

Physical Chemistry of Ionic Materials

Ions and Electrons in Solids

JOACHIM MAIER

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Preface

The book that you are about to read is, in a broad sense, concerned with the physical chemistry of solids. More specifically, it deals with the ionic and electronic charge carriers in ionic solids. The latter species are the major players in the game when one attempts a detailed understanding or deliberate tuning of kinetic properties. The charge carriers that we refer to are not necessarily identical with the charged particles that constitute the solid, but rather with the effective particles that transport charge, i.e. in the case of ionic crystals the ionic point defects, in addition to excess electrons and holes. These ionic and electronic charge carriers constitute the redox and acid–base chemistry in the same way as is the case for aqueous solutions, they permit charge and matter transport to occur, and are also reactive centres in the sense of chemical kinetics. This explains the central role of defect chemistry in this book.

The more classical introductory chapters on chemical bonding, phonons, and thermodynamics of the perfect solid may, on one hand, be considered as preparation for the key chapters which deal with thermodynamics of the real solid, as well as with kinetics and electrochemistry — both being unthinkable without the existence of defects; on the other hand, they provide the complement necessary for the book to serve as a textbook of physical chemistry of solids. (In fact the different chapters correspond to classical fields of physical chemistry but referred to the solid state.)

The structure of the book is expected to be helpful in view of the heterogeneity of the potential readership: This addresses chemists who traditionally consider solids from a static, structural point of view and often ignore the “internal life” enabled by defect chemistry, physicists who traditionally do not take pertinent account of composition as a state parameter, and materials scientists who traditionally concentrate on materials properties and may not adequately appreciate the basic role of electrochemistry.

Of course the book cannot fully cover the materials space or the world of properties. If the reader is a chemist, he or she may miss special chapters on covalent and disordered solids (e.g. polymers); the physicist will certainly find electronic properties under-represented (e.g. metals), and the materials scientist may have expected a detailed consideration of mechanical and thermal properties. Nonetheless the author is convinced — and this is based on lectures on Physical Chemistry and Materials Science given to very different audiences in Cambridge (USA), Tübingen and Stuttgart (Germany) and Graz (Austria) — that he made a germane selection to highlight the physical chemistry of charge carriers in solids. A certain preference

for examples stemming from the working group of the author is not the result of slothfulness or vanity; rather, it is based on the endeavour to concentrate on a few model materials.

The many cross-references are meant to facilitate reading; proofs or remarks that would disturb the flow of reading and belong to a different level are put into footnotes, and they should be considered when reading the text a second time.

Compared to the German version which appeared earlier (*Festkörper – Fehler und Funktion, Prinzipien der Physikalischen Festkörperchemie*; B. G. Teubner Stuttgart, 2000), the English text is — apart from a few modifications and hopefully a smaller concentration of “defects” — essentially a 1:1 translation.

I am indebted to D. Bonnell, W. B. Eberhardt, K. Funke, O. Kienzle, M. Martin, M. Rühle, E. Schönherr and A. Simon for discussions and the courtesy of providing valuable figures.

I would like to thank my co-workers and colleagues for critical remarks. In particular I appreciate helpful discussion with Jürgen Fleig, Janez Jamnik, Klaus-Dieter Kreuer, Rotraut Merkle and Roger de Souza. To Dr de Souza I am also indebted for his great help in the process of translating the German version into English. I would like to thank Barbara Reichert for the unremitting editorial assistance. Sofia Weiglein and M. Trieloff deserve thanks for their help as regards many tiny things (infinity times zero might be a very significant number). Harry Tuller (MIT Cambridge) and Werner Sitte (TU Graz) provided the hospitality, and my wife Eva the additional free time, without which this book would have never been completed. Many thanks to them.

