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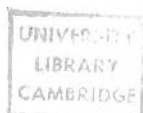
VIBRATIONS IN ELEMENTAL AMORPHOUS SEMICONDUCTORS

by

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In this thesis calculations of the vibrational spectra appropriate to structural models of the elemental amorphous semiconductors a-Ge, a-As and a-Se are presented. Simple dynamical models, involving restoring forces for bond length and angle variations only, provide information on the structure-dependence of the vibrational spectra and hence on the typical structures of the real materials. Calculations are presented for four-fold coordinated continuous random network (CRN) models of a-Ge, for a three-fold coordinated CRN model of a-As and for isolated- and interacting-chain models of a-Se.

In order to obtain a more realistic description of the structure and vibrational and electronic behaviour of a-Ge, calculations of the vibrational and electronic spectra of a series of seven CRN models are presented. The results show that the form of the vibrational spectrum is determined by the angular distortions whereas the form of the electronic spectrum is determined by the topology of the corresponding network. The vibrational spectra calculated using the more realistic dynamical model for a-Ge are also significantly different to those obtained previously using simple bond stretching and bending forces only. The results are discussed in relation to the structure of a-Ge and amorphous III-V compounds such as a-GaAs, the existence of an 'excess specific heat' at low temperatures in amorphous semiconductors, the applicability of such calculations to other systems and the modifications of the method for the calculation of infra-red and Raman spectra appropriate to the structural models.

Simple force constant models, of the type applied to the elemental

amorphous semiconductors, are also used to identify the forces chiefly responsible for the observed optical phonon anisotropies in the tin dichalcogenide layer compounds SnS_2 and SnSe_2 .

PREFACE

The research described in this dissertation was carried out in the Cavendish Laboratory between October 1974 and April 1977. This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration. When cited, the work of others is duly referenced. Neither this thesis nor a substantial part of it has been or is being submitted to any other university.

I am grateful to my supervisor Professor V Heine for his guidance over the past three years and to the Science Research Council for financial support. I have benefitted greatly from conversations with many members of the Cavendish Laboratory, particularly Dr E A Davis, Mr S R Elliot, Dr R Haydock, Mr C M M Nex, Dr W A Phillips, Dr J Robertson and Mr R D Turner. Thanks is also due to those people who were kind enough to send details of their work to me before and after publication, particularly those who supplied the coordinates of their structural models. I am also grateful to the University of Cambridge Computing Service for the use of their excellent facilities.

Much of the work presented in this thesis has been published. The references are;

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1.1 AMORPHOUS SEMICONDUCTORS

Amorphous semiconductors are a subset of those materials which are distinguished from their crystalline counterparts by structural disorder. Our particular interest in the vibrational, structural and electronic properties of elemental amorphous semiconductors is stimulated by their relative structural and compositional simplicity. They provide a convenient starting point for a detailed study of disordered solids in general. Amorphous germanium (a-Ge) is the prototype amorphous semiconductor and, along with a-As and a-Se, forms the main subject matter of this thesis. An excellent review of the tetrahedrally bonded amorphous semiconductors, describing the understanding at the time our work began, has been given by Connell (1975). We begin this thesis with an introduction to the properties of a-Ge and our methods of calculating vibrational and electronic spectra appropriate to such disordered solids.

The structural information obtained from X-ray scattering data on elemental disordered solids is the radial distribution function (RDF), the probability of finding an atom at a given distance from any other. The RDF's of sputtered and electrodeposited a-Ge obtained by Shevchik and Paul (1972) are shown in Figure 1.1. The differences between the curves arise from the different concentrations of voids in samples prepared by different techniques. For computational purposes, we consider an idealised fully-annealed amorphous phase in the same way that we consider perfect crystals without defects or impurities in calculations for the crystalline phase.

The structure of crystalline Ge (c-Ge) is diamond-cubic, as shown in Figure 1.2. Each atom is covalently bonded to four first neighbours with all bond angles at $109^{\circ} 28'$. Analysis of the RDF's of

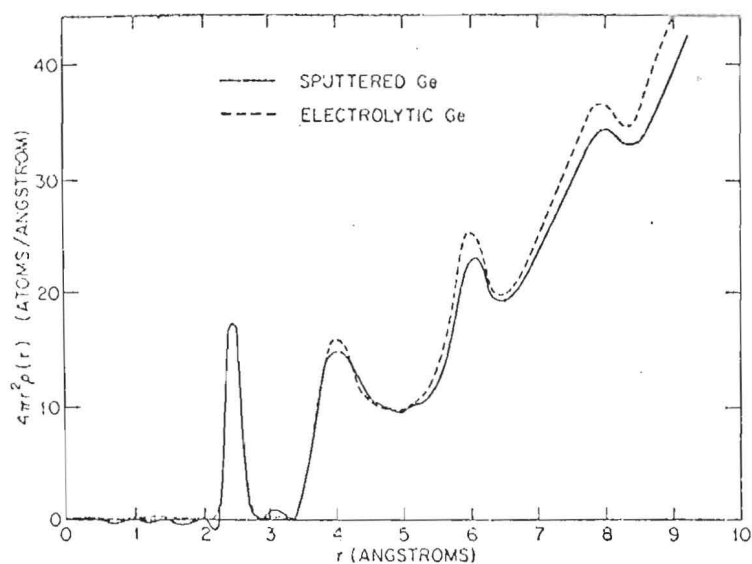


Figure 1.1 RDF's of sputtered and electrodeposited a-Ge (after Shevchik and Paul 1972).

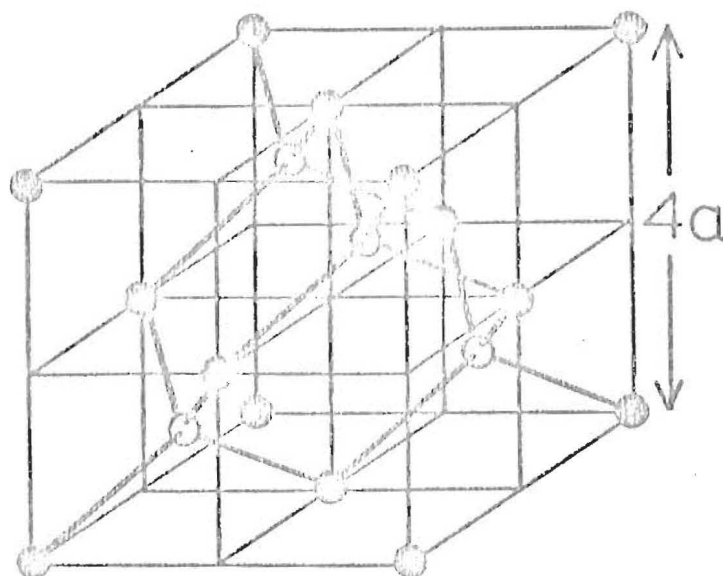


Figure 1.2 The diamond-cubic structure of c-Ge; open and filled circles denote atoms on different sublattices.



Figure 1.3 Staggered and eclipsed configurations of second neighbour bonds in four-fold coordinated systems.

Figure 1.1 shows that four-fold coordination is preserved in a-Ge (from the area under the first peak) with a negligible distribution of bond lengths but an rms bond angle distortion of about 10° . There is no peak at the crystalline third neighbour distance. Thus the atomic tetrahedra are preserved but interconnected such that the relative rotations about the common bonds vary between the staggered (dihedral angle $\phi=60^\circ$) and eclipsed ($\phi=0^\circ$) configurations of Figure 1.3. Since the RDF is a one-dimensional representation of a three-dimensional structure, the dihedral angle distribution and ring statistics cannot be uniquely deduced from it. Temkin (1974a) has shown that the presence of anywhere between 0.0 and 0.5 five-membered rings per atom (depending on the dihedral angle distribution) can be consistent with the experimental RDF.

In order to establish the typical structure of a-Ge beyond second neighbours, ball-and-stick models have been constructed based on both microcrystallites and continuous random networks (CRN's). The debate over which best models a-Ge has been decided in favour of the CRN principally by the type of argument presented by Connell (1975). He compared the experimental X-ray diffraction interference function with those appropriate to both model types, showing the very poor agreement obtained with microcrystallite models in comparison to that found with CRN's.

Polk (1971) was the first to construct a CRN model of a-Ge showing that all bonds can be satisfied without incurring a volume-dependent elastic strain energy due to bond length and angle distortions. Since then many more have been constructed, by hand and by computer, incorporating varying numbers of 5-, 6- and 7-membered rings. One of the most interesting is that due to Connell and Temkin (1974) which was constructed to model amorphous III-V and II-VI compounds and

contains only even-membered rings of bonds. The presence of odd-rings would lead to the formation of 'wrong bonds', contrary to the experimental data of Shevchik, Tejeda and Cardona (1974) - see Chapter 6. Temkin (1974b) has argued that small differences in the RDF's of a-Ge and a-GaAs can be interpreted as implying a significant number of odd-rings in the former and a negligible number in the latter. These ideas will be discussed further in succeeding chapters.

Having discussed the structure of the prototypical amorphous semiconductor a-Ge, we now go on to describe our methods of calculating vibrational and electronic spectra in both ordered and disordered systems. Although we can no longer consider phonon frequencies and electron energies as functions of wave-vector, the densities of vibrational and electronic states remain well-defined quantities in disordered systems. The aims of our work are summarised in the final part of this chapter and a plan of the thesis is outlined.

1.2 VIBRATIONAL CALCULATIONS

To calculate the normal modes of vibration of an infinite crystal of rigid atoms in the harmonic approximation, the interatomic force constants are obtained from the second derivative of an appropriate potential. Thus if l, κ and α denote unit cell, basis atom and cartesian coordinate respectively, the force constants are

$$\Phi_{\alpha\alpha'}(l\kappa, l'\kappa') = \frac{\partial^2 V}{\partial u_{\alpha}(l\kappa) \partial u_{\alpha'}(l'\kappa')} \quad (1.2.1a)$$

The 'self' force constant terms can be calculated from the sum-rule

$$\sum_{l'\kappa'} \Phi_{\alpha\alpha'}(l\kappa, l'\kappa') = 0 \quad (1.2.1b)$$

which is a consequence of invariance of the forces under a rigid lattice translation and ensures the existence of three zero-frequency modes at zero wave-vector. The equations of motion of the atoms are

$$m_{\kappa} \frac{\partial^2 u_{\alpha}(l\kappa)}{\partial t^2} = - \sum_{l'\kappa'\alpha'} \Phi_{\alpha\alpha'}(l\kappa, l'\kappa') u_{\alpha'}(l'\kappa') \quad (1.2.2)$$

where m_{κ} denotes atom mass. Considering a solution of wavevector $\underline{k}$ and amplitude $\underline{U}(\kappa, \underline{k})$, i.e.,

$$u_{\alpha}(l\kappa) = \frac{1}{\sqrt{m_{\kappa}}} U_{\alpha}(\kappa, \underline{k}) \exp \left[i \left(\underline{k} \cdot \underline{x}(l) - \omega(\underline{k})t \right) \right] \quad (1.2.3)$$

where $\underline{x}(l)$ denotes cell position, produces the system of equations

$$\omega^2(\underline{k}) U_{\alpha}(\kappa, \underline{k}) = \sum_{\kappa'\alpha'} D_{\alpha\alpha'}(\kappa\kappa'; \underline{k}) U_{\alpha'}(\kappa', \underline{k}) \quad (1.2.4)$$

where the Fourier transformed dynamical matrix $\underline{D}$ is given by

$$D_{\alpha\alpha'}(\kappa\kappa'; \underline{k}) = \frac{1}{(m_{\kappa} m_{\kappa'})^{1/2}} \sum_{l'} \Phi_{\alpha\alpha'}(l\kappa, l'\kappa') \exp \left[i \underline{k} \cdot (\underline{x}(l') - \underline{x}(l)) \right] \quad (1.2.5)$$

Thus the (squared) atomic vibration frequencies for a chosen wavevector are the roots of the $3n \times 3n$ secular equation

$$\det \left| \underline{\underline{D}}(\underline{k}) - \omega^2(\underline{k}) \underline{\underline{I}} \right| = 0 \quad (1.2.6)$$

where n is the number of basis atoms and $\underline{\underline{I}}$ is the unit matrix. The eigenvectors of $\underline{\underline{D}}$ are the mass-normalised amplitudes of vibration of the basis atoms in each cell of the crystal. A comprehensive discussion of this and many other aspects of the lattice dynamics of crystals has been given by Maradudin, Montroll, Weiss and Ipatova (1971).

For c-Ge with a basis of two atoms, such a calculation would involve the diagonalisation of a 6×6 matrix for each $\underline{k}$ -point to obtain dispersion curves and, by integration over the FCC Brillouin zone, a vibrational spectrum $N(\omega)$ - see Chapter 2. On the other hand a calculation for a CRN with no long-range order would involve a $3n \times 3n$ matrix where n is now the total number of atoms - typically 200-500. Clearly the lack of periodicity renders the machinery of the reciprocal space technique inapplicable.

In the next section we outline how electronic energy level calculations reduce to the same problem of solving a secular equation.

1.3 TIGHT-BINDING ELECTRONIC STRUCTURE CALCULATIONS

Tight-binding calculations of the electronic structure of semiconductors such as c-Ge have proved to be both simple and illustrative (see for example Weaire, Thorpe and Heine 1972). We solve the Schrodinger equation

$$\hat{H} \psi = E \psi \quad (1.3.1)$$

for the one-electron energy levels E and wavefunctions ψ of the solid by writing the potential part of the one-electron Hamiltonian operator $\hat{H}$ as the sum of atomic potentials at the sites $\underline{r}_i$. For electrons localised near atomic sites, the wavefunction ψ is well represented by a linear combination of atomic orbitals $\phi(\underline{r}_i)$ (LCAO). For a periodic system we use Bloch's theorem and write

$$\psi_{\underline{k}}(\underline{r}) = \sum_{i\alpha} e^{i\underline{k} \cdot \underline{r}_i} a_{i\alpha}(\underline{k}) \phi_{\alpha}(\underline{r} - \underline{r}_i) \quad (1.3.2)$$

where $\underline{k}$ is the electron wavevector and α distinguishes orbitals at site i . We make the following approximations which reasonably follow for localised orbitals;

A. The matrix elements

$$\langle \phi_{\alpha}(\underline{r} - \underline{r}_i) | V(\underline{r} - \underline{r}_k) | \phi_{\beta}(\underline{r} - \underline{r}_j) \rangle$$

are all zero except when $k=i$ or $k=j$ (the two-centre approximation) and i and j are near-neighbours.

B. Overlaps between orbitals on different sites are negligible and orbitals on the same site are orthogonal i.e.

$$\langle \phi_{\alpha}(\underline{r} - \underline{r}_i) | \phi_{\beta}(\underline{r} - \underline{r}_j) \rangle = \delta_{\alpha\beta} \delta_{ij}$$

C. The $\phi_{\alpha}(\underline{r})$ are approximate eigenfunctions of the atomic-like

Hamiltonian with eigenvalues E_α .

Thus the eigenenergies $E(\underline{k})$ are the roots of the secular equation

$$\det \left| \underline{H}(\underline{k}) - E(\underline{k}) \underline{I} \right| = 0 \quad (1.3.3)$$

The elements of the Hamiltonian matrix are given by

$$H_{\alpha, j \beta}(\underline{k}) = \sum_{j \beta} e^{i \underline{k} \cdot (\underline{r}_j - \underline{r}_i)} E_{\alpha \beta}(\underline{r}_j - \underline{r}_i) \quad (1.3.4)$$

where the hopping integrals are

$$E_{\alpha \beta}(\underline{r}') = \int \phi_\alpha(\underline{r}) V(\underline{r} - \underline{r}') \phi_\beta(\underline{r}') d\underline{r}$$

and the 'diagonal elements' are atomic energy levels, i.e.

$$E_{\alpha \alpha} = E_\alpha$$

The matrix elements are often parameterised but can also be calculated from first principles - see Chapter 6. Because of the extended nature of conduction states in semiconductors, the tight-binding method gives poor results for them. On the other hand, the more localised valence states are reproduced rather well as shown for a very simple such model by Weaire et al.

