Dynamical Properties of Solids

Volume 4

Disordered Solids, Optical Properties

edited by

G. K. Horton A. A. Maradudin

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Preface

In this, the fourth volume of our series, two general areas of lattice dynamics are covered. Whereas the theoretical and experimental topics considered in the preceding volumes were discussed on the basis of crystalline solids, the first two contributions to the present volume, by Weaire and Taylor and by Visscher and Gubernatis, are concerned with lattice dynamical properties of noncrystalline and disordered solids, respectively. The emphasis in these chapters is on the fundamentals of this subject, as well as a survey of its present state, with the result that we expect that these two chapters will continue to be standard references to the subject matter even after it is developed further in subsequent work. Given the current interest in amorphous materials such development is inevitable.

The remaining two chapters are devoted to optical properties of crystalline solids. In a long review, Anastassakis presents the theory and existing experimental work on morphic effects on mode properties of solids, i.e. effects induced in crystals by the application of external forces such as electric and magnetic fields and uniaxial stress and hydrostatic pressure, that are not allowed by symmetry in the absence of these forces. Although not all morphic effects are directly optical effects, the overwhelming majority of the many different kinds of morphic effects that have been studied experimentally have been examined either by the experimental techniques of infrared absorption and Raman scattering, or both. This is a subject that will undoubtedly be developed further in the future for its ability to provide information about microscopic properties of crystals unobtainable by other methods.

A topic of considerable technological importance, that at the same time provides an opportunity for fundamental research activity, is infrared absorption by multiphonon processes in highly transparent solids. This subject is reviewed by Mills, Sparks and Duthler in this volume.

We wish to thank our friends from the North-Holland Publishing Company, Dr. W. H. Wimmers, Dr. P. S. H. Bolman, Dr. William Montgomery, and Mrs. J. Kuurman for their cooperation and supervision of the publishing process.

It is also a pleasure to thank Mrs. Kathryn L. Roberts for her help in the preparation of the Subject Index for this volume.

January 1980

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CHAPTER 1

Vibrational Properties of Amorphous Solids

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1. *Introduction*

It is the nature of this subject that the definitive experiment usually proves elusive. Likewise most theories are of the type which is often entitled "An approach to..." A review of inconclusive data and speculative theory would be unenlightening. For this reason, no attempt will be made to produce an exhaustive compendium of data and hypothetical models on ever more complicated systems. We shall instead focus our attention on those few simple systems for which significant understanding has been obtained.

For details not covered in this chapter and for more complete bibliographies, the reader is referred to a number of recent reviews. The vibrational properties of non-crystalline solids have been discussed by Böttger (1974). Lucovsky (1974) and Lucovsky and Galeener (1976) have treated the vibrational properties of semiconducting glasses, and both Bell (1972) and Dean (1972) have considered the oxide glasses. Råman scattering in amorphous semiconductors is the subject of reviews by Mort (1973), Brodsky (1975) and Solin (1977). Extensive collections of both Raman and infrared results on more "traditional" oxide glasses are contained in two works by Wong and Angell (1974, 1976).

The *ingenu* reader of the current literature of this subject (for whom we are presumably writing) may find himself confronted with obstacles to understanding at a disconcertingly elementary level. The very word "amorphous" means different things to different people. Even familiar words raise questions in the mind of a critical reader. Does the term "phonon" imply the existence of a $\boldsymbol{k}$-vector? What do "acoustic" and "optical" mean when applied to vibrations in an amorphous system? Confusion abounds on such matters and, if nothing else, we hope in this chapter to achieve sufficient clarity of thought and expression to dispel some of it. Hence the short glossary presented in the next section.

1.1. A glossary of dangerous words

Acoustic

Applies to the branch of the dispersion relation for which $\omega \to 0$ as $k \to 0$. Should not be applied to a non-periodic system without suitable apologies.

Amorphous

Amorphous solids are not crystalline on any significant scale, i.e. we exclude polycrystalline solids from this category. See §2.

Band

Leaving aside its looser experimental usage, this means a set of lattice vibrations associated with a single branch of the dispersion relation $\omega(k)$. In the absence of periodicity it cannot be used in this or any other precise sense, except in those cases where there are ranges of frequency where the density of vibrational states is non-zero, separating discrete bands.

Disordered

Amorphous solids are a subset of disordered solids. Crystalline solids in which there is substitutional or compositional randomness are termed disordered, but not amorphous.

Glassy / Vitreous

Those amorphous solids which can be prepared by cooling from the liquid state are commonly called glassy or vitreous. Unfortunately this distinction is not always adhered to in the literature.

Lattice

Strictly speaking, a lattice ought to be periodic but the loose application of this word to any infinite three-dimensional structure associated with condensed matter is a relatively harmless indulgence.