Stuttgart, January 2004

Joachim Maier

Contents

1	Introduction	11
1.1	Motivation	11
1.2	The defect concept: Point defects as the main actors	14
2	Bonding aspects: From atoms to solid state	23
2.1	Chemical bonding in simple molecules	23
2.1.1	Ideal covalent bonding	23
2.1.2	Polar covalent bonding	27
2.1.3	The ionic bonding	30
2.1.4	Metallic bonding	31
2.1.5	Further intermediate forms of chemical bonding	32
2.1.6	Two-body potential functions	33
2.2	Many atoms in contact: The solid state as a giant molecule	35
2.2.1	The band model	36
2.2.2	Ionic crystals	50
2.2.3	Molecular crystals	56
2.2.4	Covalent crystals	57
2.2.5	Metallic crystals	59
2.2.6	Mixed forms of bonding in solids	60
2.2.7	Crystal structure and solid state structure	61
3	Phonons	65
3.1	Einstein and Debye models	65
3.2	Complications	69
4	Equilibrium thermodynamics of the perfect solid	72
4.1	Preliminary remarks	72
4.2	The formalism of equilibrium thermodynamics	72
4.3	Examples of equilibrium thermodynamics	86
4.3.1	Solid–solid phase transition	86
4.3.2	Melting and evaporation	88
4.3.3	Solid–solid reaction	89
4.3.4	Solid–gas reaction	89

4.3.5	Phase equilibria and mixing reactions	93
4.3.6	Spatial equilibria in inhomogeneous systems	100
4.3.7	Thermodynamics of elastically deformed solids	103
4.3.8	The thermodynamic functions of state of the perfect solid . . .	104
5	Equilibrium thermodynamics of the real solid	108
5.1	Preliminary remarks	108
5.2	Equilibrium thermodynamics of point defect formation	109
5.3	Equilibrium thermodynamics of electronic defects	125
5.4	Higher-dimensional defects	134
5.4.1	Equilibrium concentration	134
5.4.2	Dislocations: Structure and energetics	136
5.4.3	Interfaces: Structure and energetics	140
5.4.4	Interfacial thermodynamics and local mechanical equilibria . .	146
5.5	Point defect reactions	155
5.5.1	Simple internal defect equilibria	155
5.5.2	External defect equilibria	161
5.6	Doping effects	177
5.7	Interactions between defects	200
5.7.1	Associates	201
5.7.2	Activity coefficients	210
5.8	Boundary layers and size effects	217
5.8.1	General	217
5.8.2	Concentration profiles in the space charge zones	223
5.8.3	Conductivity effects	228
5.8.4	Defect thermodynamics of the interface	233
5.8.5	Examples and supplementary comments	241
6	Kinetics and irreversible thermodynamics	268
6.1	Transport and reaction	268
6.1.1	Transport and reaction in the light of irreversible thermodynamics	269
6.1.2	Transport and reaction in the light of chemical kinetics	275
6.2	Electrical mobility	283
6.2.1	Ion mobility	283
6.2.2	Electron mobility	292
6.3	Phenomenological diffusion coefficients	294
6.3.1	Ion conduction and self-diffusion	295
6.3.2	Tracer diffusion	296
6.3.3	Chemical diffusion	300
6.3.4	A comparison of the phenomenological diffusion coefficients . .	305
6.4	Concentration profiles	307

