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The Physics of Structural Phase Transitions

(2nd Edition)

结构相变物理

（第二版）

M.Fujimoto

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《国外物理名著系列》(影印版)专家委员会名单

（按姓氏笔画排序）

国外物理名著系列序言

对于国内的物理学工作者和青年学生来讲，研读国外优秀的物理学著作是系统掌握物理学知识的一个重要手段。但是，在国内并不能及时、方便地买到国外的图书，且国外图书不菲的价格往往令国内的读者却步，因此，把国外的优秀物理原著引进到国内，让国内的读者能够方便地以较低的价格购买是一项意义深远的工作，将有助于国内物理学工作者和青年学生掌握国际物理学的前沿知识，进而推动我国物理学科研和教学的发展。

为了满足国内读者对国外优秀物理学著作的需求，科学出版社启动了引进国外优秀著作的工作，出版社的这一举措得到了国内物理学界的积极响应和支持，很快成立了专家委员会，开展了选题的推荐和筛选工作，在出版社初选的书单基础上确定了第一批引进的项目，这些图书几乎涉及了近代物理学的所有领域，既有阐述学科基本理论的经典名著，也有反映某一学科专题前沿的专著。在选择图书时，专家委员会遵循了以下原则：基础理论方面的图书强调“经典”，选择了那些经得起时间检验、对物理学的发展产生重要影响、现在还不“过时”的著作（如狄拉克的《量子力学原理》）。反映物理学某一领域进展的著作强调“前沿”和“热点”，根据国内物理学研究发展的实际情况，选择了能够体现相关学科最新进展，对有关方向的科研人员和研究生有重要参考价值的图书。这些图书都是最新版的，多数图书都是2000年以后出版的，还有相当一部分是当年出版的新书。因此，这套丛书具有权威性、前瞻性和应用性强的特点。由于国外出版社的要求，科学出版社对部分图书进行了少量的翻译和注释（主要是目录标题和练习题），但这并不会影响图书“原汁原味”的感觉，可能还会方便国内读者的阅读和理解。

“他山之石，可以攻玉”，希望这套丛书的出版能够为国内物理学工作者和青年学生的工作和学习提供参考，也希望国内更多专家参与到这一工作中来，推荐更多的好书。

中国科学院院士
中国物理学会理事长

To the memory of Professor M. Takéwaki
who inspired me with fantasy in
thermodynamics

Preface to the Second Edition

In the first edition, I discussed physical principles for structural phase transitions with applications to representative crystals. Although published nearly 6 years ago, the subject matter is so fundamental in solid states and I am convinced that this book should be revised in a textbook form to introduce the principles beyond the traditional theory of ideal crystals.

Solid-state physics of perfect crystals is well established, and lattice imperfections are treated as minor perturbations. The basic theories are adequate for most problems in stable crystals, whereas in real systems, disrupted translational symmetry plays a fundamental role, as revealed particularly in spontaneous structural changes. In their monograph *Dynamical Theory of Crystal Lattices*, Born and Huang have pointed out that a long-wave excitation of the lattice is essential in anisotropic crystals under internal or external stresses, although their theory had never been tested until recent experiments where neutron scattering and magnetic resonance anomalies were interpreted with the long-wave approximation. Also, the timescale of observations is significant for slow processes during structural changes, whereas such a timescale is usually regarded as infinity in statistical mechanics, and the traditional theory has failed to explain transition anomalies. Although emphasized in the first edition, I have revised the whole text in the spirit of Born and Huang for logical introduction of these principles to structural phase transitions. Dealing with thermodynamics of stressed crystals, the content of this edition will hopefully be a supplement to their original treatise on lattice dynamics in light of new experimental evidence.

We realize that in practical crystals, a collective excitation plays a significant role in the ordering process in conjunction with lattice imperfections, being characterized by a propagating mode with the amplitude and phase. Such internal variables are essential for the thermodynamic description of crystals under stresses, for which I wish to establish the logical foundation, instead of a presumptive explanation.

Constituting a basic theme in this book, the collective motion of dynamical variables is mathematically a nonlinear problem, where the idea of *solitons* casts light on the concept of local fields, in expressing the intrinsic mechanism of distant order involved in the collective motion in a wide range of temperature. While rather primitive at the present stage, I believe that this method leads us in a correct direction for nonlinear processes, along which structural phase transitions can be elucidated in further detail. I have therefore spent a considerable number of pages to discuss the basic mathematics for nonlinear physics.

I thank Professor E. J. Samuelsen for correcting my error in the first edition regarding the discovery of the central peak.

Mississauga, Ontario M. Fujimoto
September 2003

Preface to the First Edition

Structural phase transitions constitute a fascinating subject in solid state physics, where the problem related to lattice stability is a difficult one, but challenging to statistical principles for equilibrium thermodynamics. Guided by the Landau theory and the soft mode concept, many experimental studies have been performed on a variety of crystalline systems, while theoretical concepts acquired mainly from isotropic systems are imposed on structural changes in crystals. However, since the mean-field approximation has been inadequate for critical regions, existing theories need to be modified to deal with local inhomogeneity and incommensurate aspects, and which are discussed with the renormalization group theory in recent works. In contrast, there are many experimental results that are left unexplained, some of which are even necessary to be evaluated for their relevance to intrinsic occurrence. Under these circumstances, I felt that the basic concepts introduced early on need to be reviewed for better understanding of structural problems in crystals.