Lattice vibration

In keeping with the above, we take this to mean a vibrational normal mode of an infinite three-dimensional structure.

Longitudinal, transverse

Refers to the relative orientation of polarisation vector and k-vector. In the absence of either, these terms are doubly devoid of meaning in a non-periodic system, except in the extreme low frequency regime.

Optic

Not *acoustic*. The same caveat applies in general although the existence of a discrete range of vibrational frequencies might provide some justification for the use of the term in a few cases.

Phonon

Quantised lattice vibration. We take the view, denied at least implicitly by some, that periodicity of the structure is not essential to the use of this term.

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2. *Theoretical background*

2.1. Introduction

We first consider in §§2.2 and 2.3 the two ingredients of the dynamical matrix, *structure* and *force constants*. At the present stage, only the crudest of force constant schemes are commonly applied to amorphous solids, and it seems better to review these quickly than to refer to detailed accounts elsewhere in this series.

Given both structure and forces, how is one to predict vibrational properties? The remaining sections, §§2.4–2.10, are addressed to this question and the variety of answers so far advanced.

2.2. Structure

Vibrational spectroscopy has often been presented as a probe of structure, capable of revealing the form of local atomic arrangements in cases, such as that of an amorphous solid, in which X-ray diffraction gives only limited information. It is a point of view which has probably been overemphasised and somewhat fanciful interpretations of data have sometimes been made in attempts to justify it! A major question of interest has been – *do amorphous solids have microcrystalline or continuous random structures*?

Some indication of the meaning of this question may be provided by fig. 1. The weight of evidence has in most cases come to rest on the side of

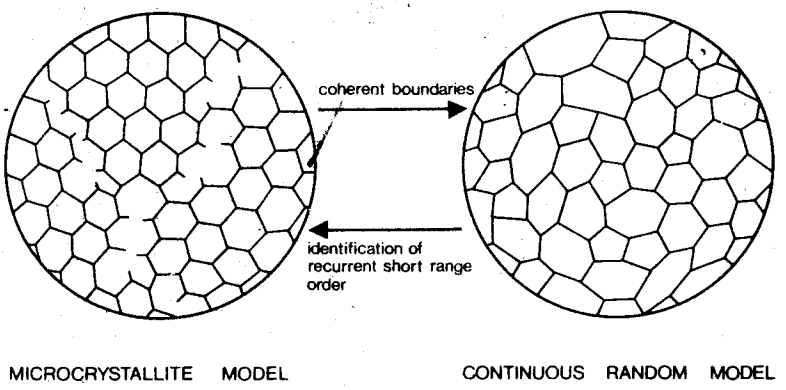

Fig. 1. Schematic diagrams of the local topology in the microcrystallite model (left) and the continuous random network model (right).

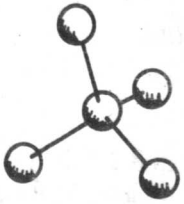

Fig. 2. Local bonding arrangement in Group IV amorphous solids where each atom has four nearest neighbours in a tetrahedral configuration.

the continous random picture, which is generally attributed to Zachariasen (1932).

In considering the details of the continuous random model, it is necessary to distinguish covalently and metallically bonded solids. In the former case it takes the form of a *random network* of nearest-neighbour bonds. For example, the random network model of amorphous Si each atom has four nearest neighbours in a tetrahedral configuration (fig. 2). It is difficult to