For c-Ge or c-GaAs choosing a basis of bonding orbitals leads to the consideration of a 4x4 matrix at each $\underline{k}$ -point, since there are only four such orbitals per unit cell (see Chapter 6). For a CRN however the matrix swells to nxn where n is the number of bonds in the network. The calculation is therefore parallel to that for the vibrational excitations of such a system. Our method of solving this particular eigenvalue problem is dealt with in the following section.

1.4 THE RECURSION METHOD

In this section we outline how we can calculate the density of vibrational (or electronic) states appropriate to a bulk amorphous solid given only the coordinates of a cluster of a few hundred atoms. Lack of periodicity means we cannot make use of reciprocal space techniques. Nor is it satisfactory just to calculate the distribution of states for the whole cluster; with only 200-500 atoms, most lie on or near the surface and would therefore give states completely untypical of the bulk solid.

The philosophy of the solution to this dilemma is that the vibrational behaviour of an atom in a system where only short-range interactions are important is determined by the local environment. It is relatively insensitive to the effects of more distant boundary conditions, as illustrated by Kelly and Bullett (1976a) for the electronic case. This phenomenon is apparent in other areas of solid-state physics, perhaps most notably the electronic structure of alloys (see Heine and Weaire 1970 and references therein). The vibrational behaviour is expressed in terms of the local density of vibrational states (DOVS) at a chosen atom i.e. the density of states of the whole cluster weighted by the amplitude squared of each mode at the atom considered. This quantity is related to the Green function which by its very nature is more sensitive to the local environment than distant boundary conditions (see Inglesfield 1972 and Kittel 1967). The local DOVS for several sites near the centre of the cluster are averaged to obtain a DOVS characteristic of the bulk solid. The results presented in subsequent chapters show that averages over five and ten central sites are almost identical, precluding further averaging. This also provides evidence that our results are not determined by special local features of the clusters used.

The partial local DOVS projected onto the displacement of atom i in direction α is evaluated from the identity

$$n_{i\alpha}(\omega^2) = -\frac{1}{\pi} \lim_{\delta \rightarrow 0^+} \text{Im} \left[G_{i\alpha, i\alpha}(\omega^2 + i\delta) \right] \quad (1.4.1)$$

where $G_{i\alpha, i\alpha}$ denotes the diagonal matrix element of the resolvent operator $[\underline{D} - \omega^2 \underline{I}]^{-1}$; i.e.

$$G_{i\alpha, i\alpha}(\omega^2) = \langle i\alpha | [\underline{D} - \omega^2 \underline{I}]^{-1} | i\alpha \rangle \quad (1.4.2)$$

(see Heine and Weaire 1970). The total local DOVS is obtained from the relation

$$n_i(\omega^2) = \sum_{\alpha} n_{i\alpha}(\omega^2) \quad (1.4.3)$$

and the averaged DOVS as a function of frequency is

$$N(\omega) = \frac{2\omega}{S} \sum_i^S n_i(\omega^2) \quad (1.4.4)$$

for S sites.

To evaluate the partial local DOVS $n_{i\alpha}(\omega^2)$ of equation 1.4.1 we employ the Recursion method of Haydock, Heine and Kelly (1972, 1975). A continued fraction expansion is obtained by the recursive definition of a new basis of orthogonal vectors $|n\rangle$ thus,

$$b_{n+1} |n+1\rangle = (\underline{D} - a_n \underline{I}) |n\rangle - b_n^* |n-1\rangle \quad (1.4.5)$$

with the initial conditions $|0\rangle = |i\alpha\rangle$, $|-1\rangle = 0$, $b_{-1} = 0$, $b_0 = 1$. Once in this tridiagonal form, $G_{i\alpha, i\alpha}(\omega^2)$ is expanded analytically to

obtain an infinite continued fraction;

$$G_{ia,ia}(\omega^2) = \frac{b_0}{\omega^2 - a_0 - \frac{|b_1|^2}{\omega^2 - a_1 - \frac{|b_2|^2}{\omega^2 - a_2 - \dots}}} \quad (1.4.6)$$

The (a_n, b_n) are evaluated from the orthonormality property of the new basis. Computationally, once the blocked, sparse matrix $\underline{D}$ is evaluated and stored, the calculation is very economical since only three vectors are involved in the recursion algorithm (equation 1.4.5) at any time.

Having calculated a finite number of coefficients, the partial local DOVS of equation 1.4.1 is evaluated by a numerical method due to Nex (1975). The (a_n, b_n) of 1.4.6 also define the power moments of $n_{ia}(\omega^2)$ and the recurrence relation for a set of polynomials orthogonal with respect to $n_{ia}(\omega^2)$. Hence rigorous bounds on integrals of the type

$$\int_{-\infty}^{\lambda} f(\lambda') n(\lambda') d\lambda'$$

can be obtained by the method of Gaussian Quadrature with one node fixed at $\lambda' = \lambda$ as shown by Akhiezer (1965). If $f(\lambda')$ is a step function, rigorous bounds on the integrated DOVS are obtained. Taking the mean of the bounds and differentiating analytically or numerically produces a smooth DOVS with a minimum of spurious oscillations. Nex's work has also provided a numerical technique for performing the sums of 1.4.3 and 1.4.4. Recalling that the set (a_n, b_n) also defines the power moments of $n_{ia}(\omega^2)$, the method can be viewed as deriving the moments for each set, summing them and then converting back to a set representing the resultant moments. Note that the final continued fraction has the

same number of levels as each of the original sets.

Calculating M levels of the continued fraction corresponds to evaluating the effect of M successive neighbour environments on the behaviour of the chosen atom (Haydock et al 1972). Since a finite cluster defines a limited number of such environments, we might expect spurious cluster-size effects in our results for large M , depending on the size of cluster used. This phenomenon is observed in our results, so each application of the method is considered on its own merits in the following chapters. In general, results obtained for larger M values in a given cluster reveal greater resolution of spectral features. Free-atom boundary conditions are used in all applications.

Note that the whole of the above argument applies to electronic structure calculations by virtue of the equivalence of the vibrational and electronic secular equations 1.2.6 and 1.3.3. The suitability of the Recursion method for these two problems hinges on the overriding importance of short-range interactions in determining the vibrational and electronic behaviour in crystalline and amorphous semiconductors.

In succeeding chapters the Recursion method is used to calculate vibrational and electronic spectra appropriate to disordered solids. In all cases the computation has the same fundamental form, a flow-chart of which is presented in Appendix 1.4. The computation times involved are proportional to the size of cluster, the number of partial densities calculated and the length of the continued fraction expansions.

1.5 PLAN OF THESIS

Having presented a background to the subject matter of this thesis, we now outline the aims of our work.

In general we wanted to evaluate the effects of structural disorder on the vibrational behaviour of elemental amorphous semiconductors by the consideration of simple dynamical models. This motivated the work presented in Chapters 2, 3 and 4, which deal with a-Ge, a-As and a-Se respectively. More specifically, we worked towards a definitive description of the behaviour of a-Ge using a very realistic dynamical model. The results indicate how the structure and vibrational and electronic properties are linked. Chapters 5 and 6 respectively deal with the vibrational and electronic properties of a-Ge within very realistic frameworks.

Throughout our work we have tried to interpret as much experimental data as possible. Chapter 7 shows how by applying a simple dynamical model of the type used for the amorphous semiconductors to the layer compounds SnS_2 and SnSe_2 we can deduce which interatomic forces are chiefly responsible for the experimentally observed anisotropies in the optically-active zone-centre modes of these crystals.

Finally, in Chapter 8 we review the successes and failures of our approach and suggest areas for further study.

2.1 INTRODUCTION

The aim of this chapter is to present the results of calculations of the vibrational spectra of three CRN models of a-Ge using the simplest dynamical model that gives a reasonable description of the phonon dispersion in c-Ge. The results show how the DOVS are modified by both topological disorder and bond-angle distortions. Interpreting them in the light of available experimental data provides information on the structural characteristics of a-Ge and a-GaAs.

Previous theoretical work by Weaire and Alben (1972) has established that the experimentally observed similarity of the DOVS for a-Ge and c-Ge arises from the preservation of short-range order in the amorphous phase. No direct measurement of the full spectrum has yet been reported, however indirect measurements of the DOVS of both a-Si and a-Ge, such as Raman and infra-red (IR) spectroscopy, reveal three features at frequencies corresponding to the transverse acoustic (TA), longitudinal acoustic and optic (LA+LO) and transverse optic (TO) regions of the crystalline spectra (for a review see Alben, Weaire, Smith and Brodsky 1975). The Raman and IR data for a-Si and a-Ge are shown in Figure 2.1 where they are compared with broadened crystalline spectra to illustrate the similarity. Weaire and Alben considered the DOVS of a tetrahedrally coordinated homopolar solid of atom mass m with a nearest neighbour bond stretching force α only. They showed that $n(\omega^2)$ consists of δ -functions at zero and $(8\alpha/m)$ and a band between them given by a tight-binding electronic s-state Hamiltonian, as illustrated in Figure 2.2b. Only the latter part depends on the ring statistics of the system. Each feature contains one state per atom, the δ -functions corresponding to flat TA and TO bands. Distortions from perfect tetrahedral symmetry

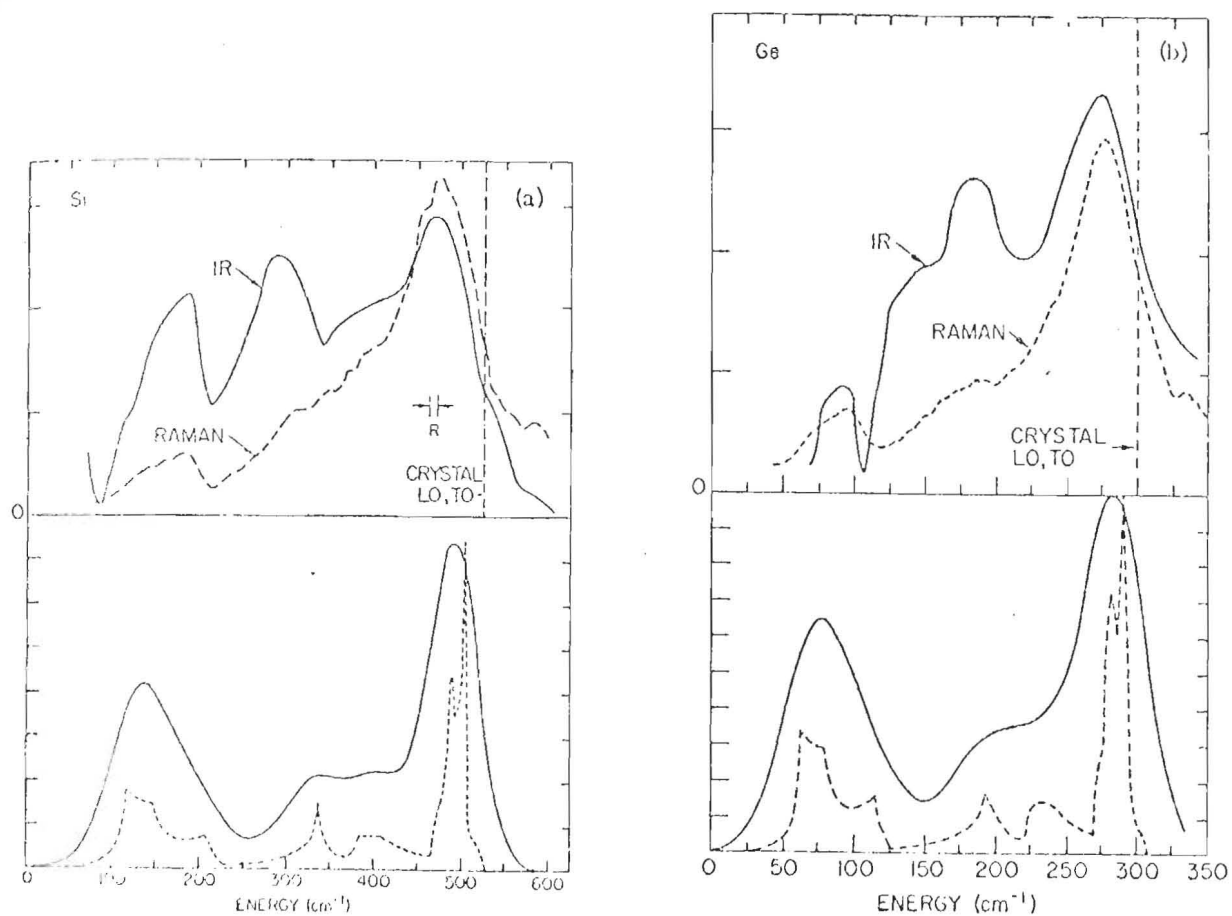


Figure 2.1 Experimental IR and Raman spectra of a-Si and a-Ge (after Alben et al 1975). In each case the experimental curves are compared with broadened crystalline phonon spectra to illustrate the similarities.

broaden the upper δ -function only; including bond-bending forces broadens both, the lower moving to higher frequency, as shown in Figure 2.2c. To see how the lower δ -function remains in the absence of perfect tetrahedral coordination, note that demanding bond lengths to be constant (giving a zero-frequency mode) places $2N$ constraints (there are two bonds per atom) on $3N$ degrees of freedom; thus there are always $3N-2N=N$ such modes i.e. one per atom. We would expect the upper δ -function to be broadened by angular distortions since the forces acting on each atom due to its nearest neighbours will have varying orientations in a CRN whereas they are always parallel in a perfect crystal. From Weaire and Alben's work, therefore, we expect angular distortions to broaden the TO feature of c-Ge and the effects of topological disorder to be evident in the LA+LO region, by virtue of its correspondence to the electronic s-band.

The CRN models used in the calculations all give good agreement with the experimental RDF of a-Ge. Some relevant structural characteristics are summarised in Table 2.1; The models are as follows.

- A. The 'Steinhardt' model (Steinhardt, Alben and Weaire 1974) contains both odd- and even-membered rings of bonds and has been energy relaxed to minimise the elastic strain in distorted bond lengths and angles, using Keating's (1966) strain energy expression.
- B. The 'Connell-Temkin' model (Connell and Temkin 1974), containing only even rings, was constructed to simulate a plausible structure of amorphous III-V and II-VI compounds, as discussed in Section 1.1. This model is not energy relaxed but the bond lengths are all constrained to lie within limits appropriate to a-Ge.
- C. The 'Polk' model (Duffy, Boudreaux and Polk 1974) has very similar structural characteristics to the Steinhardt model and has been similarly relaxed.

CRN	Number of atoms	$\frac{\Delta r_1}{r_1}$	$\Delta\theta$ (degrees)	Rings per atom		
				5	6	7
Steinhardt	201	0.008	6.66	0.39	0.89	1.05
Connell-Temkin	238	~ 0.010	10.71	0	2.30	0
Polk	519	0.024	6.87	0.38	0.93	1.04

Table 2.1 Relevant structural characteristics of the CRN's used in our calculations.

Since only these three CRN's were available to us at the time of this investigation, we also performed calculations for clusters of 27 unit cells of the BC-8 and ST-12 high pressure crystalline forms of Si and Ge. The detailed structures of these phases are discussed by Kasper and Richards (1964). We note only that they possess long-range order, containing 16 and 12 atoms per unit cell respectively, yet both display bond length and angle distortions. Since the BC-8 structure contains only even rings and the ST-12 structure contains both odd and even rings, they present a convenient 'half-way house' between c-Ge and a-Ge and therefore aid our understanding of how structural properties affect the form of the DOVS.

We note at this point the correspondence between this work and that reported by Kelly and Bullett (1976a) and by Kelly (1975) on the electronic valence band structure of a-Si (see also Chapter 6). The main conclusion of their work is that the form of the electronic spectrum is determined principally by the topological structure. In contrast, our DOVS results show dependence on both angular distortions and topological disorder.

In the next section we derive the phonon dispersion and DOVS for c-Ge by both the reciprocal space and Recursion methods. After comparing the results of the two approaches, we go on to consider the results of our CRN calculations and the structure of a-Ge.

2.2 CRYSTALLINE GERMANIUM

The simplest rigid-ion force constant model which describes the principal features of the phonon dispersion in c-Ge is that originally due to Born (1914). This model includes central and non-central interactions between nearest neighbour atoms only and has been widely used in the study of vibrations in a-Ge (see for example Thorpe 1973, 1974, Alben et al 1975, Chen, Vetelino and Mitra 1975 and Beeman and Alben 1977).