Phase transitions in crystals should, in principle, be the interplay between order variables and phonons. While it has not been seriously discussed so far, I have found that an idea similar to charge-density-wave condensates is significant for ordering phenomena in solids. I was therefore motivated to write this monograph, where basic concepts for structural phase transitions are reviewed in light of the Peierls idea. I have written this book for readers with basic knowledge of solid state physics at the level of *Introduction to Solid State Physics* by C. A. Kittel. In this monograph, the basic physics of continuous phase transitions is discussed, referring to experimental evidence, without being biased by existing theoretical models. Since many excellent review articles are available, this book is not another comprehensive review of experimental results. While emphasizing basic concepts, the content is by no means theoretical, and this book can be used as a textbook or reference material for extended discussions in solid state physics.

The book is divided into two parts for convenience. In Part One, I discuss basic elements for continuous structural changes to introduce the model of pseudospin condensates, and in Part Two various methods of investigation are discussed, thereby revealing properties of condensates. In Chapter 10, work on representative systems is summarized to conclude the discussion, where the results can be interpreted in light of fluctuating condensates.

I am enormously indebted to many of my colleagues who helped me in writing this book. I owe a great deal to S. Jerzak, J. Grindley, G. Leibrandt, D. E. Sullivan, H.-G. Unruh, G. Schaack, J. Stankowski, W. Windsch, A. Janner and E. de Boer for many constructive criticisms and encouragements. Among them, Professor Windsch took time to read through an early version of the manuscript, and gave me valuable comments and advice; Professor Unruh kindly provided me with photographs of discommensuration patterns in K_2ZnCl_4 systems; and Dr. Jerzak helped me to obtain information regarding $(NH_4)_2SO_4$ and $RbH_3(SeO_3)_2$, and to whom I express my special gratitude. Finally I thank my wife Haruko for her continuous encouragement during my writing, without which this book could not have been completed.

"It was like a huge wall!" said a blind man.
"Oh, no! It was like a big tree." said another blind man.
"You are both wrong! It was like a large fan!" said another.
Listening to these blind people, the Lord said, "Alas! None of you have seen the elephant!"

From East-Indian Folklore.

A Remark on Bracket Notations

Somewhat unconventional bracket notations are used in this monograph. While the notations $\langle Q \rangle$ and $\langle Q \rangle_s$ generally signify the spatial average of a distributed quantity Q over a crystal, the notation $\langle Q \rangle_t$ indicates the temporal average over the timescale t_o of observation.

In Chapters 8 and 9, the *bra* and *ket* of a vector quantity v, i.e. $\langle v|$ and $|v\rangle$, respectively, are used to express the corresponding row and column matrices in three-dimensional space to fascilitate matrix calculations. Although confusing at a glance with conventional notations in quantum theory, I do not think such use of brackets is of any inconvenience for discussions in this book.

Guelph, Ontario
April 1996

M. Fujimoto

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Part II Experimental Studies

Part I

Basic Concepts

A structural phase transition can take place in a crystal when some distortion or reorientation in the *active groups* is collectively developed, which is characterized macroscopically by a change in lattice symmetry. Landau defined the *order parameter* in terms of irreducible representations of the symmetry element signifying the structural change, whereas the origin for phase transitions can be attributed to a physical change in the active group. Being considered as ordering phenomena in crystals, structural phase transitions should, in principle, be closely related to a spontaneous deformation in the lattice. We can therefore consider the interplay between active groups and their hosting lattice, which is responsible for a structural change at a specific thermodynamic condition. On the other hand, Cochran introduced the concept of soft phonons to deal with lattice stability, which was, nevertheless, deduced from two competing interactions of polar order variables in his model ionic crystal.

Although generally acceptable, there is still some confusion about these concepts when applied to structural problems as originally implied. Therefore, I have reconsidered their physical implications in practical crystals, so that critical anomalies observed by various experiments can be interpreted in terms of these interacting counterparts participating in phase transitions. It is also a significant fact that critical phenomena are so slow in timescale that observed results showed anomalies often conflicting with their thermodynamic interpretation. Generally, observed anomalies depend on the timescale of experiments, which is, nevertheless, considered as infinity in most statistical arguments based on the *ergodic* hypothesis. In reviewing thermodynamic concepts, we therefore pay specific attention to the timescale of observation, which is competitive with the characteristic time for critical fluctuations.

In Chapter 1, thermodynamic principles for isotropic media are reviewed for structural problems, whereas in Chapter 2, statistical concepts for ordering processes are reconsidered for typical order-disorder phenomena. In Chapter 3, classical *pseudospins* are proposed for binary structural transformations in crystals, where their anisotropic correlations in low dimensions are discussed for the singular behavior at transition points. The role played by soft phonons is discussed in Chapter 4, where the concept of *condensates* is introduced for the critical region, representing complexes of pseudospins and soft phonons. In Chapter 5, dynamics of condensates and their nonlinear character in the ordering process are discussed in relation to long-range order developing with decreasing temperature. The *soliton* is a promising concept for ordering processes, and hence the related mathematics is sketched in some detail, although the application to structural problems is still in its infancy at the present stage. Although constituting a recent topic of nonlinear physics, actual ordering processes are, by far, more complex than a simplified mathematical model can explain.