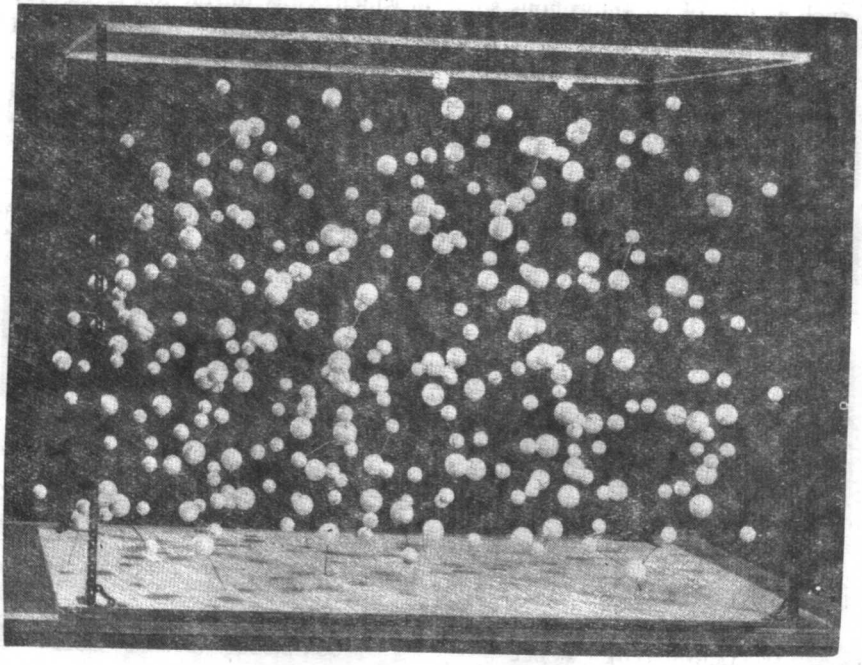

Fig. 3. Random network model of glassy SiO_2 (large spheres represent Si atoms) where the silicon atoms are tetrahedrally coordinated and the oxygen atoms are two-fold coordinated. (Photograph courtesy of Bell and Dean 1972; Crown Copyright.)

convey the nature of this model descriptively. Interested readers are strongly recommended to build one themselves! In doing so, they will be struck by the ease with which such networks can be built for sufficiently low coordination numbers. One does not need to contrive to meet the local bonding requirements by foresight or repeated building. A celebrated handbuilt model is shown in fig. 3.

Ultimately, any particular random network model should be specified by a table of coordinates. Statistical measures of structure, such as the radial distribution function, cannot uniquely specify the model. They are, of course, useful in any attempt to analyse its properties. Ring statistics, in particular, have a peculiar fascination for many people and much emphasis has been laid on them in characterising particular models.

As for amorphous metals, these are now considered to conform rather well to the Bernal model (Bernal and Mason 1960), which is the dense random packing of hard spheres. Here we cannot uniquely define nearest-neighbour shells.

2.3. Force constants

In the course of internecine disputes on the finest details of the dispersion relations of crystalline solids, the wood is often obscured by the trees. Let us therefore state emphatically that *the broad features of the vibrational spectrum of most solids are dominated by nearest-neighbour central forces.* For qualitative purposes, it is therefore forgivable to contemplate the very simple *central force* expression for the potential energy associated with atom displacements u_i,

$$V = \frac{1}{2} \sum_{\substack{ij \\ \text{neighbours}}} \alpha_{ij}\left[(\boldsymbol{u}_i - \boldsymbol{u}_j)\cdot \boldsymbol{r}_{ij}\right]^2. \tag{2.1}$$

Here α_{ij} is the force constant associated with the atoms i and j, often taken (in an elemental amorphous solid) to be equal for all nearest-neighbour pairs ij. The vector $\boldsymbol{r}_{ij}$ connects the equilibrium positions of atoms i and j. Different classes of solid part company when we attempt to improve upon (2.1). For *metals*, longer-range central forces with an oscillatory dependence on range may be incorporated and can in a few instances be calculated from first principles (Heine and Weaire 1970). For covalently bonded solids, semi-empirical schemes are used to incorporate short-range *non-central forces*. Thus, in the simplest (axially symmetric) *Born model*, we add to (2.1) a term of the form

$$\sum_{\substack{ij \\ \text{neighbours}}} \beta_{ij}(\boldsymbol{u}_i - \boldsymbol{u}_j)^2, \tag{2.2}$$

where again β_{ij} might be taken to be equal for all nearest-neighbour pairs ij. This may be called a *bond bending* term, as contrasted with the *bond stretching* term (2.1). The above form is quite satisfactory for many purposes but entails difficulties associated with rotational invariance. This complication may be avoided entirely by using forces which are derived from an *ad hoc* expression for the potential energy (as a function of atom positions) which is *manifestly* rotationally invariant. Following Keating (1966), we may choose to write an expression quadratic in the change of the scalar products of nearest-neighbour bond vectors from their equilibrium values. This, when expanded in terms of displacements, gives for each pair of nearest neighbours a term proportional to

$$\sum_{i\Delta\Delta'} [(\boldsymbol{u}_i - \boldsymbol{u}_{l\Delta})\cdot\boldsymbol{r}_{\Delta'}(l) + (\boldsymbol{u}_i - \boldsymbol{u}_{l\Delta'})\cdot\boldsymbol{r}_{\Delta}(l)]^2. \tag{2.3}$$

Finally, the valence force field model deals with lengths and angles rather than scalar products. Martin (1970) argues persuasively in support of the superiority of the Keating model, at least for Group IV semiconductors, but it is for our purposes a marginal consideration.

