THERMODYNAMICS OF POINT DEFECTS AND THEIR RELATION WITH BULK PROPERTIES

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SERIES **DEFECTS IN SOLIDS**

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PREFACE

During the past few years the authors have published a number of papers relating to the study of point defects in solids. This book is to a large extent a unified compilation of these publications. Some of them dealt purely with thermodynamics; within the context many so-called "anomalous effects" have found a natural explanation. In most cases the difficulties in the interpretation of the experimental data arose from assumptions uncritically adopted in standard thermodynamic concepts. It therefore became evident that a careful separation of the thermodynamical definitions of defect parameters from any assumptions whatsoever was absolutely necessary. Furthermore thermodynamics impose some fundamental constraints on the various defect parameters, whose consideration is essential not only to experimentalists but also to theorists.

In recent publications the authors also studied the problem whether an explicit connection between defect parameters and bulk macroscopic properties really exists. Zener and others made such an attempt long ago. The question is of technological interest because one could then predict the temperature and pressure dependence of the parameters knowing only macroscopic properties as the volume and the elastic constants. The authors have suggested that such a connection really exists. By comparing the values of various defect parameters with bulk properties they noticed that certain connections repeatedly appeared. With time an empirical law was found describing correctly a large quantity of experimental data, many of them obtained through completely independent techniques. The basic relation is the formula $g = cB\Omega$, where g is the Gibbs defect energy, B is the isothermal bulk modulus and Ω the "mean" atomic volume. The coefficient c is practically temperature and pressure independent and is fixed only by the defect mechanism and the matrix material. The authors labelled the above relation the $cB\Omega$-model, and for a long time they considered it an empirical law.

The consistency with which this model applies to increasingly more cases led to the idea that we were not dealing with a coincidence, but that a deeper general law lay hidden within. A revision of the thermodynamics of defects showed that a hitherto unknown formula exists connecting defect parameters (Gibbs energy and volume) to bulk properties (B, and the pressure derivative dB/dP). Inserting usual numerical values into this formula it simplifies, to a very good approximation, to the $cB\Omega$-model, which can therefore be considered as a special case of a general thermody-

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namical law. The bounds of its errors can be determined and were found to permit the use of this approximation for nearly all experimental situations.

In view of the above remarks the text of this book has been divided into two relatively independent sections. In Part 1 we give a strict review of the thermodynamics of point defects and the basic philosophy for the correct analysis of the experiments, while carefully avoiding unwarranted assumptions. It starts with a brief review of general thermodynamics of solids in order to aid readers who are less familiar with the subject. Part 2 studies the connections of defect parameters with bulk properties, which is in essence the $cB\Omega$-model. In the first chapters of this part it is presented as an empirical model supported by a large quantity of experimental data. A strict theoretical basis of the model is given in the last chapter. This division enables the reader to select the point he is specially interested in without having to go through the whole book.

The $cB\Omega$-model finds important practical applications in Metallurgy, as it permits the prediction of diffusion coefficients under conditions of temperature and pressure when diffusion measurements are difficult. For such extreme conditions the measurements can be replaced by the much easier elastic and expansivity experiments. As the $cB\Omega$-model develops new theoretical connections between the defect parameters, a number of experiments is proposed on various aspects of defects.

Another interesting application is found in the field of Geophysics; certain solids emit electrical currents when the pressure reaches the value at which the relaxation time for the attainment of thermodynamic equilibrium becomes very short. This theoretical result became the impulse for experiments on the variation of the electrical field in the earth during periods of high seismicity. They led to the detection of transient electric pulses that can serve for the prediction of earthquakes.

Since the completion of the main text of this book a number of experiments has been published referring to point defects. The connection between defects and bulk properties seems to become a promising tool in the study of geophysical questions. Furthermore, pressure-induced currents observed in the earth have been exceedingly well exploited in making short-term predictions of the epicenter and the magnitude of earthquakes. Some of these newest data are described in the Appendix.

Professors David Lazarus and Larry Slifkin went through a large part of the manuscript and have made many instructive comments.

April 1985   P.A.V. and K.D.A.

To the memory of my father Antonios (P.A.V.)

CONTENTS

1 | INTRODUCTION

1.1   Scope and organisation of the book

The present book starts with a part on strict definitions of the formation and migration parameters and on the laws that connect them. It is separated from the second part which is based on the "$cB\Omega$-model"; this model is simply a proposal which states that the formation g^f (or migration g^m or activation g^{act}) Gibbs energy is proportional to $B\Omega$, where B is the isothermal bulk modulus and Ω the mean volume per atom. As will be seen, the proportionality constant – labelled c^f (or c^m or c^{act}) – depends on the process but is *not* an empirical quantity; it has a definite physical meaning and can be shown to be practically temperature and pressure independent. As will be proven in ch. 14 the $cB\Omega$-model is of thermodynamical origin; in this sense the second part of the book can be considered a natural continuation of the first.