6.5	Diffusion kinetics of stoichiometry change	312
6.6	Complications of matter transport	319
6.6.1	Internal interactions	319
6.6.2	Boundary layers and grain boundaries	332
6.7	Surface reactions	338
6.7.1	Elementary processes	338
6.7.2	Coupled reactions	340
6.7.3	Phenomenological rate constants	347
6.7.4	Reactivity, chemical resistance and chemical capacitance . . .	361
6.8	Catalysis	362
6.9	Solid state reactions	367
6.9.1	Fundamental principles	367
6.9.2	Morphological and mechanistic complications	378
6.10	Nonlinear phenomena	382
6.10.1	Irreversible thermodynamics and chemical kinetics far from equilibrium, and the special role of autocatalysis	382
6.10.2	Nonequilibrium structures in time and space	388
6.10.3	The concept of fractal geometry	393
7	Solid state electrochemistry:	
	Measurement techniques and applications	399
7.1	Preliminary remarks: Current and voltage in the light of defect chemistry	399
7.2	Open circuit cells	404
7.2.1	Equilibrium cells: Thermodynamic measurements and potentiometric sensors . .	404
7.2.2	Permeation cells and chemical polarization: Measurement of transport parameters and chemical filters . .	413
7.3	Cells under current load	418
7.3.1	Electrochemical pumps, conductivity sensors and other applications	418
7.3.2	Measurement cells	424
7.3.3	Bulk and phase boundary effects	426
7.3.4	Stoichiometry polarization	444
7.3.5	Coulometric titration	460
7.3.6	Impedance spectroscopy	462
7.3.7	Inhomogeneities and heterogeneities: Many-point measurements and point electrodes	473
7.4	Cells generating current	481
7.4.1	General	481
7.4.2	Fuel cells	482
7.4.3	Batteries	487
7.4.4	Tables	495

10	Contents
8	Bibliography
500	
Index	527

1 Introduction

1.1 Motivation

It may seem odd to ask the reader in the first sentence of the book he or she has just opened to put it down for a moment (naturally with the intention of picking it up and reading it again with greater motivation). Consider, however, your environment objectively for a moment. The bulk of it is (as we ourselves are to a large degree) made up of solid matter. This does not just apply to the materials, from which the house in which you live is built or the chair in which you may be seated is made, it also applies to the many technical products which make your life easier, and in particular to the key components that are hidden from your eyes, such as the silicon chip in the television set, the electrodes in the radio battery, and the oxide ceramics in the oxygen sensors of modern automobiles. It is the rigidity of solids which endows them with characteristic, advantageous properties: The enduring structure of our world is inconceivable without solid matter, with its low diffusion coefficients at least for one component (the reader may like to consider for a moment his or her surroundings being in spatial equilibrium, i.e. with all diffusion barriers having been removed). In addition and beyond the mere mechanical functionality, solids offer the possibility of subtly and reproducibly tailoring electromagnetic, chemical and thermal functions.

The proportion of functional materials and, in particular, electrical ceramics in daily life is going to increase enormously in the future: Chemical, optical or acoustic sensors will analyse the environment for us, actuators will help us influence it. More or less autonomous systems, controlled by computers and powered by an autarchic energy supply (battery) or by an “electrochemical metabolism” (fuel cell) are by no means visions for the distant future. Wherever it is possible, attempts are being made to replace fluid systems by solid ones, for instance, liquid electrolytes by solid ion conductors. In short: The importance of (inorganic or organic) solids can hardly be overestimated (even if we ignore the crowning functionality of biopolymers, as (almost)¹ done in this book). Furthermore, solid state reactions were not only of importance for and during the creation of our planet, they also constitute a large portion of processes taking place, nowadays, in nature and in the laboratory.

Perhaps you are a chemistry student in the midst of your degree course or a chemistry graduate already with a complete overview of the syllabus. You will then certainly agree that the greater part of a chemist's education is concerned with liquids and, in particular, with water and aqueous solutions. Solids, when they are considered, are almost always considered from a naive “outer” point of view, i.e. as chemically invariant entities: Interest is chiefly concerned with the perfect structure and chemical bonding; in aqueous solutions it either precipitates or dissolves. Only the surface is considered as a site of chemical reactions. The concept of a solid having an “internal

¹See Section 6.10 of Chapter 6 for systems far from equilibrium.

chemical life”, which makes it possible for us to tailor the properties of a solid, in the same manner that we can those properties of aqueous solutions, sounds — even now — somewhat adventurous.

On the other hand, solid state physicists have influenced the properties of semiconductors such as silicon, germanium or gallium arsenide by defined doping in a very subtle way. If the reader is a physicist, I believe he or she would agree that the role of composition as a parameter is not sufficiently appreciated in physics. Even though internal chemical equilibria are sometimes considered and doping effects are generally taken into account, concentration is still too strongly focused on singular compositions and electronic carriers. In fact, a large number of functional materials are based on binary or multinary compounds, for which stoichiometric effects play an enormous role.

