronic structure and spectroscopy of defects and impurities in the more ionic crystals. Underlying the spectroscopy of these localized centers, however, should be an understanding of their local geometry and the electronic structure of the ground state. Electronic spectroscopy alone gives some, but not enough, of this information, and it must be supplemented by other methods such as electron spin resonance, electron-nuclear double resonance, nuclear quadrupole resonance, infrared and Raman spectra, and thermodynamic measurements. The great generality and the precise meaning of thermodynamic quantities give them a position of special significance in this field, as will be shown in detail in the first parts of the chapter.

The electronic states associated with defects and impurities are localized on a very few atoms, unlike the Bloch states of the perfect crystal. The localization is caused by a change in potential at one or a few lattice sites compared to the pure crystal and could be described

in some cases as a perturbation of the band structure, as has been done in a famous paper by Koster and Slater.⁽¹⁾ On the other hand, the potential changes due to impurity substitution are caused by definite chemical differences between host and guest atom and are usually fairly large. Localized states entirely unrelated to host crystal band structure are introduced by transition metal impurities in non-transition metal compounds, for example. A useful classification of localized states can be based on the types of atomic orbitals available to electrons in impurity atoms, relative to those available in the host crystal.

The most localized impurity states are those of the $4f$ shell in rare earth atoms. Except for the splitting of degeneracies by a few hundred cm^{-1} and shifts of the same amount, the energy levels of the rare earth ions in ionic crystals are the same as those of the free atoms.⁽²⁾ The $4f$ shell is also able to preserve its identity in semiconductors and metals.

As the number of radial nodes for a given l value increases, the orbital becomes more extended in space. Thus the $5f$ shell of the actinide series is more strongly perturbed than the $4f$ shell, and crystal field splittings are of the order of 1000 cm^{-1} .⁽³⁾

In the first transition series, Sc to Zn, where the $3d$ orbitals are being filled, the atomic degeneracies are split by $5000\text{--}25,000 \text{ cm}^{-1}$ in crystals, while in the second and third series greater splittings are observed.⁽⁴⁾

The metals at the ends of the three transition groups have moderately stable $4s$, $5s$, or $6s$ orbitals because the d^{10} shells do not shield as well as p^6 shells of the pre-transition metals. Therefore the $4s$ and $4p$, $5s$ and $5p$, and $6s$ and $6p$ orbitals of post-transition metals are localized sufficiently well to be identified as atomiclike states when they occur as ions in crystals. The $ns\text{--}np$ separation is considerably less than in the free atoms, however, and is strongly dependent on the environment.⁽⁵⁾

Even a bromide ion impurity in a NaCl lattice shows a distinct spectrum at lower energy than the band gap of NaCl, and thus it must have well-localized states. The $5p$ shell in this case is part of a highly electronegative atom. On the other hand, only weakly localized behavior is exhibited when electropositive metals such as potassium occur as impurities in NaCl.⁽⁶⁾

Another example of poorly localized impurity states is given by the levels resulting from the substitution of phosphorus in a germanium crystal. The wave functions of these states extend over many

unit cells, and are best characterized as perturbed Ge conduction band levels.⁽⁷⁾

In the transition groups of elements, by which we mean both *d* and *f* series, both the initial and final states of a spectroscopic transition may be highly localized. At energies high enough, however, stronger transitions occur in which either the initial or final state is localized, but the other is not as well localized. The latter states are related to the band structure of the crystal, though they are modified by the presence of the impurity. The name "charge-transfer transition" is often given to these processes, implying that an electron is transferred from one atom to another, or to a group of other atoms.⁽⁸⁾

Closely related to charge-transfer transitions are the spectroscopic processes in "donor-acceptor pairs." These are two impurities, usually acting mutually as charge compensators in the crystal lattice, and an electron is transferred from one to the other. This type of system is the basis for phosphor behavior.⁽⁹⁾