The potential between atoms i and j is written as

$$V_{ij} = \frac{3}{2} \beta \left[(\underline{u}_i - \underline{u}_j) \cdot \underline{r}_{ij} \right]^2 + \frac{1}{2} (\alpha - \beta) \left[\underline{u}_i - \underline{u}_j \right]^2 \quad (2.2.1)$$

where $\underline{u}_i$, $\underline{u}_j$ are the displacements of i , j and $\underline{r}_{ij}$ is a unit vector connecting them. Proceeding as described in Section 1.2, the force constant tensor for two atoms on the x-axis is

$$\Phi_{100} = \begin{bmatrix} -(\alpha + 2\beta) & 0 & 0 \\ 0 & -(\alpha - \beta) & 0 \\ 0 & 0 & -(\alpha - \beta) \end{bmatrix} \quad (2.2.2)$$

illustrating that the central force constant is $(\alpha + 2\beta)$ and the non-central one is $(\alpha - \beta)$. Following Cochran (1966), we derive the dynamical matrix for unit mass, $\underline{\underline{D}}$;

$$\underline{\underline{D}} = \left| \begin{array}{ccc|ccc} 4\alpha & 0 & 0 & -4\alpha P & 4\beta Q & 4\beta R \\ 0 & 4\alpha & 0 & 4\beta Q & -4\alpha P & 4\beta S \\ 0 & 0 & 4\alpha & 4\beta R & 4\beta S & -4\alpha P \\ \hline & \text{complex} & & 4\alpha & 0 & 0 \\ & \text{conjugate} & & 0 & 4\alpha & 0 \\ & & & 0 & 0 & 4\alpha \end{array} \right| \quad (2.2.3)$$

where

$$\begin{aligned}
 P &= C_x C_y C_z + i S_x S_y S_z & S_x &= \sin(k_x a) \\
 Q &= S_x S_y C_z + i C_x C_y S_z & C_x &= \cos(k_x a) \text{ etc} \\
 R &= S_x C_y S_z + i C_x S_y C_z \\
 S &= C_x S_y S_z + i S_x C_y C_z
 \end{aligned}$$

Solving the secular equation for $\underline{k}=(k,0,0)$ gives the dispersion relations

$$\omega^2 = 4\alpha \pm 4 \left[\alpha^2 C_x^2 + \beta^2 S_x^2 \right]^{1/2} \quad (2.2.4a)$$

for transverse modes (each doubly-degenerate) and

$$\omega^2 = 4\alpha \left[1 \pm C_x \right] \quad (2.2.4b)$$

for longitudinal modes (each singly-degenerate). For zero non-central forces $\alpha=\beta$ and equation 2.2.4a becomes

$$\omega^2 = 4\alpha \pm 4\alpha$$

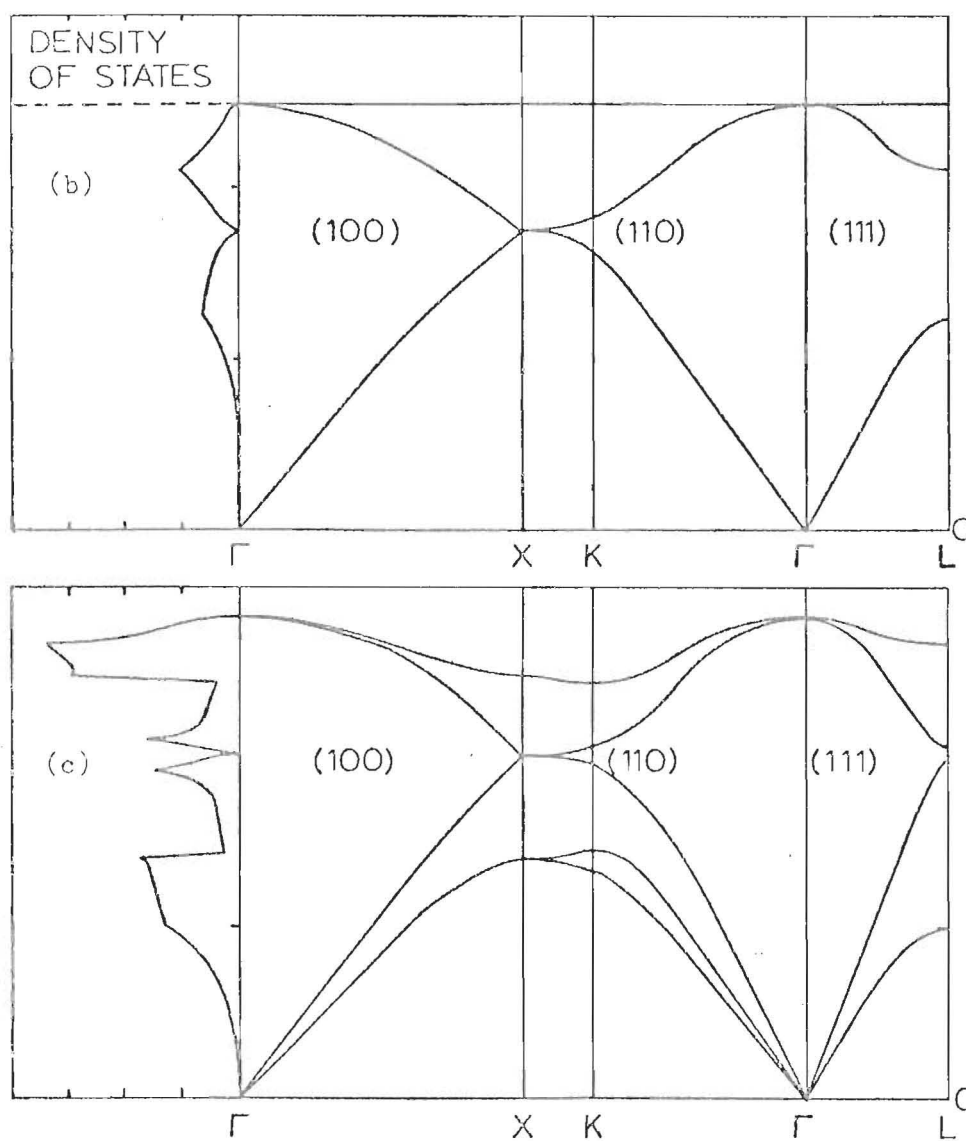
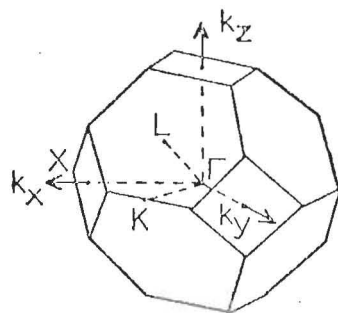
i.e. flat bands at $\omega^2=0$ and 8α , as shown by Weaire and Alben. Figure 2.2 shows the FCC Brillouin zone and the dispersion curves and DOVS for the cases of $\alpha=\beta$ i.e. central forces only and $\beta/\alpha=3/4$ which lies in the range of values appropriate to c-Ge. The DOVS were obtained by integration over the zone by the method of Gilat and Raubenheimer (1966). The dispersion curves and DOVS for $\beta/\alpha=3/4$ reproduce the general behaviour found in experiments on c-Ge - see Chapter 5.

We now consider a comparison of these results with those of the Recursion method. The input to this calculation is a set of cluster coordinates from which the dynamical matrix is derived. The force constant tensor ϕ_{ij} for a given pair of atoms is given by the unitary

Figure 2.2 a) The FCC Brillouin zone.

b) Dispersion curves and DOVS for c-Ge with central forces only.

(a)



c) Dispersion curves and DOVS for c-Ge with $\beta/a=3/4$.

transformation

$$\Phi_{ij} = \underline{R} \Phi_{100} \underline{R}^{-1} \quad (2.2.5)$$

where Φ_{100} is given by 2.2.2 and $\underline{R}$ rotates the vector (1,0,0) to an orientation parallel to the interatomic unit vector $\underline{r}_{ij}$ of the CRN. Thus, variations in the force constants due to bond length and angle variations are omitted but the characteristic connectivity and imperfect tetrahedral coordination of the cluster are included. We continue to work within the harmonic approximation.

Figure 2.3 shows the results of the calculation for a 344-atom cluster of the diamond-cubic structure with $\beta/\alpha=3/4$, for different lengths of the continued fraction expansion. As expected, the resolution increases with the number of levels, until at 20 all important features are adequately resolved (see the comparison plot of Figure 2.6). We hesitate to increase the number of levels further since we have already included environments of the central atoms well outside the 344-atom cluster. Further calculation will produce spurious peaks in the spectrum (Nex, Private communication). The agreement of Figure 2.6 is very good except in the region of critical points, as expected from the use of such a small cluster. This result stresses the importance of the local environment in determining the form of the DOVS. The agreement could of course be improved by the use of a larger cluster, but the present size was chosen to facilitate comparison with the CRN results.

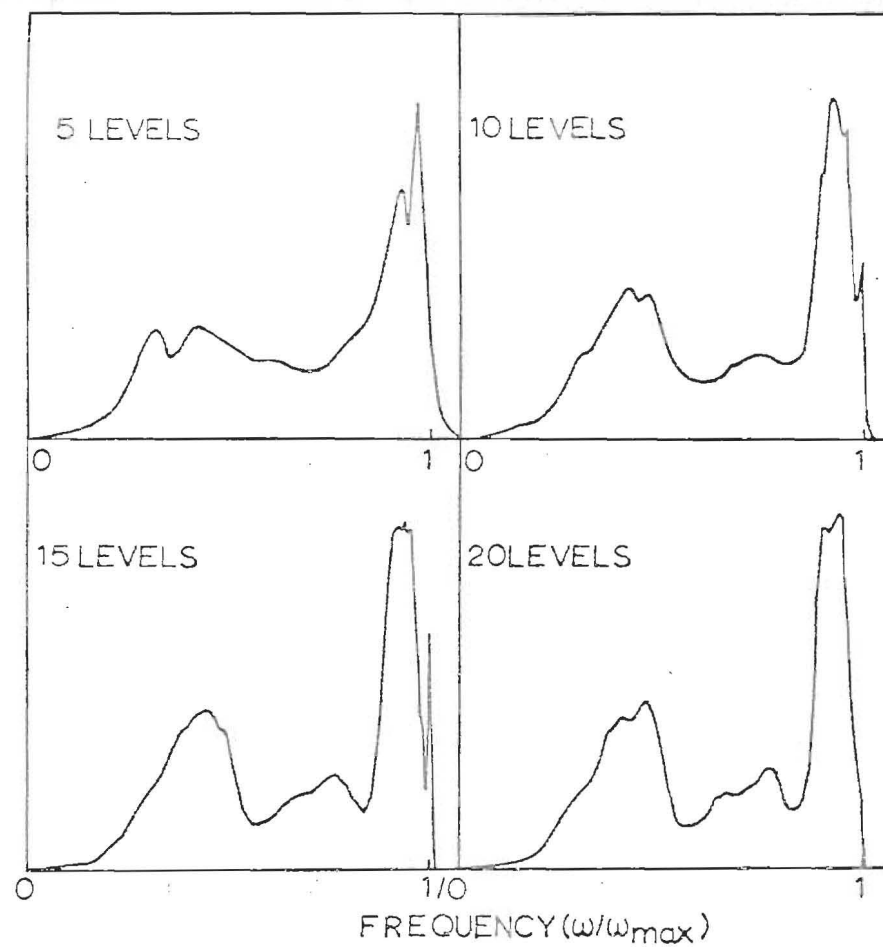


Figure 2.3 Vibrational spectra for a 344-atom diamond-cubic structure cluster calculated using the Recursion method; the different plots illustrate the increased resolution obtained with more levels of the continued fraction expansion.

2.3 RECURSION RESULTS

As a prelude to presenting the results for the case of $\beta/\alpha=3/4$, we consider the DOVS in the limit of central forces only. These are shown in Figure 2.4 for the three CRN's of Table 2.1, where the zero-frequency δ -functions have been omitted. The frequency scale is in units of the maximum crystalline frequency. Each spectrum has been calculated to 20 levels of the continued fraction, averaged over 10 central sites of the network. These results illustrate the differences arising from structural variations in the manner predicted by Weaire and Alben.

The retention (and even widening) of the dip in the LA+LO-like region of the Connell-Temkin model result mirrors the effect found by Kelly (1975) and Alben, von Heimendahl, Galison and Long (1975) in their calculations of the s-band electronic structure for this CRN. The dip for an even-ringed structure arises from the symmetry of the eigenvalues of the s-state Hamiltonian for an isolated ring about a central value of energy (or frequency squared), as discussed originally by Joannopoulos and Cohen (1973). The eigenvalues are

$$E_n = -2h \cos\left(\frac{2n\pi}{N}\right) \quad n=0,1,\dots,N-1 \quad (2.3.1)$$

where h is the nearest-neighbour s-state hopping integral. Interactions between such ring states in the bulk produce broadening but the minimum is retained. If odd-rings are present, the eigenvalue distribution is not split in this way and the dip is significantly (but not totally) filled in, as seen for the Steinhardt and Polk models.

The broadening of the TO-like feature is greater for the Connell-Temkin model than either the Steinhardt or Polk CRN's by virtue of its larger rms bond angle distortion. This is stressed by the bond angle

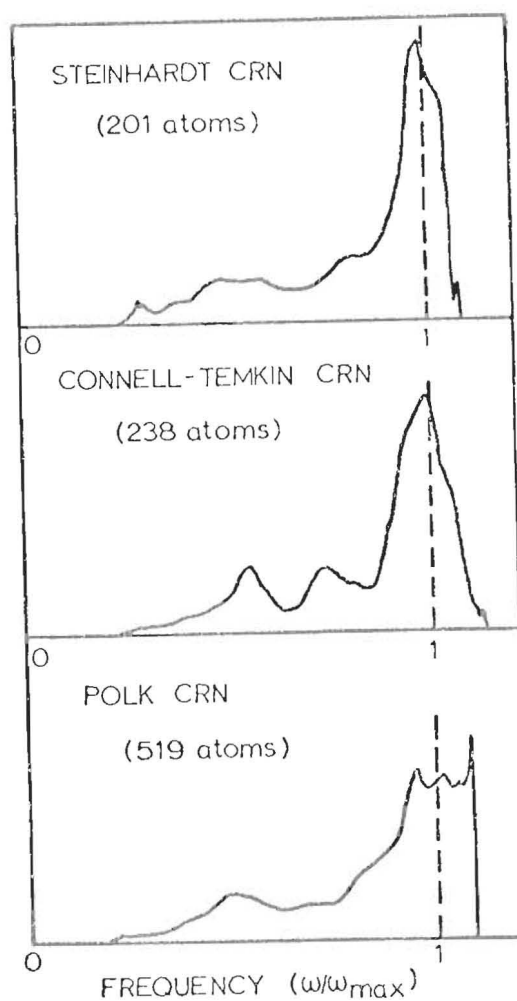


Figure 2.4 DOVS for the CRN's of Table 2.1 calculated with central forces only; the zero-frequency δ -functions have been omitted.

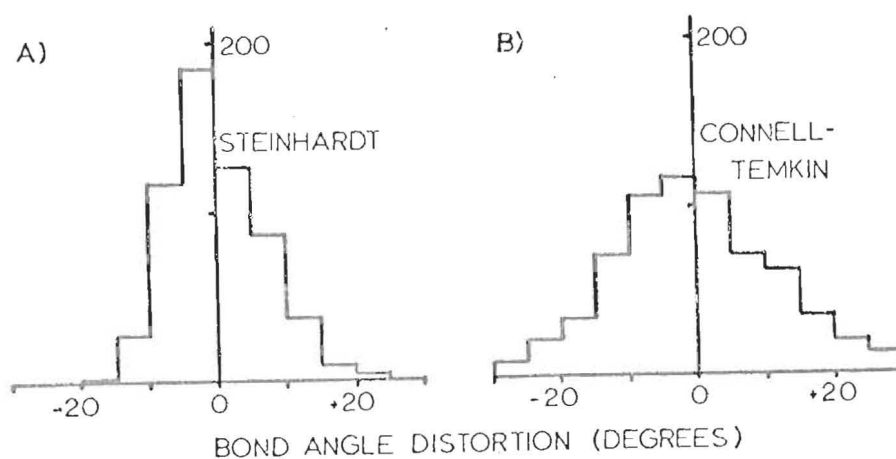


Figure 2.5 Bond angle distortion histograms for the Steinhardt and Connell-Temkin models.

distortion histograms of Figure 2.5. Note that the differences between the Steinhardt and Polk model DOVS are undoubtedly due to the different sizes of the models since they are very similar in other respects (see Table 2.1). For a given number of levels of the continued fraction expansion, there are bound to be different degrees of convergence for clusters of very different sizes.