Lastly this text is addressed to materials scientists for whom the mechanical properties frequently and traditionally are of prime interest. Electrochemical aspects are generally not sufficiently considered with respect to their importance for the preparation and durability of the material and optimization of its function. Thus, the fields of ceramics, in general, and electroceramics, in particular, are addressed.

The chemistry and physics of defects play a key role in the following text [1,2]. After all, in the classical examples of water in chemistry and silicon in physics it is not so much the knowledge of the structure or of the chemical bonding that has made it possible to carry out subtle and controllable tuning of properties, but rather the phenomenological knowledge of the nature of relevant particles, such as H_3O^+ ions, OH^- ions or foreign ions in water that determine its acid–base and redox chemistry. In the case of silicon the relevant particles are conduction electrons and electron holes, which, on account of their properties, determine the (redox) chemistry and the electronic properties.

Focusing on such relevant particles leads to the generalized concept of defect chemistry that permits the treatment of internal chemical processes within the solid state (in this context Fig. 1.1 is illustrative). In processes, in which the structure of the

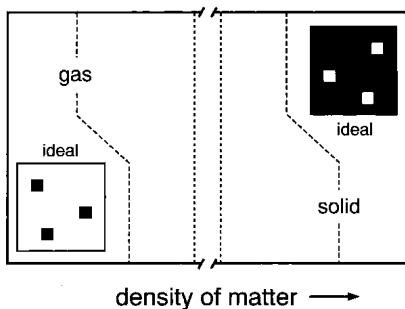


Fig. 1.1: In the same way as the treatment of ideal gases is simple — since the particles are dilute and uncorrelated (l.h.s.) —, the treatment of the solid state becomes equally simple from the viewpoint of the (dilute) defects (r.h.s.). (The portion of matter increases from the left to the right, while the portion of vacancies correspondingly decreases.)

phase does not alter, the perfect state can be regarded as invariant and all the chemical occurrences can then be reduced to the behaviour of the defects, that is, the deviations from the perfect state. The foundation stone of defect chemistry was laid

by Frenkel, Schottky and Wagner [1,2] as early as the 1930s; there is an extensive technical literature covering the field [3–14], but in chemistry and physics it has not yet become an adequate and generally accepted component of our training. In this sense this text is intended to motivate the chemist to deal with the internal chemistry of solid bodies. I hope that the effort will be rewarded with a density of “aha experiences” that will be adequate to compensate for the trouble caused by the physical language which is sometimes necessary. The physicist should be stimulated by the text to examine the internal equilibria of solid materials, changes in their composition and, in particular, the properties of more complex materials. The motivation here ought to be the fact that the formalism of defect chemistry is largely material independent, at least as long as the defect concentrations are sufficiently low, and that it offers a universal phenomenological description in such cases. Finally the text is intended to help the materials scientist to optimize the functional properties of materials, but also to understand the preparation and degradation of structural materials.

If this attempt at motivation is an “attack on open doors”, then the sentences I have written may at least act as a guide for the path ahead.

The text concentrates on ionic materials and on electrical and electrochemical properties in order to keep the contents within bounds. On the whole, we will refer to a “mixed conductor”, for which ion and electron transport are both important and with regard to which the pure electronic conductor and the pure ionic conductor represent special cases. We will specifically address material transport with regard to its significance for electrochemistry and reaction kinetics. Whenever necessary, indications of the generality of the concepts are interspersed. In order to make the treatment reasonably complete, references are given whenever a detailed consideration is beyond the scope of the book.