Pairs of identical transition group atoms situated at nearest cation sites in a crystal display exchange interactions which have been related to the magnetic behavior of the corresponding transition metal compound. Nonidentical pairs, or a transition metal impurity in a transition metal crystal, also show interesting exchange effects, both in the ground and in excited states.⁽¹⁰⁾

Atomic or ionic vacancies act as donors or acceptors in crystals. The absence of an atom leaves weakly bound states which result in the occurrence of low-energy optical transitions. The most familiar of these is the anion vacancy, which becomes the *F* center when it captures an electron.⁽¹¹⁾

Complexes formed between an *F* center and a transition metal or rare earth ion have been observed, and have interesting properties. For example $\text{Ce}^{3+} + F$ center⁽¹²⁾ in a CaF_2 crystal displays photochromic behavior. An *F* center with a neighboring alkali or alkali-earth ion different from the host cations is called an F_A center, and much has been learned from them about electrons near defects.⁽¹³⁾

A great deal of chemistry depends on which atomic orbitals in the range of valence energies are able to remain localized when the atom becomes part of a crystal or molecule. Our scheme for classifying localized states depends on being able to identify these localized valence orbitals. An illustration of the differences between the radial extent of different atomic orbitals is shown for the gadolinium atom in Figure 1.⁽¹⁴⁾ Gadolinium has three valence electrons, one *5d* and two *6s*. As an impurity in a CaF_2 crystal in the presence of only a

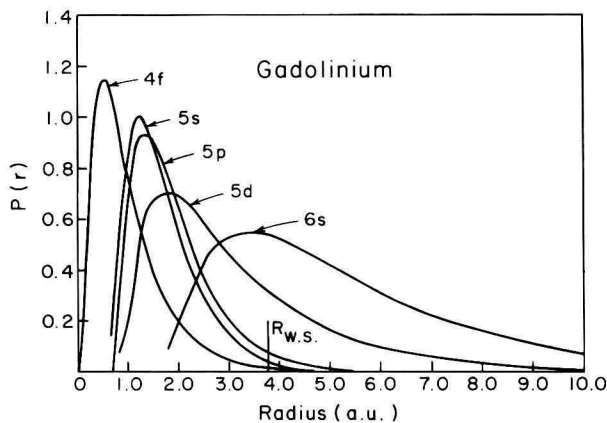


Fig. 1. The radial probability distribution $P(r) = \psi(r)^2 \cdot 4\pi r^2$ of electrons in the outer parts of the 4f, 5s, 5p, 5d, and 6s orbitals of atomic Gd. The radius of the Wigner-Seitz sphere (approximately one-half the nearest-neighbor distance in the metal) is shown for comparison.⁽¹⁰⁾

weak acceptor, it can exist in the divalent state with one electron in the 5d orbital and seven in the 4f orbitals. With a somewhat stronger acceptor it reaches the usual trivalent state when the 5d orbital is empty. The 4f shell is so localized that it has nearly the same magnetic and spectroscopic properties whether the atom is part of a metal or an ionic compound. Thus, as Figure 1 shows, the 4f orbital does not have significant amplitude at half the interatomic distance in the metal, while the 5d orbitals of neighboring metal atoms overlap strongly. In compounds, the 5d orbitals, if occupied, are strongly perturbed by the orbitals of the electronegative partners and the 6s orbitals are essentially completely mixed with them, giving the compound its ionic nature.

The radial extent of the orbitals relative to interatomic distances therefore gives a good indication of the chemical behavior of the valence electrons.

There is more to the story, however, because Figure 1 does not show the large kinetic energy associated with the f and d orbitals. Thus the 4f electrons are less tightly bound than the 5s and 5p electrons even though the 4f orbitals are on the average closer to the nucleus. Kinetic energy is manifested in the node patterns of f and d orbitals, which in turn leads to "crystal field splitting." The number of nodes is not affected by the introduction of the atom into a solid and it remains as an identifying feature of the nature of localized atomic orbitals.