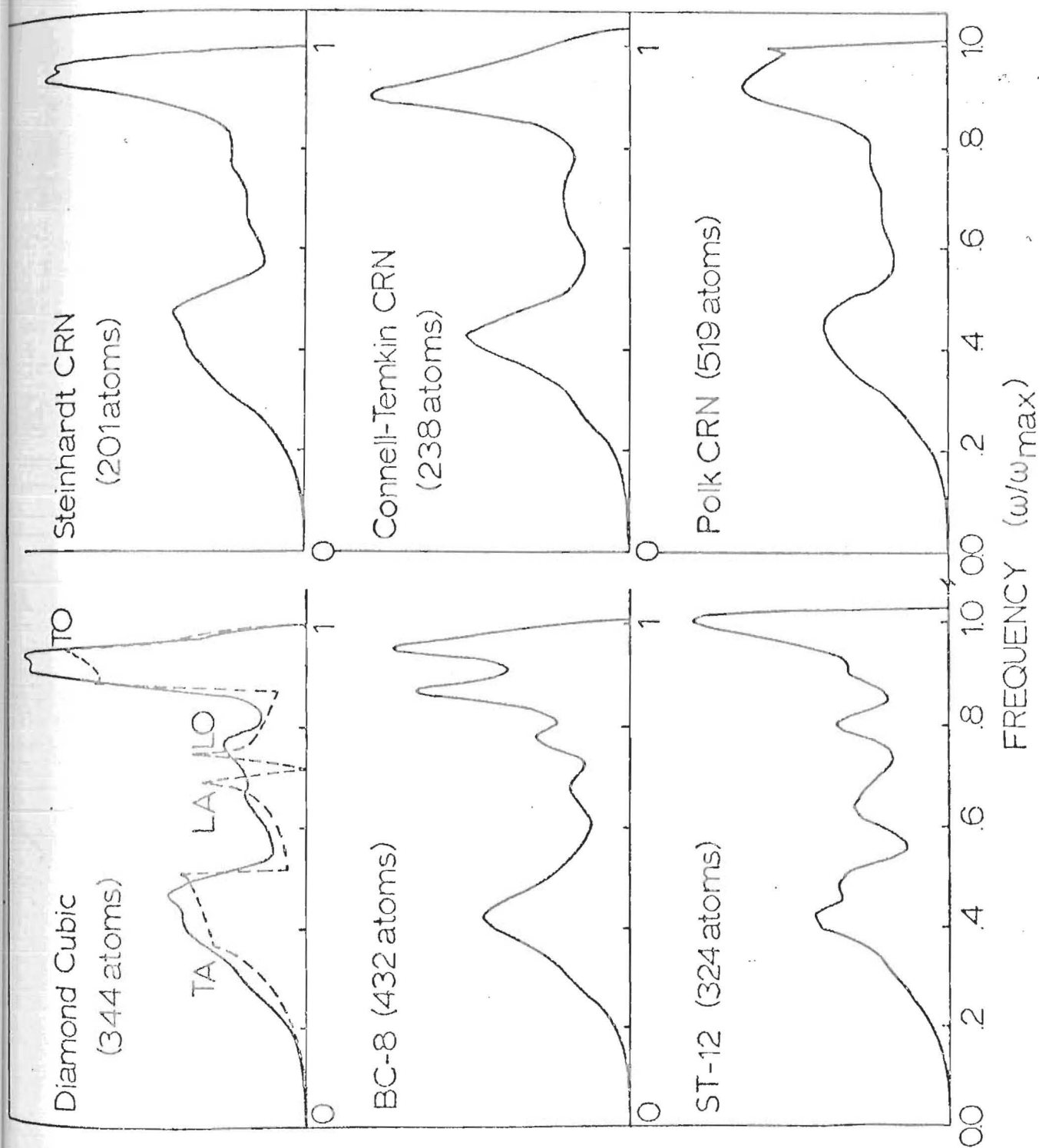
Consider now the DOVS for the case of $\beta/\alpha=3/4$ shown in Figure 2.6. The results for c-Ge calculated by both Recursion method and Brillouin zone integration (the broken line) are repeated for comparison with those for the BC-8 and ST-12 structures and the Steinhardt, Connell-Temkin and Polk CRN's. The BC-8 and ST-12 results are averages over the unit cells whereas the CRN spectra are averages over 10 central sites; averages over 5 and 10 sites were indistinguishable for each of the CRN's. All spectra are calculated from 20 levels of the continued fraction expansion.

Each of the CRN spectra reveal the same basic distribution of modes as the crystalline spectrum, as a result of the similar short-range order. They do however differ in detail in ways reflecting their structural differences. The BC-8 and ST-12 results display sharp features arising from long-range order, which are typical of crystalline vibrational spectra. They are however useful in interpreting the CRN results, as shown below.

Strictly, the LA+LO-like regions of the spectra can no longer be discussed in terms of the Weaire-Alben result. The sharp LA and LO features of the crystalline DOVS are washed out by disorder but a small LA+LO-like dip can still be detected in the Steinhardt and Polk model results. The TA-like and TO-like regions of the spectra are the most interesting areas of the CRN results.

The TA-like peaks of the BC-8 and Connell-Temkin results are

Figure 2.6 DOVS for the diamond-cubic, BC-8 and ST-12 forms of Ge and the CRN's of Table 2.1 calculated using the Recursion method; the diamond-cubic result is compared with that from Brillouin zone integration (the broken line).



noticeably symmetric whereas the Steinhardt, Polk and ST-12 spectra display broader asymmetric such peaks. Thus the TA-like peak shape gives a clear distinction between models with only even rings and those containing both odd and even rings. The crystalline TA peak is broad and flat due to van Hove singularities arising from the X and L points of the FCC zone. On introducing disorder but retaining only even rings, the peak becomes symmetric, whereas also including odd rings in the structure restores some asymmetry.

The structures containing odd-rings of bonds display TO-like peaks with comparatively steep high frequency edges. The TO-like peak of the Connell-Temkin model result does not reveal this behaviour; it does however peak at a lower frequency than in the Steinhardt or Polk results and is broad enough to envelope the crystalline zone-centre mode frequency. This observation of a steeper high-frequency side to the TO-like peak of the DOVS for systems with larger concentrations of odd rings is corroborated by Thorpe's (1974) results for isolated 5- and 6-membered rings, obtained using a self-consistent cluster calculation. Our results are also in good agreement with those of Beeman and Alben (1977).

2.4 STRUCTURAL INTERPRETATIONS

The experimental Raman and IR spectra of a-Si and a-Ge shown in Figure 2.1 are now tentatively interpreted in the light of the results of our DOVS calculations. Our conclusions regarding the typical structures of a-Ge and a-GaAs are in general agreement with those reached by other methods. The Raman and IR spectra of disordered solids are related to the DOVS via frequency-dependent matrix elements (see Section 5.4 and Alben et al 1975) and the situation is further complicated by the inevitable variations in force constants in the real materials. Nevertheless, it appears that meaningful comparisons can still be made. In general, Raman spectra are less complicated by matrix element effects than IR spectra but both indicate that the TA-like features are asymmetric and the TO-like features peak at about 90% of the zone-centre frequency but also envelope that frequency in a-Si and a-Ge.

The results of Figure 2.6 therefore suggest that a-Ge contains odd-membered rings but fewer in number than the Polk or Steinhardt models, with an rms bond angle distortion of 10° or more. The concentration of odd-membered rings would have to be reduced not only to ensure a larger bond angle distortion but also to contribute to the absence of a steep high-frequency side to the TO-like peak.

These conclusions are in general agreement with those derived from both structural and electronic considerations. Connell and Temkin (1974) for example, claimed that a linear combination of the RDF's of theirs and the Polk model would fit the experimental RDF better than either model alone. Kelly and Bullett (1976a) also claim that the topological structure of a-Ge is that of the Polk model but with fewer odd rings (see Chapter 6). The rms bond angle distortion of about 10° is also consistent with the RDF analysis of Shevchik and Paul (1972).

Since the shape of the TA-like features of the calculated spectra

clearly distinguish structures with and without odd rings, it is interesting to compare the data for a-Ge with the Raman spectrum of a-GaAs presented by Lannin (1974). The TA-like feature of the a-GaAs result is symmetric and the TO-like peak appears to be broader than the corresponding feature of the a-Ge Raman spectrum. We therefore tentatively suggest that a-GaAs contains very few odd-membered rings which is consistent with the valence band photoemission results of Shevchik et al (1974).

2.5 DISCUSSION

The results presented above illustrate the usefulness of our approach for the calculation of vibrational spectra appropriate to structural models of disordered solids. The applicability of the method is tested further in subsequent chapters using different structural and dynamical models. As pointed out in Section 2.3, however, there is some danger in comparing the spectra calculated to the same accuracy using clusters of very different sizes. In all subsequent applications therefore clusters of very similar sizes have been considered.

Since no force constant variations were included in our calculations and good general agreement with the available experimental data was obtained, it appears that such effects are small in a-Ge. We might expect this since the nearest neighbour central force dominates the dynamics and bond lengths are effectively unchanged in the amorphous phase. Angular distortions, however, can be significant so it seems that force constants which are not expected to vary greatly in magnitude must be chosen if we wish to continue with this approach. This is to be preferred because of the difficulties of developing a simple yet physical method of estimating force constants as functions of bond lengths etc. It also appears that anharmonic effects are not of great importance in a-Ge. The validity of our approach is tested further in the following chapters on a-As and a-Se.

3.1 INTRODUCTION

In this chapter the results of calculations of the vibrational spectra of a single layer of the rhombohedral crystalline As structure and a three-fold coordinated CRN model of the structure of a-As are presented. In this case bond stretching and bending forces as defined by Keating (1966) are used. Comparing the two spectra stresses that the three-dimensional CRN is based on the buckling of a single two-dimensional layer of pyramidally-bonded atoms. Comparing the network result with experimental data for a-As suggests that it is a good model of the typical structure of a-As in all but some topological aspects.

As for a-Ge, the typical structure of a-As beyond second neighbours is not yet known with certainty. In a-Ge this would be specified by the dihedral angle* distribution, but in a-As (as in a-Se) the situation is further complicated by the existence of two types of near-neighbours in the corresponding crystalline phase - see Figure 3.1a. The unit cell of rhombohedral As can be viewed as a distorted cube; in addition to three first neighbours in the same layer, each atom has three second neighbours in the adjacent layer, as shown in Figure 3.1. The RDF of a-As, as measured by Krebs and Steffen (1964), reveals a first neighbour distance and coordination number unchanged from that of the crystal but a drastic reduction in the number of second neighbours. The changes are consistent with a loss of inter-layer correlations and an rms bond angle deviation of about 10° . Further evidence in line with this interpretation is revealed in the optical properties of the two phases. Rhombohedral As

* i.e. the angle between second neighbour bonds when projected onto a plane perpendicular to their common first neighbour bond.

is semi-metallic whereas a-As is a semiconductor with a gap of about 1.2 eV, indicating a lower coordination in the amorphous form. A detailed discussion of these and other properties of a-As has been given by Greaves (1975).

On the basis of the experimental data, Greaves and Davis (1974) modelled the structure of a-As with a 533-atom three-fold coordinated CRN with an rms bond angle distortion from the crystalline value of 97.2° of about 10° . The model can be viewed as a buckled single layer of rhombohedral As (see Figure 3.1b), the inter-layer bonds being neglected apart from ensuring that non-bonded neighbours are not unrealistically close. During construction the dihedral angles were allowed to vary without restriction to achieve complete connectivity. As a result, although all interior atoms are fully coordinated, the topology of the model is characterised by cavern-like voids and atoms connected into a large variety of odd and even membered rings. The experimentally observed density deficit of about 12% compared to the rhombohedral form is well reproduced by the model which gives good agreement with the experimental RDF. Elliot and Davis (1976) have recently improved the RDF agreement by energy relaxation of the CRN using the same energy expression used for the vibrational calculations presented below - see Keating (1966).

We are fortunate in having the experimentally determined one-phonon density of states for a-As, deduced from their inelastic neutron scattering data by Leadbetter, Smith and Seyfert (1976). The spectrum is shown in Figure 3.2. The Raman and IR spectra of a-As have been measured by Lannin (1976) and Lucovsky and Knights (1975) respectively. Lucovsky and Knights showed that the general form of the DOVS can be obtained by broadening the normal mode spectrum of a pyramidal As_4 molecule, calculated using bond stretching and bending force constants. Their argument illustrates the division into regions of bond bending (low

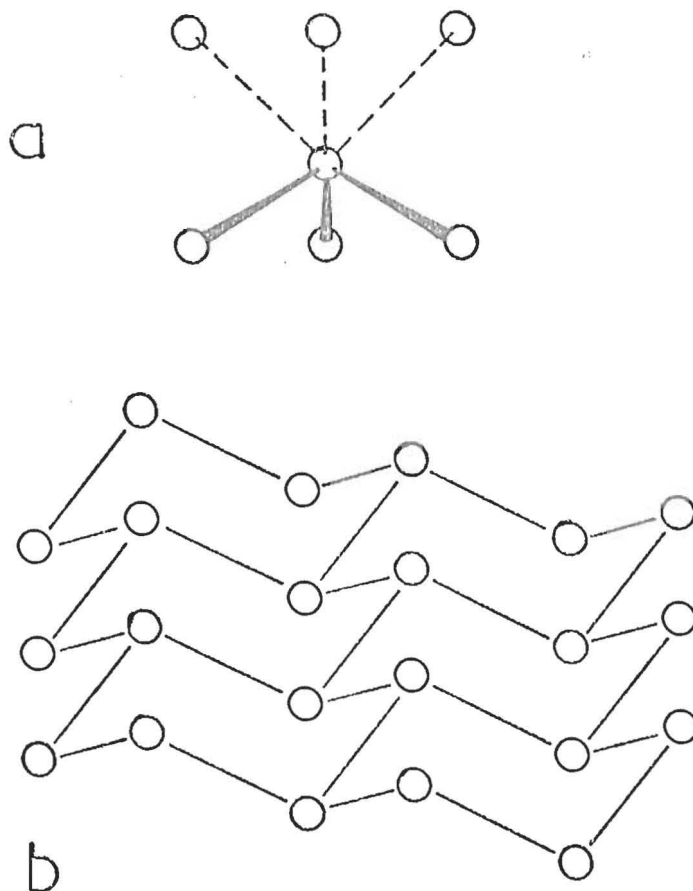


Figure 3.1 a) The near-neighbour environment in rhombohedral As.
b) The structure of a single layer of rhombohedral As.