We start with an extensive introduction to the perfect solid, its bonding and its vibrational properties, knowledge of which is necessary for understanding the physical chemistry of the processes involved. In order not to lose sight of the purpose of the book these sections have been kept as simple as possible (but as precise as necessary). The same applies to the general thermodynamic and kinetic sections, which also serve to introduce the formal aspects. Nevertheless, in view of the heterogeneity of the potential readership, this detailed mode of presentation has been chosen deliberately in order to be able to assume a uniform degree of knowledge when discussing defect chemistry. Some material may be repeated later in the text and this is intended to ensure that some chapters can be omitted by the advanced readers without loss of internal consistency.

The text will have fulfilled its purpose in an ideal manner, if it not only conveys to the reader the elegance and power of the defect concept, when it not only puts him or her in the position of being able to recognize the common aspects of different properties and processes such as doping and neighbouring phase effects, ionic and electronic conductivity, passivation and corrosion of metals, diffusion and reaction processes, synthesis kinetics and sintering kinetics in solids, electrode reactions and

catalysis, sensor processes and battery processes; but also puts the reader in the position to optimize the solid state “strategically” at the “writing desk” in those situations in which the desired parameters are already known.

1.2 The defect concept: Point defects as the main actors

As already mentioned, phenomenological understanding of condensed phases with regard to the tunability of chemical and electrical properties implies knowledge of the defects as the relevant particles and their interactions, rather than (or at least in addition to) knowledge of the structure of the perfect state. This is known to be the key to phenomenological understanding of the aqueous phase and to control its chemical and electrical properties. In pure water these defects or “chemical excitations” are H_3O^+ and OH^- ions. Let us consider the first row in Fig. 1.2. As shown, it is advantageous, in a purely phenomenological sense, to subtract from

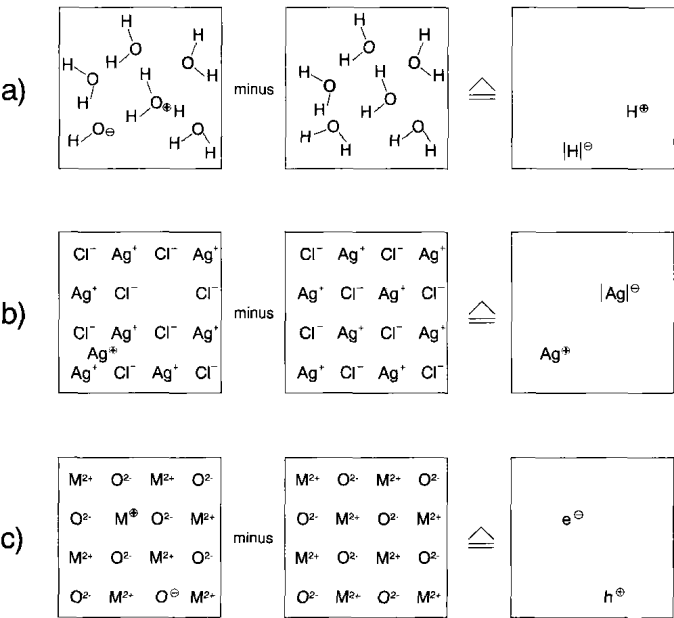
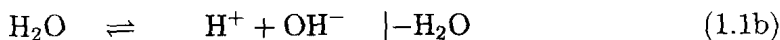
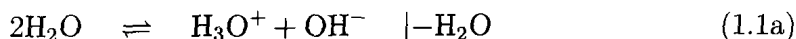


Fig. 1.2: a) If the basic compositionally unperturbed structure (chemical ground structure) is subtracted from the real structure, the point defects shown on the right remain. Naturally each is surrounded by a distorted region (effective radius of the point defect) which affects at least the immediate neighbourhood. In the case of fluid phases (see above) this procedure can only be regarded as an instantaneous picture. Owing to the absence of defined sites no distinction is made between various types of defect reactions as is done in the solid state. b) Frenkel disorder is sketched in the second row. c) The third row shows the case of purely electronic disorder whereby localized charge carriers are assumed for the sake of clarity [14].

the real structure the instantaneous perfect water structure. We are left with an excess proton and a missing proton, i.e. a “proton vacancy”. This is also the result of subtracting the H_2O molecule completely (Eq. (1.1c)) from the autoprotolysis

reaction² according to

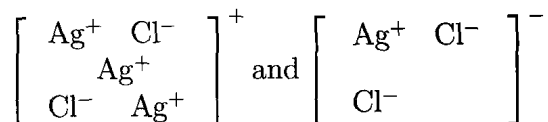


Here $|\text{H}|^-$ denotes a proton vacancy³.

