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RIGIDITY AND BOOLCHAND INTERMEDIATE PHASES IN NANOMATERIALS

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Editors:

M. Micoulaut
M. Popescu

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An Historical Perspective

Glasses as materials have been known for thousands of years, but it was only about a thousand years ago that glass blown for windows began to be developed. The practical applications of window glass were so valuable that it soon became second only to metals as mankind's most useful class of materials. It was not until the 20th century that polymers (plastics) appeared (1920's), followed finally by semiconductors in the 1940's.

The development of theory, which came much later, has followed a parallel chronology, except for network glasses! The theory of metals began in the 1920's and 1930's, and that of polymers in the 1930's, while the theory of semiconductors really began in the 1950's. Although Kauzmann made some stabs in the 1940's at a general theory of glasses, the special properties of network glasses were left behind, rather mysteriously, considering that window glass is so common. Of course, Kauzmann and many others (like Moynihan, who introduced the now very popular idea [even in string theory!] of energy landscapes in the 1960's) were fully aware of the importance of network glasses, but everyone faced the same problem: how to come to grips with the global problems that extended networks pose.

The present book is actually the third book in a series[1,2] that was begun in 1998 by M. F. Thorpe, a pioneer in this field who has since moved on from network glasses to proteins. Those problems are now being solved by the theoretical methods described in this book and its predecessors. These methods are largely topological; although topology was formerly a branch of mathematics largely neglected by physicists, it has recently become much more important, not only for network glasses, but also for the description of many other networks, such as the cosmic web (clusters of galaxies forming filamentary networks), social networks based on the Internet, and of course proteins and drugs. Among all these applications network glasses retain their position of importance, both as prototypical examples exhibiting systematic trends dependent on chemical bonding, and as a field rich in practical applications.

The most important development in this field since this series began is the discovery in 1999 of the Reversibility Phase by Boolchand, which is the central topic of this book. This discovery was made possible in part by theory, but theory did not predict it! As is so often the case, the fact that theorists had some new ideas stimulated experiments, which in turn surprised theory. This has led to a reconsideration of the theoretical ideas about network topology that began around 1980. While the early theory was not wrong, it is now being done much better, and quite close connections with technology are visible. This in itself is a great accomplishment, considering that for most of the last thousand years, there was no theory at all of network glasses.

The greatest problem an experimentalist, or theorist either, faces is finding a good direction at the start. This can be a problem in a field with little or no data, but as network glasses have shown, it can also be a problem in a field already mature technologically. The influence theory can have is enormous, and it need not always be beneficial (Lysenkoism was partly responsible for the failure of Soviet agriculture). Perhaps the strongest and most attractive feature of this book is the close relationship it establishes between good theory, successful practice and applications.

J. C. Phillips
Member of the National Academy of Sciences, USA

1. *Rigidity Theory and Applications*, Ed. M. F. Thorpe and P. M. Duxbury (Kluwer Academic/Plenum, New York, 1999).
2. *Phase Transitions and Self-Organization in Electronic and Molecular Networks,* Ed. J. C. Phillips and M. F. Thorpe (Kluwer Academic/Plenum, New York, 2001).

Foreword

Almost eight years ago, in June 2001, Professor Punit Boolchand communicated a report on the Intermediate Phase at the First International Workshop on Amorphous and Nanostructured Chalcogenides held in Bucharest. The paper entitled "*Discovery of the intermediate phase in chalcogenide glasses*" was published in a special issue[1] of the Journal of Optoelectronic and Advanced Materials and it was recognized by the Boris T. Kolomiets Award. In network glasses this unusual Intermediate Phase (IP) phase lies compositionally between elastically flexible and the stressed rigid phases. Its discovery has intrigued glass scientists by its special properties, some of which are: 1. The melt to glass transition is thermally reversible; 2. The apparently stress-free character of IP networks; 3. Giant photo-contraction seen in obliquely deposited amorphous thin-films. The present viewpoint is that the IP features reflect a self-organization process in its formation.

Recent observation of IPs in modified oxides and H-bonded networks, suggest that their occurrence is generic, well beyond covalent materials, to structurally disordered networks.

The IP is now often referred to as "*Boolchand phase*", and has expectedly stimulated a growing body of theoretical and experimental papers in the last few years. We believe, therefore, that a book on network rigidity generally, and the IP in particular would be timely for bringing this fascinating subject to the diverse community of glass scientists. The present issue in the series "*Optoelectronic Materials and Devices*" is a collection of contributions dealing primarily with aspects of rigidity transitions. We are spurred in this endeavor by the presently poorly understood (and sometimes magical for us) unique features of the *Boolchand phase*; and we hope that this collection fairly describes this state of understanding and will encourage new studies of it and its potential technological implications

The rigidity theory of glasses pioneered by J.C. Phillips and M.F. Thorpe offers a practical computational scheme, namely, the Maxwell constraint counting procedure, and has been central to many contemporary calculations on non-crystalline solids, particularly on chalcogenide and oxide glasses. Large challenges remain however (as discussed in this book), having to do with the need to improve the approximate mean-field procedure and to

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[1] J. Optoelectron. Adv. Mater. **3**(3), 703-720 (2001)