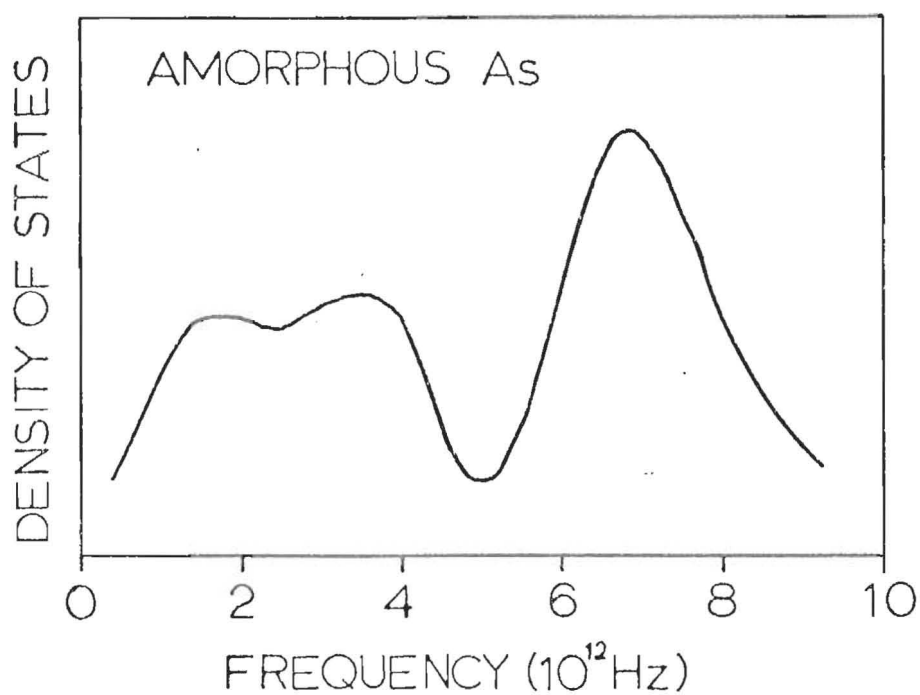


Figure 3.2 Experimental density of vibrational states of a-As
(after Leadbetter et al 1976).

frequency) and stretching (high frequency) motions seen in Figure 3.2 and supports the modelling approach of Greaves and Davis. As for a-Si and a-Ge, the Raman and IR spectra of a-As appear to be related to the DOVS by smoothly varying matrix elements.

Comparisons of the results of electronic structure calculations with X-ray and ultraviolet photoelectron spectra (XPS/UPS) have already provided information on the structure of a-As. Robertson (1975b) has interpreted the filling of the dip in the valence s-states on going from rhombohedral to amorphous As as evidence for odd membered rings in the latter. Since the bond angles are close to 90° we expect little s-p hybridisation so the consideration of pure s-states is valid. Thus in the single-layer approximation we expect the isolated ring states argument of Section 2.3 to apply. Kelly and Bullett (1976b) have reproduced the qualitative differences between the crystalline and amorphous XPS data using the Greaves-Davis CRN and Slater-Koster (1954) hopping integrals calculated from first principles. They interpret the differences as arising from the removal of inter-layer bonding giving a local two-dimensional character to the a-As electron density of states.

In the next section we describe our calculations and present our results, which are subsequently discussed in respect of the structure of a-As.

3.2 CALCULATIONS AND RESULTS

Following Keating, the potential energy of the solid under elastic deformation is written

$$V = \frac{1}{2} \sum_l \left[4\alpha \sum_i \left\{ \underline{X}_{li} \cdot (\underline{u}_l - \underline{u}_i) \right\}^2 + \beta \sum_{j \neq i} \left\{ \underline{X}_{li} \cdot (\underline{u}_l - \underline{u}_j) + \underline{X}_{lj} \cdot (\underline{u}_l - \underline{u}_i) \right\}^2 \right] \quad (3.2.1)$$

where $\underline{X}_{li}$ is a unit vector between atoms l and i , $\underline{u}_l$ is the displacement of l and the summations are over all atoms l and their nearest neighbours i and j . Note that α and β are not the same quantities as defined in Chapter 1, they are bond stretching and bending force constants defined in a manner ensuring their translational and rotational invariance. Proceeding as usual the force constant tensors are

$$\begin{aligned} \Phi_{xy}^{''''}(A, B) = & -8\alpha X_{AB} Y_{AB} \\ & -\beta \left[\sum_{AN} (X_{AB} + X_{HAN}) Y_{BAN} + \sum_{BN} (Y_{BA} + Y_{BBN}) X_{BBN} \right] \end{aligned} \quad (3.2.2a)$$

for first neighbours A, B and

$$\Phi_{xy}^{''''}(A, BN) = \beta X_{BA} Y_{BBN} \quad (3.2.2b)$$

for second neighbours A, BN . Here $\underline{X}_{AB} = (X_{AB}, Y_{AB}, Z_{AB})$ where A and B are first neighbours and AN and BN denote their other first neighbours respectively. Note that this scheme results in each atom interacting with three first neighbours and six second neighbours in a three-fold

coordinated system.

A single layer of the rhombohedral As structure constitutes a planar hexagonal lattice with two atoms per primitive cell, as shown in Figure 3.3a. The translation vectors are

$$\underline{t}_1 = (2A, 0, 0) \quad \underline{t}_2 = (A, 3B, 0) \quad (3.2.3)$$

where

$$A = \sin\left(\frac{1}{2}\theta\right)$$

$$B = \frac{1}{\sqrt{3}} \sin\left(\frac{1}{2}\theta\right)$$

$$C = \left[1 - \frac{4}{3} \sin^2\left(\frac{1}{2}\theta\right)\right]^{1/2} = \text{layer thickness} \quad (3.2.4)$$

θ is the pyramidal bond angle (97.2° in the crystal layer) and the bondlength is taken as the unit of length. The reciprocal lattice vectors are

$$\underline{g}_1 = 2\pi \left(\frac{1}{2A}, -\frac{1}{6B}, 0\right) \quad \underline{g}_2 = 2\pi \left(0, \frac{1}{3B}, 0\right) \quad (3.2.5)$$

These generate the Brillouin zone shown in Figure 3.3b. The 6×6 dynamical matrix deduced from the structure and equations 3.2.2 as outlined in Section 1.2 is listed in Appendix 3.2.

The DOVS histogram calculated by sampling 2600 uniformly distributed points in the irreducible zone bounded by the path Γ -M-K- Γ is shown in Figure 3.4 (the first frame). The ratio of force constants is $\beta/\alpha=1$, which lies in the range of values appropriate to this simplified model. The general form of the spectrum derives from the two-dimensional character of the system, the division into equally weighted bands of acoustic and optic modes being obvious.

The dynamical matrix used in the Recursion calculation for a given set of coordinates is constructed using equations 3.2.2. For a cluster with bond length and angle distortions, unchanging force constants are

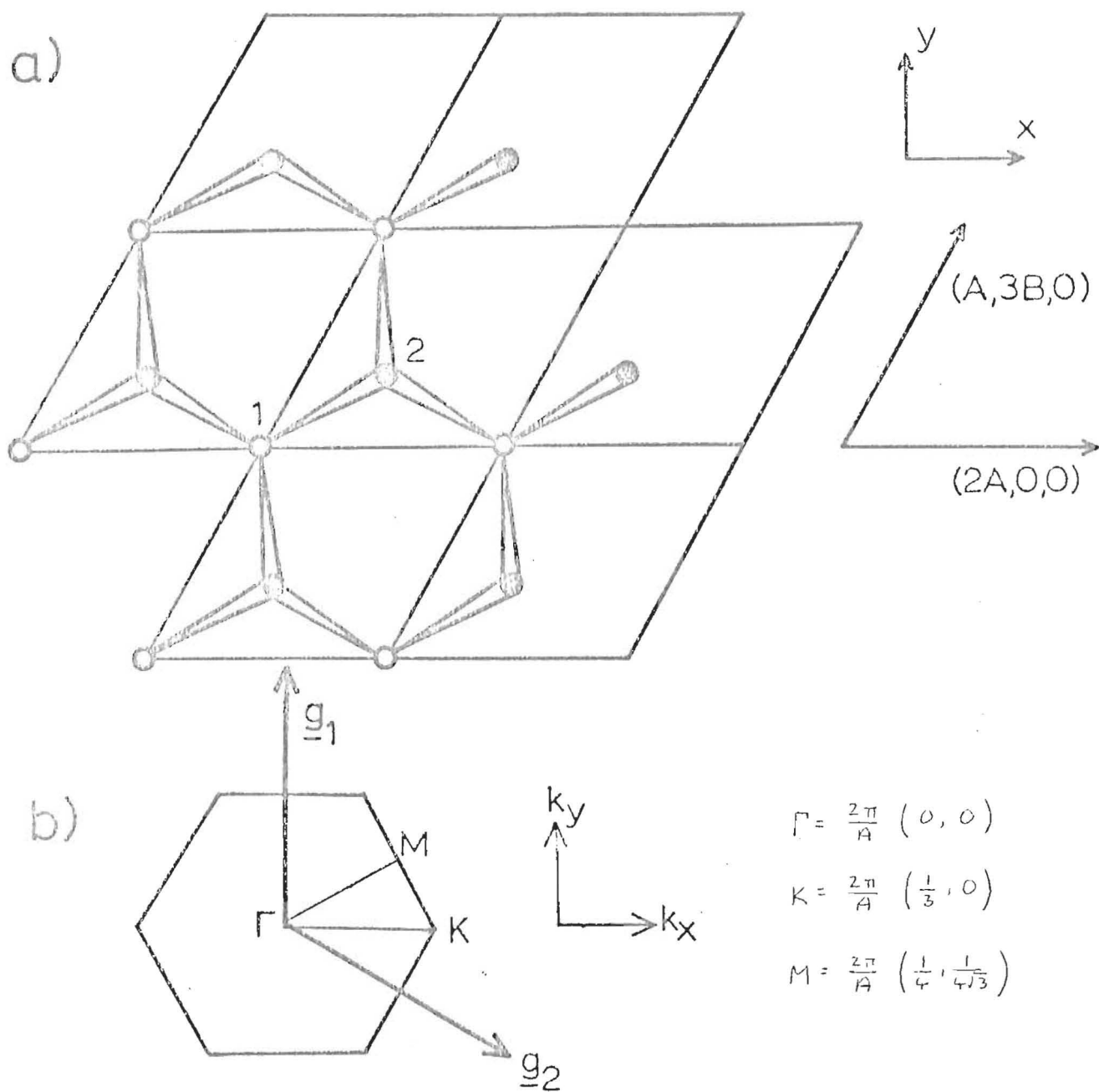


Figure 3.3 a) The hexagonal lattice of a single layer of rhombohedral As; The basis atoms are marked 1 and 2.

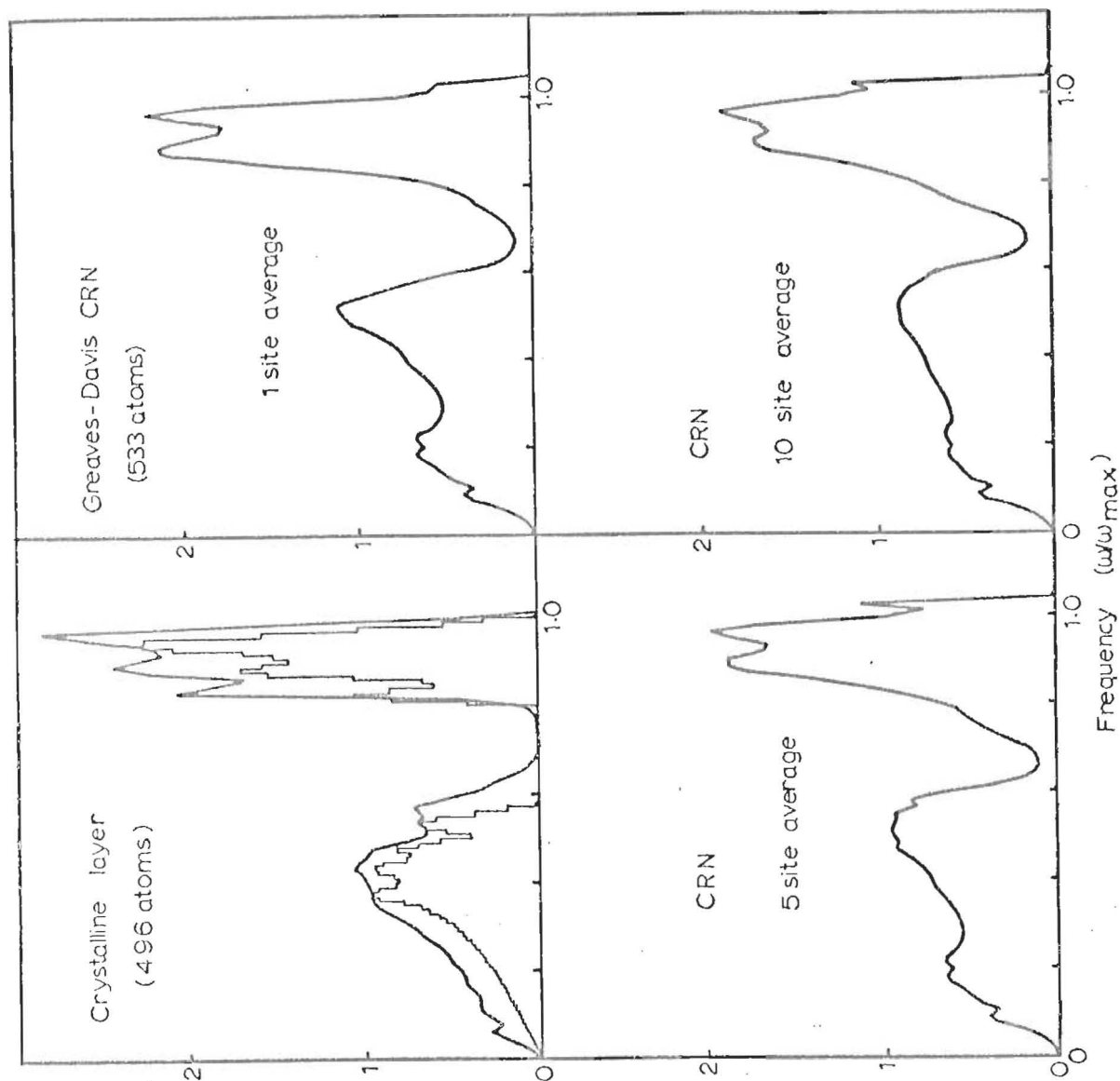
b) The corresponding Brillouin zone; the irreducible 1/12th of the zone is bounded by the path Γ -K-M- Γ .

assumed. The result of the method applied to a 496-atom cluster of the single layer structure (Figure 3.1b) is shown in Figure 3.4 for comparison with the histogram result. The number of levels of the continued fraction is 15. This was found to give adequate resolution of the bending and stretching mode bands and the gap between them.

The DOVS appropriate to the Greaves-Davis CRN are also shown in Figure 3.4 for averages over one, five and ten central sites of the network. The differences between the averages for five and ten sites are small but still noticeably greater than those obtained for the CRN models discussed in Chapter 2. We attribute this to the greater variation in local environment in the more cavernous three-fold coordinated CRN. The overall distribution of modes in the ten-site average is in good agreement with the experimental DOVS of Figure 3.2. We note the following points;

1. The lower frequency band has been reshaped towards the twin-peaked form of Figure 3.2.
2. The band gap has been filled with states mainly derived from the much-broadened upper band; the ratio of peak heights is now very similar to that of the experimental data.
3. The upper band displays a significantly steeper high-frequency edge than the corresponding feature of the experimental result.

Figure 3.4 Vibrational spectra for a single layer of rhombohedral As and the Greaves-Davis CRN model of a-As calculated using the Recursion method; the histogram is the reciprocal space result for the single layer which has a different normalisation for clarity.



3.3 DISCUSSION

An important feature of the results of Figure 3.4 is an illustration of the way in which the space-filling Greaves-Davis CRN has been derived from the buckling of a single two-dimensional layer. It is often difficult for anyone who has not seen the model to appreciate this. The spectra show how the single-layer DOVS has been transformed into a form giving good agreement with the data for bulk a-As, without the introduction of longer-range forces. The neglect of inter-layer interactions is consistent with the original approach of Greaves and Davis and it appears that a significantly better description of the lattice dynamics of rhombohedral As is necessary before a more realistic calculation for a-As becomes either feasible or worthwhile. We are, however, in the frustrating position of having data on the DOVS of a-As but not on the phonon dispersion in rhombohedral As.

Consider now the structural implications of a comparison of the experimentally determined DOVS of a-As with the Recursion result for the Greaves-Davis CRN. To evaluate within our simple model the influence of network topology on the vibrational spectrum, we can call upon our experience with four-fold coordinated CRN's (see Chapter 2). Since the higher-frequency side of a peak of bond stretching modes appears to be steeper for models with more odd rings of bonds, the results suggest that the Greaves-Davis model contains too many odd rings. Apart from this, the quality of the agreement suggests it to be an accurate representation of the atomic arrangements in a-As.