Let us now consider disorder in a crystalline phase, to be specific, in solid AgCl. In this case some silver ions have left their regular sites⁴, and hence, left vacancies behind. As one can see (Fig. 1.2b), there is a very close analogy to Eq. (1.1). Even the nature of the driving force for the internal dissociation, namely the gain in entropy of configuration, is identical. The “subtraction” of the perfect structure as an invariant yields an excess cation (Ag^\cdot) and a cation vacancy ($|\text{Ag}|'$) as the relevant particles. Just as in Eq. (1.1c) we can write



The old-fashioned charge designations (dot and dash) denote the relative charges: The crystal segments containing the defects such as



are positively or negatively charged in an absolute sense, but the local positive or negative charge at the proper defect-site — interstitial or vacant site — represents a charge relative to the perfect situation. This differentiation between absolute and relative charge was naturally not necessary for H_2O .

²It is naturally possible to formulate the whole of aqueous acid–base chemistry in water in this minimal notation. Eq. (1.1c) would also formally describe autoprotolysis in liquid ammonia. An analogous Cl^- disorder reaction would be suitable for describing the dissociation of SOCl_2 :



instead of



Conversely, these considerations emphasize that internal acid–base chemistry of solids involves point defects [15]. In Chapter 5 we will see that such acid–base reactions, together with redox-reactions, constitute defect chemistry.

³According to Eq. (1.1c) we could also refer to the OH^- ion (more precisely to the difference of OH^- and H_2O) as a proton hole or an anti excess-proton. The following joke may be instructive in this context: A mathematics teacher notices that 10 pupils left the class-room even though only 9 have been in. His comment: If one pupil enters the room, the occupation is zero and the world is in order again.

⁴Perfect AgCl is dissociated in the sense that it consists of ions; but it is not dissociated into free particles since Ag^+ and Cl^- are trapped in their deep Coulomb potentials. The latter, “superionic” dissociation is described by Eq. (1.2).

The disorder in the electron shells is to be comprehended in an analogous manner. Here the bonding electrons, more precisely the valence electrons, have left their “regular” positions and have been excited into the conduction band. This also creates excess particles and missing particles, which are conduction electrons (e') and electron holes (h'). Let us take a metal oxide with the (perfect) composition MO as our model compound and for the purpose of better visualization assume that, to a good approximation, the valence band is composed of the oxygen p-orbitals, while the conduction band is composed of the outer metal orbitals. Hence, the reaction can also be formulated as an internal redox reaction

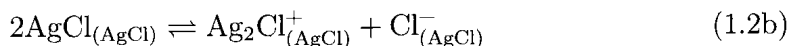


The minimal notation (subtraction of the perfect phase MO on both sides of the equation, see Fig. 1.2c) then becomes

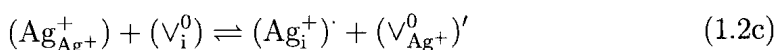


In silver chloride this corresponds to the charge transfer from Cl^- to Ag^+ . The advantage of the notation used in Eq. (1.3b) is that it is independent of such detailed bonding considerations. The building element formulation of Eqs. (1.2a), (1.3b) and also of Eq. (1.1c) is an adequate notation for the thermodynamic, i.e. phenomenological treatment and emphasizes the superposition of perfect and defect components in energetic questions.