The "thermodynamical definitions" of defect parameters given in Part 1 are consistent with the general spirit of Thermodynamics and do not assume any restrictions on their temperature and pressure variation apart from those imposed by thermodynamical laws (e.g. from the third law that states that the formation entropy of a vacancy has to tend to zero for $T \rightarrow 0$ K for a pure solid etc.). These thermodynamical definitions, although being of major importance for a consistent analysis of the experimental data, do not lead by themselves to a description of the data. In an analysis one has anyhow to go one step further, i.e. to adopt some "assumptions" concerning the temperature and pressure (volume) dependence of some thermodynamical parameters. This is now the point where a dilemma emerges. In order to realise whether these assumptions are plausible or not, one usually has to go back to the microscopic picture of these parameters. This is achieved by Statistical Thermodynamics; for this reason the statistical definitions of the formation and migration parameters are also given in the first part of the book. However, there is the difficulty that the "statistical definitions" are easy only for harmonic or quasi-harmonic solids but not for real solids. This shortcoming may be serious when one is making microscopic calculations but *not* for the scope of the present book which only examines if the above assumptions are reasonable or not. The $cB\Omega$-model will be found to be able to replace them by others which are physically more acceptable. In the block diagram of fig. 1.1 an attempt is made to compare them; it is restricted to

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Usual assumptions		Physically acceptable assumptions	
The isobaric formation entropy s^f does not depend on T	The formation volume v^f does not depend on P	The isochoric formation entropy s^* does not depend on T	The formation volume v^f depends on P in a manner at least comparable to the bulk volume
g^f varies linearly with P and T		g^f is proportional to $B\Omega$	
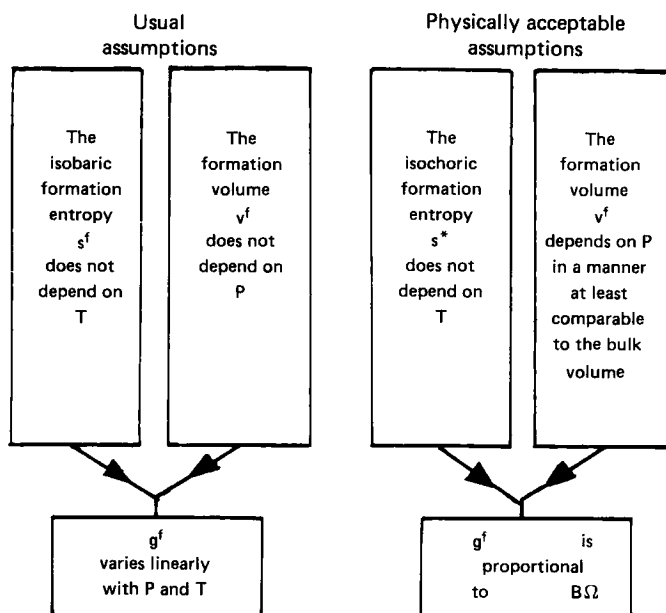
Fig. 1.1. Comparison of usual assumptions with physically acceptable assumptions.

the formation process but analogous comments are valid for the migration process. A brief discussion concerning their comparison is given below.

In the framework of the usual assumptions the formation entropy s^f and enthalpy h^f are accepted as temperature independent and the formation volume v^f is arbitrarily taken as temperature and pressure independent. This set of "current assumptions" is from a thermodynamical point of view absolutely self-consistent; attention is drawn, however, to the point that if one changes even only one of these assumptions' (e.g. that s^f depends on temperature) and retains the others, the above self-consistency is immediately destroyed from a thermodynamical viewpoint. It has been repeatedly realised that the above "set of assumptions" is correct *only* for a pure harmonic solid. But we know that solids expand, that their isothermal bulk modulus B decreases with temperature, that C_P differs from C_V and so do many other properties which are characteristic of the real (i.e. anharmonic) behaviour. A direct consequence of the anharmonicity is the incontestable fact that some *isobaric* defect parameters are quite different from the *isochoric* defect parameters (see ch. 3). Therefore it is at least questionable whether harmonic assumptions can describe real (i.e. anharmonic) solids. It is reasonable to expect that they do *not*.

A strange confusion often arises concerning this point; when the experimental data of real solids cannot be satisfactorily described from these harmonic assumptions the data are considered as showing "anomalous behaviour", as for example in the case of nonlinear Arrhenius plots. However, these cases should be considered anomalous only if these harmonic assumptions were actually able to describe the behaviour of a real solid.