A possible cause of this odd ring excess may derive from the free rotations of the dihedral angles allowed during the construction process. A large body of evidence suggests that there is a preferred magnitude of the dihedral angle along chain-molecular units in a-Se and a-Te (see Chapter 4). Such a situation is also likely in a-As, involving a

preference for the staggered configuration, which is typical of the rhombohedral structure. Staggered dihedral angles are present in the chair-like 6-fold rings of Figure 3.1b whereas eclipsed angles are more typical of 5-fold rings of bonds. Such a preference may well influence the ring statistics of the real system. The neglected inter-layer bonds also place constraints on the atomic positions, but it is difficult to see how this relates directly to the intra-layer topology.

4.1 INTRODUCTION

In this chapter the results of calculations of the vibrational spectra of models appropriate to the structures of a-Se and a-Te are presented. An explanation for the excess low-temperature specific heat observed in amorphous Se compared to trigonal Se is also given.

Crystalline Se occurs in a trigonal form, consisting of spiral chains (see Figure 4.1), and two monoclinic forms, consisting of 8-membered rings packed in different ways. Crystalline Te occurs only in the trigonal form. Both chains and rings have bond angles (θ) and dihedral angles (ϕ) of 105° and 102° respectively (see Figure 4.2); the sign of ϕ is constant along a chain but alternates around a ring. The RDF of a-Se (Kaplow, Rowe and Averbach 1968) indicates that the bondlength is as in the more molecular monoclinic forms and the bond angles have a very small distribution about the crystalline value; further information cannot be deduced uniquely. Long, Galison, Alben and Connell (1976) have modelled the structure of a-Se/a-Te with convoluted two-fold coordinated chains of atoms. No rings or broken chains are present in the body of the model, which was energy-relaxed with Van der Waals forces acting between the chains. The model gives reasonable agreement with the RDF, exhibiting a random distribution in ϕ . On the other hand, Richter (1972) claims good RDF agreement with flat zig-zag chains, thus advocating a fixed value of ϕ at 180° in a-Se.

Structural information on a-Se has also been inferred from experimental UPS/XPS data. Joannopoulos, Schluter and Cohen (1975) infer an increased inter-chain distance and the presence of 6-fold rings from their Empirical Pseudopotential Method (EPM) calculations of the electronic structure of trigonal Se and Te. Shevchik (1975) claims a decrease in the average dihedral angle from 105° to that for 6-fold rings i.e. about 78° from

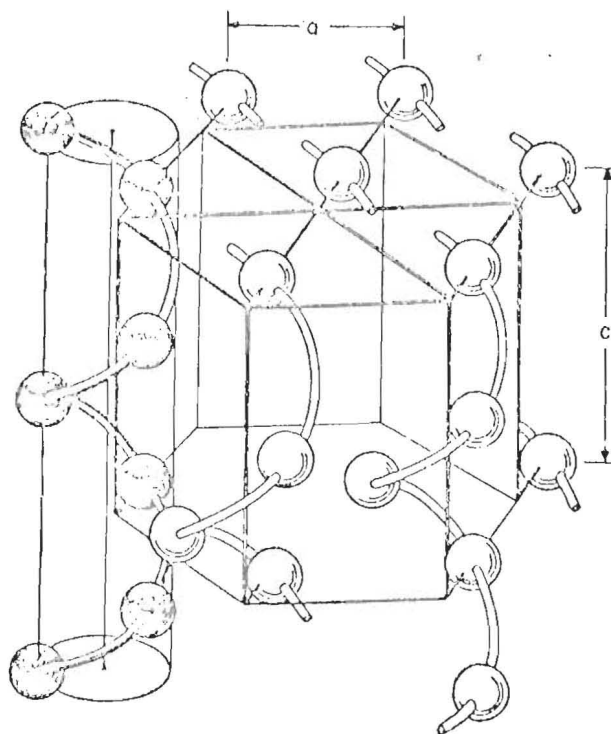


Figure 4.1 The spiral chain structure of trigonal Se and Te.

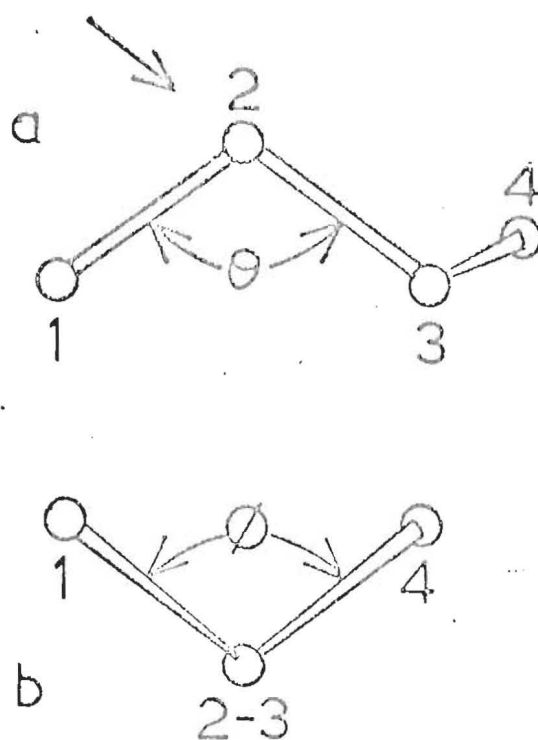


Figure 4.2 Bond angle θ (a) and dihedral angle ϕ (b) for a chain or ring of Se atoms.

the results of tight-binding calculations. Robertson (1975a, 1976) has shown that the reversal in magnitude of two p-bonding peaks in the electronic spectrum of amorphous compared to trigonal Se/Te is best explained by the presence of dihedral angles of alternating or random sign. He rules out large variations in the magnitude of ϕ on the basis of a minimum in the rotational energy curve $E(\phi)$ at the crystalline value of 102° . Even in the case of alternating ϕ this does not necessarily produce closed rings of bonds because of bond angle distortions. The calculations of Bullett (1976) are in excellent agreement with these conclusions.

Brodsky, Gambino, Smith and Yacoby (1972) measured the Raman spectrum of a-Te and interpreted their results in terms of disordered chains since only trigonal Te is stable. They ascribed the differences between the a-Te and c-Te Raman spectra to increased chain separations in the amorphous phase, in agreement with the observed density deficit. The same applies to the IR and Raman spectra of a-Se presented by Lucovsky (1973) and shown in Figure 4.3. Beeman and Alben (1977) have used the structural model of Long et al (1976) to calculate the DOVS and Raman and IR spectra appropriate to a-Se. Their IR result does not reproduce the peak at about 120cm^{-1} ; our results attribute this feature to the existence of a constant magnitude of ϕ in a-Se and a-Te.

The 'excess specific heat' of amorphous compared to trigonal Se at temperatures of about 10K observed by Berton and Lasjaunais (1973) is typical of the effect found in many disordered solids (a fuller discussion of 'excess specific heat' is given in Chapter 5). The results of model calculations show qualitatively that this is a result of increased inter-molecular separations in the amorphous phase.

In the next section a suitable dynamical model for trigonal Se and Te is developed. The model is then applied to the DOVS of a-Se and a-Te.

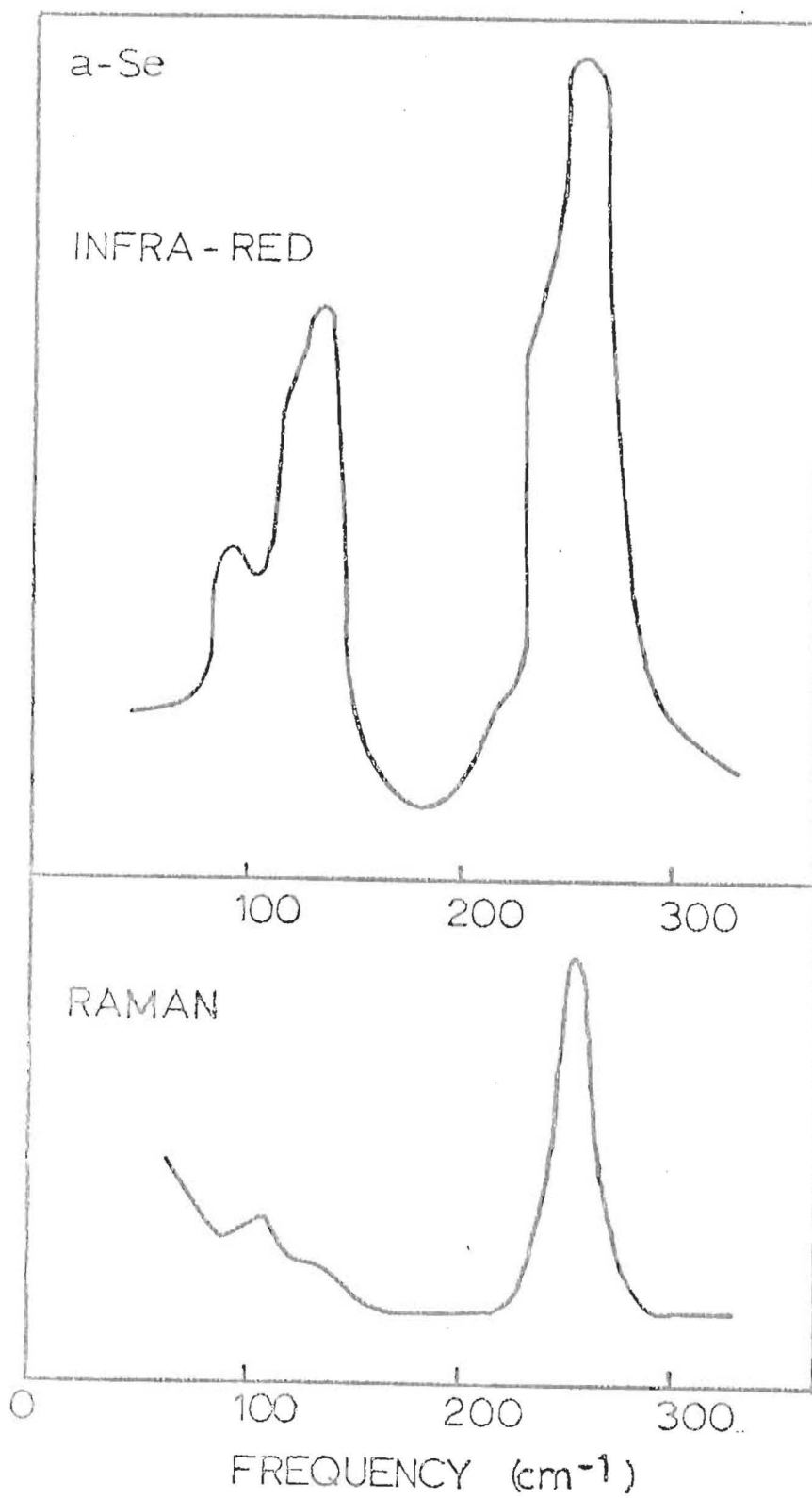


Figure 4.3 Experimental IR and Raman spectra of a-Se
(after Lucovsky 1973).

4.2 DYNAMICAL MODEL

Phonon frequencies in trigonal Se and Te along several high-symmetry directions of the hexagonal Brillouin zone have been measured by neutron scattering techniques (Teuchert, Geick, Landwehr, Wendel and Weber 1975 and Powell and Martel 1975), yet no accurate model of the lattice dynamics has been developed. Valence force field models are as successful as any in describing the general form of the dispersion but not the detailed differences between Se and Te (see Martin, Lucovsky and Helliwell 1976). We use here the simplest such model that ensures no zero-frequency modes away from the zone-centre; in the notation of Section 3.2, the Keating strain energy expression is

$$V = \frac{1}{2} \sum_l \left[4\alpha \sum_i \left\{ \underline{\chi}_{li} \cdot (\underline{u}_l - \underline{u}_i) \right\}^2 + \beta \left\{ \underline{\chi}_{li} \cdot (\underline{u}_l - \underline{u}_j) + \underline{\chi}_{lj} \cdot (\underline{u}_l - \underline{u}_i) \right\}^2 + 4\gamma \sum_{i'} \left\{ \underline{\chi}_{li'} \cdot (\underline{u}_l - \underline{u}_{i'}) \right\}^2 + \delta \sum_{(ij)'} \left\{ \underline{\chi}_{li'} \cdot (\underline{u}_l - \underline{u}_{j'}) + \underline{\chi}_{lj'} \cdot (\underline{u}_l - \underline{u}_i) \right\}^2 \right] \quad (4.2.1)$$

where the summations are now over all atoms l , their two intra-chain neighbours i, j and their four inter-chain neighbours i', j' (see Figure 4.1). α, β and γ, δ are intra- and inter-chain stretching and bending force constants respectively. The same force δ is used for the three inter-chain bond angles that are close to 90° ; the force for the inter-chain angle close to 180° is omitted. The corresponding force constant tensors have the same form as in equation 3.2.2.

The trigonal structure of Se has three atoms per unit cell. The primitive translation vectors are

$$\underline{t}_1 = (a, 0, 0) \quad \underline{t}_2 = \left(\frac{1}{2}a, \frac{\sqrt{3}}{2}a, 0 \right) \quad \underline{t}_3 = (0, 0, c) \quad (4.2.2)$$

where a and c are defined in Figure 4.1. The reciprocal lattice vectors

are

$$\mathbf{q}_1 = \frac{2\pi}{a} \left(1, -\frac{1}{\sqrt{3}}, 0 \right) \quad \mathbf{q}_2 = \frac{2\pi}{a} \left(0, \frac{2}{\sqrt{3}}, 0 \right) \quad \mathbf{q}_3 = \frac{2\pi}{c} (0, 0, 1) \quad (4.2.3)$$

These vectors generate the Brillouin zone shown in Figure 4.4. The 9x9 dynamical matrix for computing the phonon frequencies at any point in this zone is listed in Appendix 4.2.

The force constants obtained by least-squares fitting the experimental phonon frequencies at the Γ , A, H and K points of Se and Te are shown in Table 4.1. Also presented are the atom masses and the cell dimensions (from Martin et al 1976). The force constants indicate stronger inter-chain forces in Te than Se. Neither fit to the dispersion curves is as accurate as that obtained by Martin et al but our simple model describes the general features well. Figure 4.5 illustrates the dispersion along Γ -A-H-K- Γ for Se; the results for Te differ only in that the bands are closer which can be attributed to the stronger inter-chain forces in our simple model. The vibrational spectra obtained with this model for Se and Te are considered in Section 4.4.

Figure 4.4 The hexagonal Brillouin zone of the trigonal Se/Te structure.