Unfortunately the formulation suffers from a lack of vividness precisely on account of the high degree of abstractness. From a descriptive point of view, structure element formulation is to be preferred. Nonetheless, descriptions utilizing very detailed structural elements, as in Eq. (1.1b) or Eq. (1.1a), are not employed in the case of ionic solids, although the disorder in AgCl (Eq. (1.2a)) could certainly be analogously formulated as the “dissociation reaction of the lattice molecule” according to



(the lower index refers to the perfect state), or even — by analogy to $H_9O_4^+$ — by inclusion of further regular neighbours (see Chapter 5). The author has resisted, for two reasons, the temptation to select such a “molecular” notation: Firstly, the field of the “internal chemistry” of solids is already conceptually overloaded, and secondly, such a chemical notation would be clumsy for complicated solids or in kinetic considerations. Instead the conventional Kröger–Vink notation [3] is used: It also considers structural elements, in that it refers to absolute structures, but “boiled down” to only the “atomic” particles actually reacting. That means in the case of our silver chloride example that the anion-sublattice is completely omitted from the description, while, on the other hand, vacancies (here in the cation-sublattice) are explicitly taken into account as structural elements using the symbol ∇ . So instead of Eq. (1.2a) or (1.2b) we write



or abbreviated by the omission of all absolute charges



The superscript in Eq. (1.2d) again represents the relative charge, i.e. the difference between the charge in the real case and that in the perfect case ($' \hat{=} -1$, $\cdot \hat{=} +1$). An effective charge of zero is not indicated or is sometimes indicated by means of a cross ("×"). The subscript denotes the crystallographic position in the perfect structure (i: interstitial site). Specifically Eq. (1.2d) indicates that a silver ion (Ag^+) has moved from a regular silver ion position (subscript Ag) to a vacant (V stands for vacancy) interstitial site (subscript i) where it becomes an interstitial silver ion $\text{Ag}_{\text{i}}^{\cdot}$ and leaves a vacancy (V_{Ag}') in the silver ion lattice. The regular components such as Ag_{Ag} , V_{i} or Cl_{Cl} do not carry an effective charge, while the interstitial silver ion bears the relative charge +1 ($= +1 - 0$) and the silver vacancy the relative charge -1 ($= 0 - (+1)$). Structure element notation is not used in the case of electronic defects, rather the building element notation of Eq. (1.3b). This has the advantage that, firstly, the formulation is independent of the nuances of the bonding and that, secondly, a possible double counting of electronic states⁵ is avoided. Since an ionic crystal is a rigid body with well-defined sites and the picture is only slightly complicated by vibrations (or rotations) about the equilibrium state, it is possible (and necessary) to distinguish in contrast to the fluid phase water, between several defect types, as will be discussed in Section 5.5.

In addition to defects intrinsically formed in pure substances by thermal disorder, defects are also generated by the incorporation of foreign substances. Hence, the (substitutional) incorporation of a D^{2+} cation in place of an M^+ cation leads to a point defect $(\text{D}_{\text{M}}^{2+})' \equiv \text{D}_{\text{M}}'$, while the (additive) interstitial incorporation of a cation of higher valence leads to a defect with a higher effective charge, namely $\text{D}_{\text{i}}^{\cdot}$. Although dissolved foreign substances are similarly important in liquids, it is necessary to point out another basic difference between liquid and solid phases: The simultaneous dissolution of cations and anions does not normally constitute a difficulty in the case of deformable fluids, and electroneutrality is automatically guaranteed. The normal case in the solid state is that either only the anion or the cation (here D^{2+}) is soluble. The dissolution of D^{2+} then takes place either by substitution of M^+ or by taking up an unoccupied interstitial position⁶. The change in charge must be compensated by creation of another defect. Thus, the introduction of D^{2+} (by substituting⁷ for an M^+ or by occupation of a free interstitial position) is associated with the formation of negatively charged ionic and electronic defects

⁵The electronic shell is included in the symbol for the element.

⁶As in organic chemistry, it is possible to distinguish between addition, substitution and elimination reactions (in and on the "giant molecule solid"). Rearrangement reactions also occur (cf. phase transitions).

⁷Such substitution reactions also play a role in aqueous solution: The precipitation reaction,