Semi-empirical models of such simplicity are rather *passé* in the context of crystalline systems. Much more elaborate schemes have been developed, involving a multiplicity of disposable parameters, although these have in turn been replaced by *shell models* which yield similar results with less extravagant use of adjusted force constants. This is achieved by the use of extra degrees of freedom representing, in a crude classical sense, valence electrons. For Group IV semiconductors Weber's *bond charge model* (1974), which is in the same spirit but uses bond charges rather than atom-centred shells, is the latest and perhaps ultimate refinement of this empirical tradition. For crystalline Si and Ge, it leaves few mysteries unveiled.

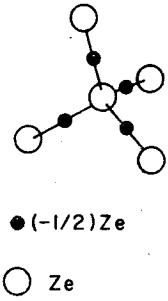

Fig. 4. Schematic representation of the bond charge model as applied to Group IV amorphous semiconductors.

Fig. 4 illustrates the general nature of this model. Recently it has been applied to amorphous Group IV semiconductors by Meek (1977), as described in §4.2.

Finally, highly ionic solids can only be reasonably described by a model which includes long-range coulomb forces between ions. This is elementary in principle but in practice it has been difficult to analyse the effects of such forces in an amorphous solid.

2.4. The problem

How can we analyse the vibrational properties of a given random network model? In discussing this question we shall concentrate for the moment on the phonon density of states $n(\omega)$, which we define to be the density (as a function of frequency) of vibrational normal modes.

In the study of *crystals* this may be obtained by integration of $\boldsymbol{k}$-space, once the dispersion relations $\omega(\boldsymbol{k})$ have been determined. The latter may be calculated by the diagonalisation of a secular matrix of dimensions $3n \times 3n$, where n is the number of atoms per unit cell.

In a disordered system, the absence of periodicity implies that Bloch's theorem is not applicable, and we are confronted with the necessity of using a much larger secular matrix. Strictly (and somewhat absurdly), it may be said that the dynamical matrix must have dimensions dictated by the number of atoms in an experimental sample, but clearly a much more reasonable number (10^2?, 10^3?) should give results characteristic of an infinite sample, for most purposes. Just how many atoms constitute an effectively infinite sample, in this case, depends in part on the *boundary conditions* used. In some early work in this field (Dean 1972, Bell 1972) atoms were either fixed or left free on the surface of a chosen random network cluster. The surface/volume ratio is rarely small enough for this to be done without the introduction of spurious features arising from the surface. Apart from some special methods in which boundary conditions are not relevant, we must therefore ensure that the boundary conditions are such as to minimise surface features and/or make a projection of the *local* density of states at the centre of the cluster. Suitable boundary conditions include the *periodic* case (which entails a somewhat demanding model-building exercise, rarely executed satisfactorily!) or the use of effective fields (§2.8).

We thus envisage a calculation of the eigenvalues of a dynamical matrix of dimension 10^2 or more. This is feasible (up to about 10^3 or so), by any one of a number of methods, direct or indirect, to be reviewed in the sections which follow.

What are the limitations of such an approach?

Firstly, calculations for any finite sample of practical size cannot tell us anything about the low-frequency (Debye) regime.

Brute force cannot, of itself, give much qualitative insight, and must therefore be supplemented by more simplistic *ad hoc* models which are analytically tractable and can be tested against it.

Numerical methods can also be expensive, although objections on such grounds are often hypocritical, since it is not exactly cheap to employ theorists chewing pencils in a search for more elegant approaches!

Attempts to devise simpler models fall into various categories. Firstly there are those that are based on an analysis of the normal modes of molecules representative of the local groupings of atoms in the solid. Secondly there are calculations for *pseudo*-lattices, which have tree-like branching structures, and have the advantage of providing analytically soluble models. Thirdly, one may attempt to use calculations for *crystals* as a basis for predicting the properties of an amorphous solid, usually by considering the effects of random local distortions. This last approach is often given a formal basis by means of the "Gubanov transformation" by which atoms of a crystal are placed in 1 : 1 correspondence with those of an amorphous solid. No amount of formal labelling and mathematical window-dressing can make this more than an empty gesture, in our opinion.

There have also been studies (both experimental and theoretical) of crystalline polymorphs with large unit cells with a view to providing a "half-way house" between the simplicity of such crystal structures as diamond cubic and the complexity of the random network.

All of these methods take liberties with the *structure*. Sometimes one can simplify the form of the vibrational Hamiltonian instead, discarding, for example, all but the nearest-neighbour central forces. One may thus arrive at a model for which analytic proofs of exact results are available, providing a skeletal framework for understanding the main features of more realistic calculations.

Finally, the low-frequency regime (§5) requires special arguments based on the continuum approximation and the consideration of the possibility of "tunnelling modes". This remains the least satisfactory area of theory.

2.5. Diagonalisation

It would hardly be appropriate to devote much space here to a discussion of methods of finding eigenvalues, but it does deserve some attention, if only to indicate that considerable progress is still being made in this field.

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