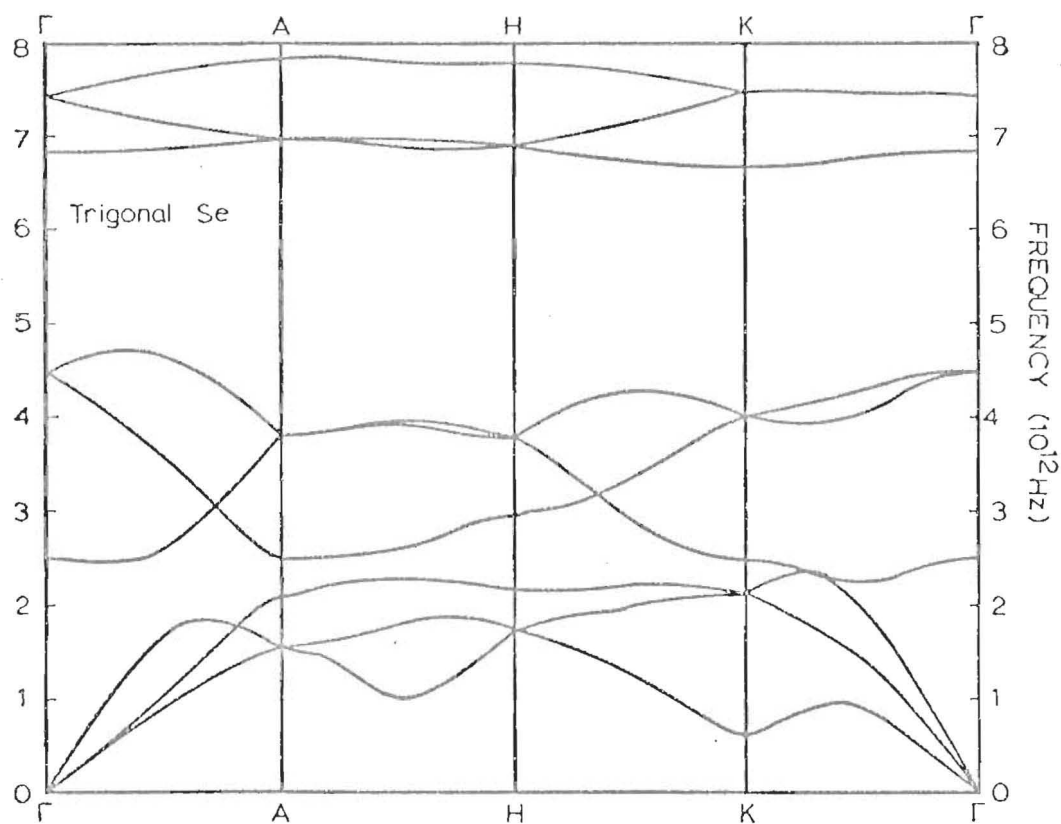
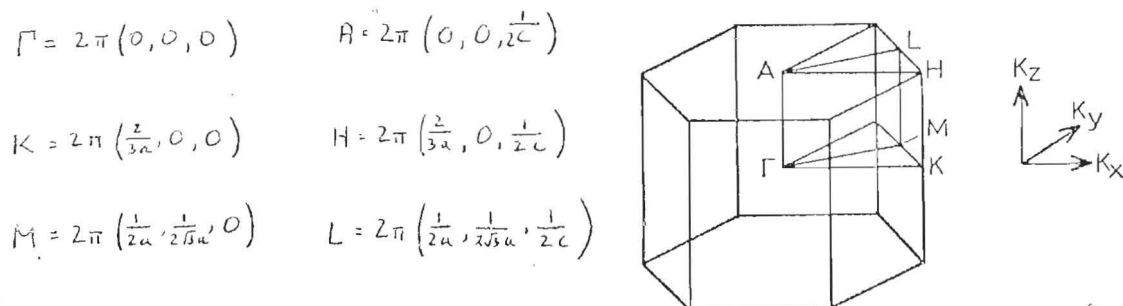


Figure 4.5 Phonon dispersion along some symmetry directions of the trigonal Se Brillouin zone calculated using the force constant model described in the text.

	Se	Te
a	$4.366 \times 10^{-10} \text{ m}$	$4.457 \times 10^{-10} \text{ m}$
b	0.984×10^{-10}	1.174×10^{-10}
c	4.954×10^{-10}	5.929×10^{-10}
r_1	2.373×10^{-10}	2.835×10^{-10}
r_2	3.436×10^{-10}	3.495×10^{-10}
m	$1.31115 \times 10^{-25} \text{ kg}$	$2.11884 \times 10^{-25} \text{ kg}$
α	$0.156 \times 10^5 \text{ Nm}^{-1}$	$0.664 \times 10^4 \text{ Nm}^{-1}$
β	0.142×10^5	0.845×10^4
γ	0.151×10^4	0.124×10^4
δ	0.159×10^3	0.939×10^3

Table 4.1 Structural parameters and fitted force constants for trigonal Se and Te.

4.3 ISOLATED CHAINS

In this section the DOVS of a series of isolated chains of atoms with constant bond lengths and angles but varying dihedral angles are presented. These calculations were performed in order to determine whether the vibrational data for α -Se are consistent with Robertson's model of the structure. From Table 4.1, the force constant ratio $\beta/\alpha=1$ is appropriate to both Se and Te for the purposes of model calculations; γ and δ are both zero. The spectra are calculated by the Recursion method for a series of 51-atom chains, accurate to 20 levels of the continued fraction.

To test our method, in Figure 4.6 we compare the Recursion result for a chain with constant dihedral angle $\phi=102^\circ$ with a histogram obtained by sampling 1000 points along the zone corresponding to an infinite chain of the trigonal crystal. The agreement is very good, particularly in respect of the zero-frequency δ -function, the band gap and the characteristic one-dimensional van Hove singularities at the extrema of the upper band. The δ -function, lower band and upper band correspond to chain twisting, bending and stretching modes respectively, each feature being of equal weight.

Results for chains of different dihedral angle distributions are shown in Figure 4.7 where the ϕ -independent δ -functions have been omitted. Each spectrum reveals the same basic form as the 'crystalline' result due to invariant bond lengths and angles, however there is a notable ϕ -dependence of the peak at the top of the lower-frequency band ($\omega/\omega_{\max}=0.5$). In (a) the 'crystalline' result is repeated; (b) is the DOVS obtained by averaging over 5 atoms each from the centres of 5 chains with the random distribution $-180^\circ \leq \phi < +180^\circ$ (25 atoms in all); (c) and (d) correspond to chains with ϕ constant at 180° (Richter 1972) and 78° (Shevchik 1975) respectively; (e) is the result from averaging over 5 atoms each from 3 chains (15 atoms in all) with ϕ at the crystalline

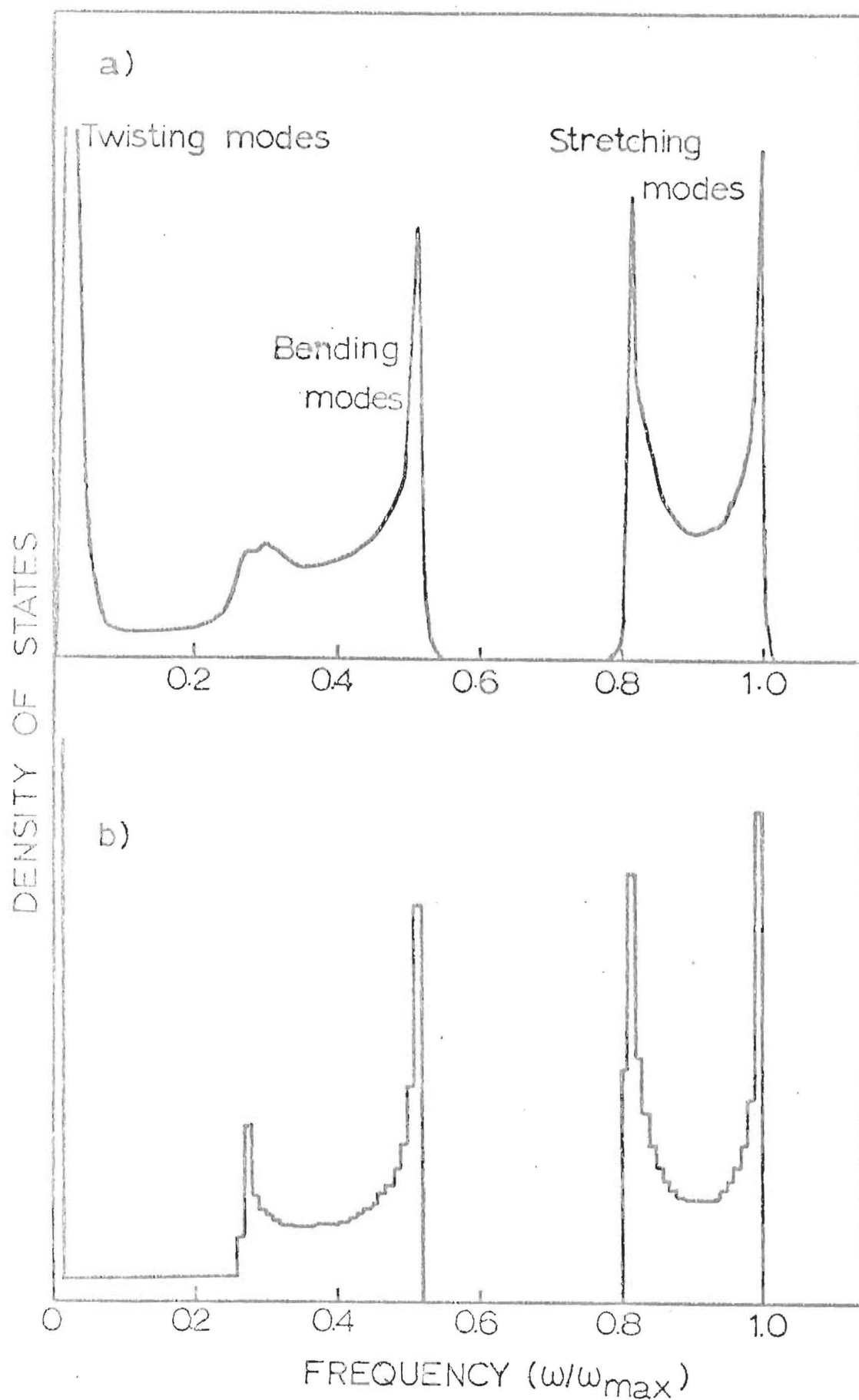


Figure 4.6 Comparison of the DOS of an isolated chain of Se calculated by (a) the Recursion method and (b) sampling along the zone.

magnitude but random in sign, as suggested by Robertson.

These results show a clear correlation between the occurrence of a peak at the upper edge of the lower band and a constant magnitude of the dihedral angle along the chains. The peak is much less sensitive to randomisation in the sign of ϕ than the magnitude. It was also found that result (a) of Figure 4.7 is identical with that obtained for chains with ϕ normally distributed about 102° with a standard deviation of up to about 10° ; significantly larger deviations produce smoothing as in result (b).

The results of Figure 4.7 therefore indicate that the features at about 120cm^{-1} in the IR and Raman spectra of Figure 4.3 are due to a constant magnitude of ϕ in a-Se. In comparing our results with the experimental data, we must remember that the data refer to a real solid whereas the calculations were performed for isolated chains. The effects of inter-chain interactions on the DOVS are two-fold. Firstly, the zero-frequency δ -function broadens and moves to higher frequencies; this is unlikely to produce a peak at the upper limit of the twisting/bending mode band since the inter-chain forces are weak (as indicated by the density deficit) and the disorder of the system will tend to produce a broad range of twisting mode frequencies. The second effect will be a smoothing of the typical one-dimensional features of the spectrum (see Section 4.4). Note also that the IR and Raman spectra are related to the DOVS by frequency dependant matrix elements. It might therefore be suggested that the prominent peak in the IR spectrum of a-Se at about 120cm^{-1} is a matrix element effect. We counter this by arguing that such a large IR activity must be supported by a corresponding increase in the density of modes. Further evidence has been furnished by Dultz, Hochheimer and Muller-Lierheim (1973). They measured the Raman spectrum of fibrous sulphur, a form containing (ideally) disordered chains of sulphur atoms, and also found a peak at the upper edge of the lower frequency band.

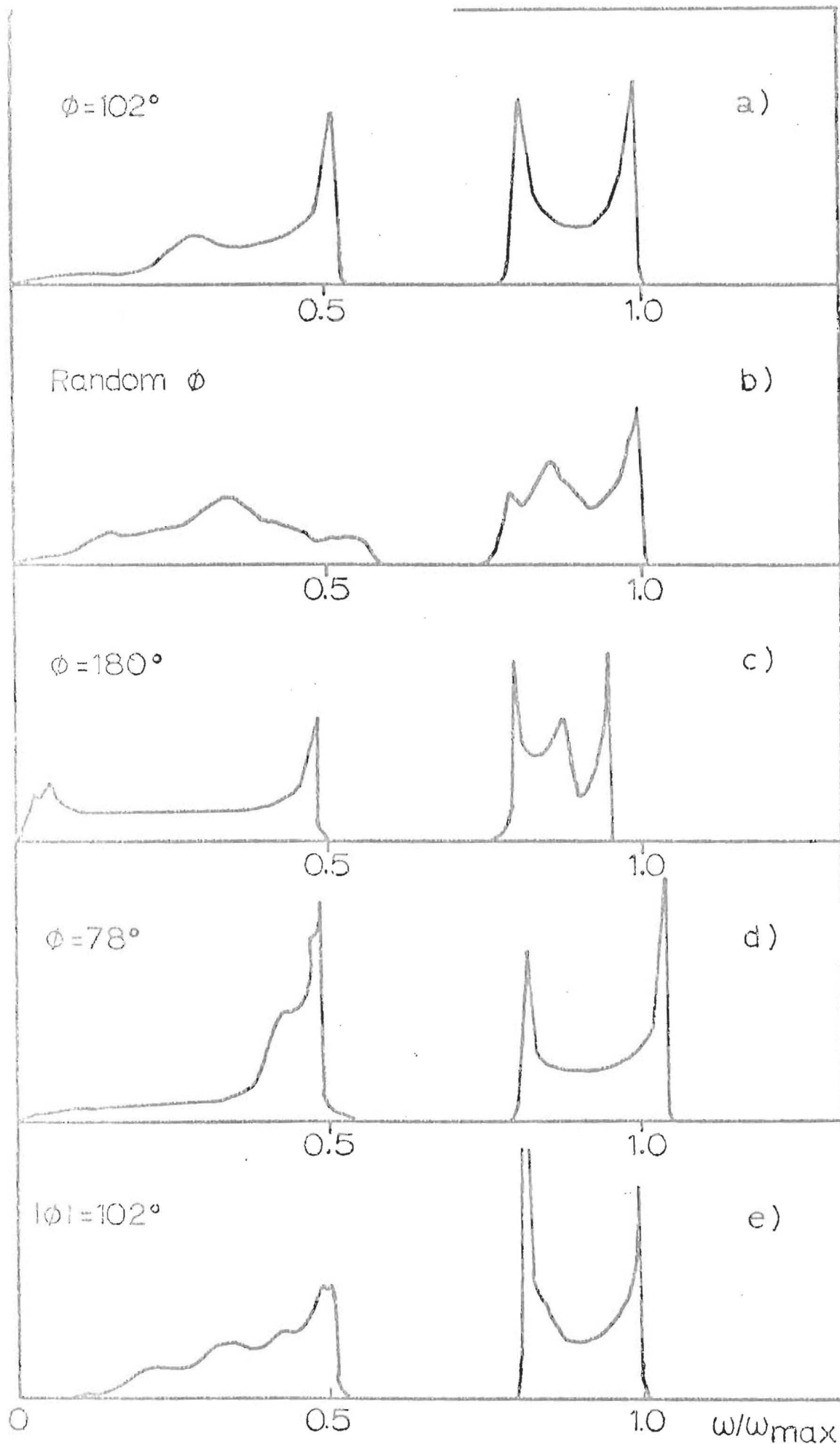


Figure 4.7 DOVS for the series of chains of varying dehdral angle

distribution described in the text.

Comparing their result to the DOVS of a flat zig-zag chain (Figure 4.7c), they identified this feature as evidence for the flat chain structure. The results of Figure 4.7, however, show that a constant dihedral angle of any magnitude will produce this result.

Having interpreted the experimental data in terms of a constant magnitude of ϕ in a-Se and a-Te, we note that the dynamical model used is too simple to provide information on the magnitude itself. We merely reiterate Robertson's argument that significant deviations from 102° are unlikely. Finally, the results suggest that a broader distribution of ϕ about 102° will be found in a-Te, within the limits of the roughly 10° rms distribution suggested by the calculations. Such a distribution will occur in a system of interacting chains relaxing to a structural energy minimum; the broader distribution is expected in a-Te because of the relatively stronger inter-chain forces in Te (see Table 4.1 and Lucovsky 1972).

4.4 INTER-CHAIN EFFECTS

Berton and Lasjaunais (1973) have reported an increase in the low-temperature (about 10K) specific heat of a-Se compared to trigonal Se and identified the magnitude of the specific heat in the latter as arising from the low frequency acoustic modes of the DOVS. Consider therefore modelling a-Se by trigonal Se with reduced inter-chain restoring forces. The DOVS for trigonal Se and Te with (a) the force constants of Table 4.1 and (b) the inter-chain force constants reduced by half are shown in Figure 4.8. The spectra were obtained by sampling 4120 points in the irreducible Brillouin zone and smoothing the resultant histogram. As expected, on increasing the inter-chain distance, i.e. decreasing the inter-chain forces, the chain twisting modes separate out from the lower band, moving to lower frequencies to produce an 'excess specific heat' at about 10K. In the limit of $\gamma=6=0$ they form the zero-frequency δ -function of Figure 4.6. The excess specific heat therefore is consistent with increased inter-chain separations in the amorphous phase, as are the density deficit and the IR and Raman data discussed in Section 4.1. Note how in our simple dynamical model calculation the optic mode band decreases in frequency as the inter-chain forces are reduced; a realistic model of the lattice dynamics should produce an increase in these frequencies, as revealed by the IR and Raman data for a-Se and a-Te. Lasjaunais (Private communication) has also found that the magnitude of the excess specific heat depends on the details of sample preparation. This lends further support to our explanation since details of the inter-chain correlations are inevitably dependant on the conditions of preparation.