Another example of such an inconsiderate use of the word "anomalous" is the case of curved $\ln D$ versus P isothermal plots. In such cases many workers interpret this phenomenon as resulting from a coexistence of two cooperating mechanisms for each of which the activation volume v^{act} is assumed pressure independent. However, a definite confusion reigns in this respect. Once one uses the word "activation volume" one must recall its correct thermodynamical definition $v^{\mathrm{act}} = (\partial g^{\mathrm{act}}/\partial P)_T$; this definition does not preclude a pressure variation of v^{act} and hence a curved "$\ln D$ versus P plot", even when a single mechanism is operating; the "anomaly" arises at the very moment the assumption is adopted that v^{act} is pressure independent.

In order to prove the inacceptability of the current assumptions when applied to real solids we shall discuss two of them, (1) the temperature independence of the entropy s^{f}, (2) the pressure independence of the formation volume v^{f}. We will do this in the light of the quasiharmonic approximation which, as generally accepted, is undoubtedly an important progress with respect to the pure harmonic approximation.

(1) Temperature independence of s^f. The entropy s^{f} as mentioned is currently assumed to be temperature independent; how far is this justified? The statistical meaning of s^{f} is given by: $s^{\mathrm{f}} = -k\Sigma_i \ln[\omega_i'(V)/\omega_i(V^0)]$, where ω_i' are the frequencies of the real volume V after the vacancy was produced and ω_i those of the "isobaric ideal lattice", i.e. at a different volume V^0. As the temperature increases while the external pressure remains constant both the volumes V and V^0 of the real and the ideal crystal (usually) increase; we are quite sure that in these two solids the frequencies ω_i' and ω_i vary upon heating predominantly due to their volume variation. It seems therefore totally unjustified or at least difficult to accept that the sum $\Sigma_i \ln[\omega_i'(V)/\omega_i(V^0)]$ does not change, e.g. when the solid is heated from $T_{\mathrm{M}}/2$ up to T_{M} where T_{M} is the melting temperature. There is no physical argument to guarantee that the above complicated sum (and therefore the formation enthalpy) remains constant. In order to get a feeling how dubious this assumption is, we recall the simple Grüneisen theory: for the temperature interval from $T_{\mathrm{M}}/2$ to T_{M} the volume of mono-atomic crystals increases by ~ 5% and hence the mean frequencies of both crystals are reduced typically by $\gamma \times 5\% \approx 15\%$ for $\gamma \approx 3$.

On the other hand one could replace the above "assumption" by another which is physically more acceptable: upon *isochoric* heating the sum $-k\Sigma_i \ln[\omega_i'(V)/\omega_i(V)]$, where the frequencies ω_i' and ω_i now refer to the same macroscopic volume V can be well considered as temperature independent. This is physically plausible because – according to the physical basis of the quasiharmonic approximation – the frequencies are explicit functions *only* of the macroscopic volume; therefore, due also to the fact that upon *isochoric* heating there is direct experimental confirmation that the frequencies exhibit only a very small explicit temperature dependence, one is led to the conclusion that the sum $-k\Sigma_i \ln[\omega_i'(V)/\omega_i(V)]$ can well be considered temperature independent. (This sum as we shall see is simply the thermal entropy s^* for an *isochoric* production of a vacancy.) Combining now this "physically acceptable assumption" with the well-known fact that $(\partial B/\partial T)_V$ is also temperature independent (which is also theoretically justified in the quasiharmonic approximation [1]) one is directly led – by thermodynamics (see ch. 14) – to the conclusion that the Gibbs formation energy g^f should be linear with respect to $B\Omega$ where the coefficient of $B\Omega$ has to be *temperature independent* (recall for V = constant).

(2) *Pressure independence of* v^f. Another current assumption is that the formation volume v^f is pressure independent. The thermodynamical meaning of v^f is that it represents the variation $V - V^0$ where V^0 is the initial volume and V the real volume after the production of a vacancy under isothermal and isobaric conditions. There is no doubt that both V and V^0 have to decrease upon compression. There is no guarantee however that their difference, i.e. v^f, also remains constant. From a purely physical point of view the assumption accepting v^f as pressure independent (i.e. that the compressibility κ^f of the volume v^f is zero) is equivalent to saying that the isothermal compressibility κ of the crystal *decreases* after the introduction of vacancies under isobaric conditions. (see eq. 3.57). This is really dubious and contrary to common sense because one expects physically the compressibility to *increase* and not to decrease upon creation of vacant sites; one could assume at least that the compressibility remains almost the same which – from thermodynamics – directly leads to the conclusion that the compressibility κ^f of the formation volume is comparable to the bulk compressibility κ. When one now combines: *either* the physically plausible assumption that $\kappa^f = \kappa$ with the fact that dB/dP is pressure independent (which is exactly valid in the quasiharmonic approximation [1]), *or* the reasonable physical assumption that κ^f exceeds κ only by a few times (clearly justified from the microscopic point of view) with the well-known fact that dB/dP varies only slightly upon isothermal compression, one can directly derive from thermodynamics (see ch. 14) that g^f is linear in $B\Omega$