No low temperature specific heat data for trigonal or amorphous Te have yet been reported, however our argument clearly predicts a similar effect to that found with a-Se due to the reduced inter-chain forces suggested by the Raman measurements of Brodsky et al (1972).

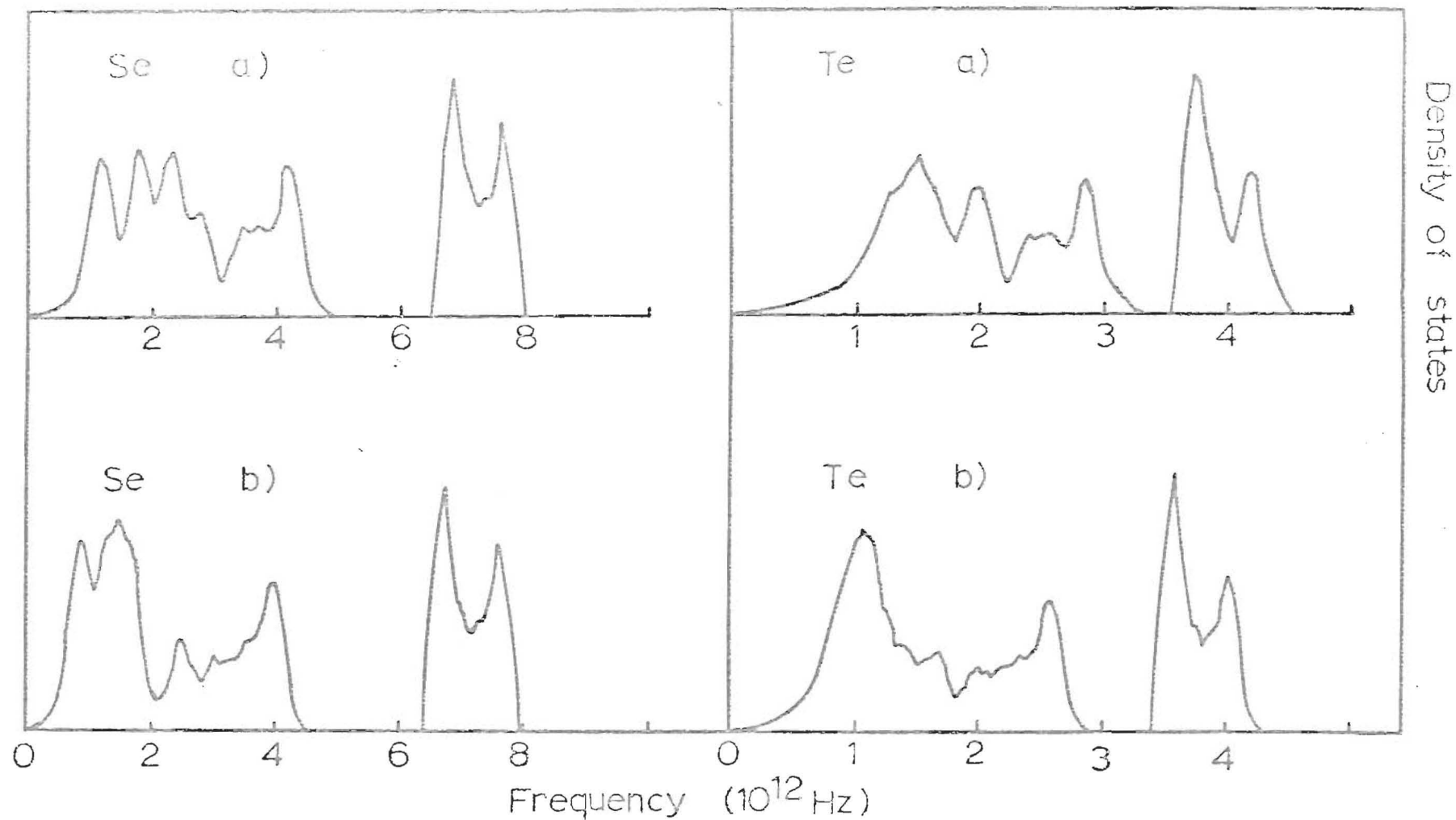


Figure 4.8 Vibrational spectra for trigonal Se and Te calculated with (a) the force constants of Table 4.1 and (b) the inter-chain force constants reduced by half.

Full calculations of the DOVS appropriate to structural models of a-Se/a-Te are not yet practical due to the lack of such models and a realistic description of the lattice dynamics of trigonal Se and Te. The inter-chain correlations are still rather uncertain, however the intra-chain structure seems to be well resolved.

5.1 THE BOND-CHARGE MODEL

In this chapter we present vibrational spectra appropriate to a-Ge calculated using a short-range version of Weber's (1974, 1977) adiabatic bond-charge model (SR BCM) of the lattice dynamics of Group IV semiconductors. A further refinement is the use of a series of seven CRN's with gradually varying structural characteristics. Since Weber's model describes the phonon dispersion in c-Ge very well, we expect it to provide a realistic description of the DOVS of the amorphous phase. The extent to which this aim is realised is discussed, as are general considerations of 'excess specific heat' in glassy solids, towards the end of this chapter.

The Born model of the lattice dynamics of c-Ge presented in Chapter 2, like all such simple models, does not adequately describe the transverse acoustic (TA) branches of the phonon spectrum (see Figure 2.2c). In the Group IV semiconductors, as in the zincblende structure crystals, these branches have very low frequencies and are very flat away from the zone-centre (Nilsson and Nelin 1971). Herman (1959) showed that to reproduce the high shear elastic constants and the TA flattening requires interactions out to sixth neighbours in a Born-like scheme. A shell-model fit to the dispersion curves was made by Cochran (1959), who modelled the valence electron response to the atomic motions with interactions involving massless shells concentric with the ion cores. Although the SR interactions are limited to nearest neighbours, the adiabatically moving shells transmit effective long-range interactions between the cores, producing flat TA branches. A more fundamental treatment of the lattice dynamics of c-Ge is Martin's (1969) dielectric screening model, based on the bond-charge theory of covalent solids developed by Phillips

(1968). The argument is that since c-Ge can be described as nearly-free-electron-like, the bare ion-ion interaction is expected to be screened by the diagonal elements of the inverse dielectric function $\epsilon^{-1}(\underline{k}+\underline{G}, \underline{k}+\underline{G}')$, as in simple metals. The existence of a band gap reveals incomplete screening, there being a net charge of $4/\epsilon_0$ at each ion. To achieve complete screening, Phillips located charges of $-2/\epsilon_0$ in the bonds, representing the effects of off-diagonal elements of ϵ^{-1} . Martin showed that the metal-like screening produces SR ion-ion forces and the BC interactions stabilise the diamond structure against shear. Martin's simple BCM involves a first neighbour central force and Coulomb interactions with the BC's fixed midway between the ions. The flat TA branches are not reproduced.

Weber's adiabatic BCM successfully incorporates certain elements of these preceding theories to give the most physical description of the phonon dispersion in the Group IV elements and III-V compounds to date. The metal-like binding is modelled by a central ion-ion force, the covalency being mirrored in SR and Coulomb interactions involving the BC's, which are now allowed to move adiabatically. Including an ion-BC central force (to stabilise the BC's at the bond-centres) and a BC-ion-BC angle bending force, while allowing the magnitude of the BC to vary, leaves four parameters to be determined by fitting to experiment. The ion-ion central force dominates the dispersion curves except the TA branches, which correspond to modes in which the bond length variations are very small. Thus in TA vibrations only very small forces are transmitted between the ions, which therefore vibrate like Einstein oscillators at frequencies determined only by the very weak effective ion-BC coupling. Dispersionless TA branches are formed, provided the effective ion-BC coupling is weak compared to the BC-BC coupling. In the long wavelength acoustic modes, the BC's move in phase with the ions and the strong BC-BC forces produce

the stability against shear.

Given that the adiabatic BCM describes the TA phonons so well in c-Ge, our chief motivation for applying it to a-Ge is a desire to explain the observed shift of the TA-like modes to lower frequencies in the amorphous phase. This shift has been detected in low-temperature specific heat data (King, Phillips and deNeufville 1974) and preliminary inelastic neutron scattering experiments (Axe, Keating, Cargill and Alben 1974); King et al have also shown the shift to be consistent with the Raman data. In detail, the c-Ge TA peak is broadened and uniformly reduced in frequency by a factor of about 15%. No such shift was observed in our Born-model results of Chapter 2. Comparison of the BCM calculations for a series of CRN's with full inelastic neutron scattering data for a-Ge should also provide an indication of which CRN best models the structure of a-Ge, as was attempted in Chapter 2. Finally, we expect the results of such a realistic calculation to reveal any important weaknesses in the use of simplified short-range dynamical models in DOVS calculations for disordered solids.

The coordinates of the series of CRN's used in the BCM calculations were generated by Beeman and Bobbs (1975) by restructuring the even-ringed Connell-Temkin (C-T) model. This effectively involves scrambling the centre of the model to introduce odd rings and increased angular distortions. Thus a series of five CRN's, C-T B to C-T F, were generated with increasing odd-ring concentrations and rms angular distortions. Supplementing the series with the Steinhardt model, yields seven equally-sized CRN's which are ideal for investigating the correlations between structure and vibrational (and electronic) properties. The important characteristics of the models are summarised in Table 5.1.

CRN	Number of atoms	$\frac{\Delta r_1}{r_1}$	$\Delta\theta$ (degrees)	Rings per atom			Wrong Bonds (%)
				5	6	7	
Connell-Temkin	238	0.013	9.1	0	2.432	0	0.0
C-T B	238	0.014	10.2	0.059	2.270	0.156	1.4
C-T C	238	0.014	10.6	0.158	2.090	1.313	3.0
C-T D	238	0.015	10.8	0.189	1.955	0.469	4.2
C-T E	238	0.015	11.6	0.336	1.506	0.808	7.0
C-T F	238	0.015	13.3	0.398	1.287	1.008	8.4
Steinhardt	201	0.007	6.8	0.430	0.889	0.989	9.9

Table 5.1 Structural characteristics of the seven CRN's used in our SR BCM calculations for a-Ge.

5.2 CALCULATIONS

Weber's original BCM involves long-range Coulomb interactions which cannot be included in our Recursion calculation. Instead we use an equivalent SR model, justified by the fact that the near-neighbour contribution to the Madelung constant constitutes about 8/9ths of the total (see Weber 1974, 1977). Coulomb interactions extending beyond nearest neighbours are neglected, the rest being absorbed into the SR forces. We write the crystal potential as

$$\begin{aligned}
 V = \frac{1}{2} \sum_A \left[4\alpha \sum_{AN} \left\{ \chi_{\alpha AN} (u_A - u_{AN}) \right\}^2 + \beta \sum_{B \geq BN} \left\{ \chi_{\alpha B} (u_A - u_{BN}) + \chi_{\alpha BN} (u_A - u_B) \right\}^2 \right. \\
 \left. + 4\gamma \sum_B \left\{ \chi_{\alpha B} (u_A - u_B) \right\}^2 \right] \quad (5.2.1) \\
 + \frac{1}{2} \sum_B \left[4\gamma \sum_{\alpha} \left\{ \chi_{\alpha B} (u_B - u_{\alpha}) \right\}^2 + \delta \left\{ r_0 \Delta \Theta_B \right\}^2 \right]
 \end{aligned}$$

where the summations are over adjacent atoms and bonds A, B and their like neighbours AN, BN. α and γ are atom-atom and atom-BC central force constants and β and δ resist changes in the BC-atom-BC and atom-BC-atom angles respectively, as shown in Figure 5.1. Since the latter is a 180° angle, the Keating scheme produces only a central force, so the δ contribution is in terms of the half-bond length r_0 and the change in the angle from 180° , $\Delta \Theta_B$. The force tensors involving α , β and γ are of the same form as before; the terms in δ are

$$\Phi_{x_j}^{\delta} (A1, A2) = \delta \left[\delta_{xy} - \chi_{\alpha A1} \chi_{\alpha A2} \right] \quad (5.2.2a)$$

$$\Phi_{x_j}^{\delta} (A1, B) = -2\delta \left[\delta_{xy} - \chi_{\alpha A1} \chi_{\alpha B} \right] \quad (5.2.2b)$$

where B denotes the bond between atoms A1 and A2 and δ_{xy} is the

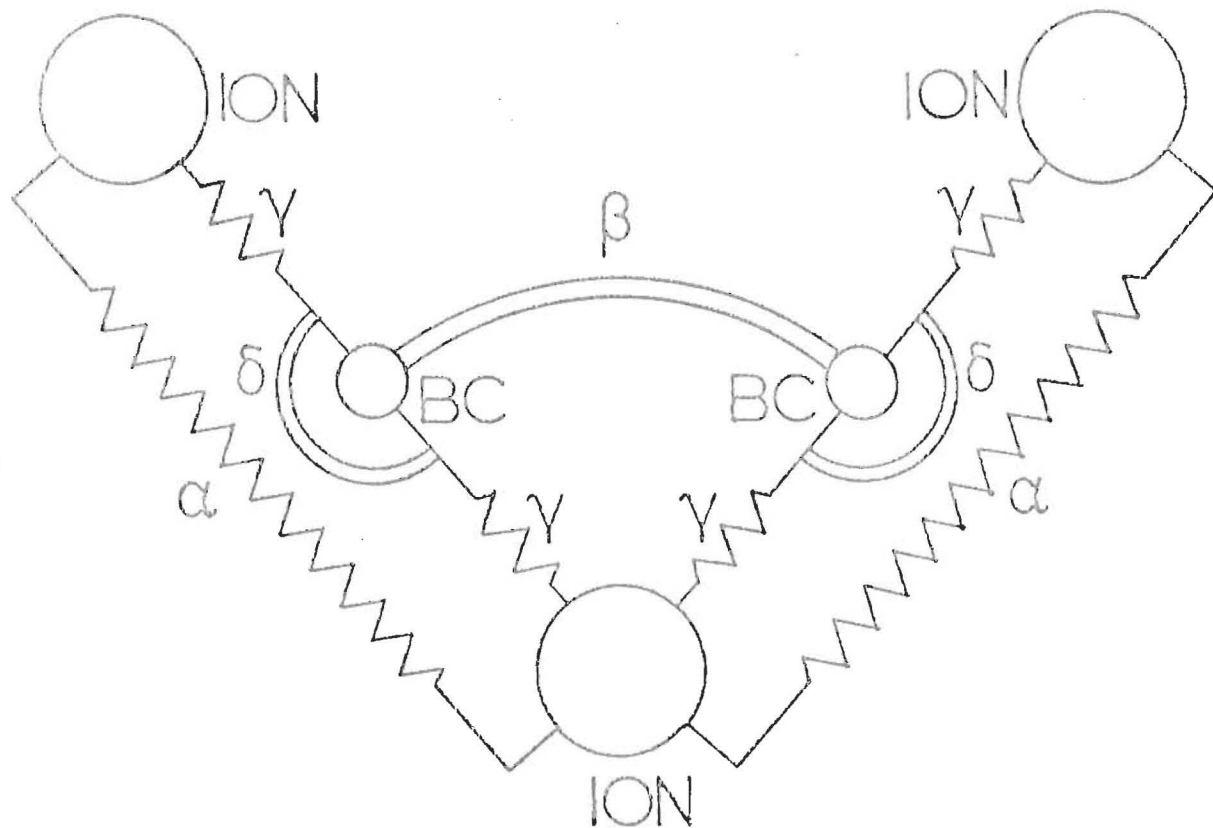


Figure 5.1 The force constants α , β , γ and δ of our short range version of Weber's adiabatic BCM.

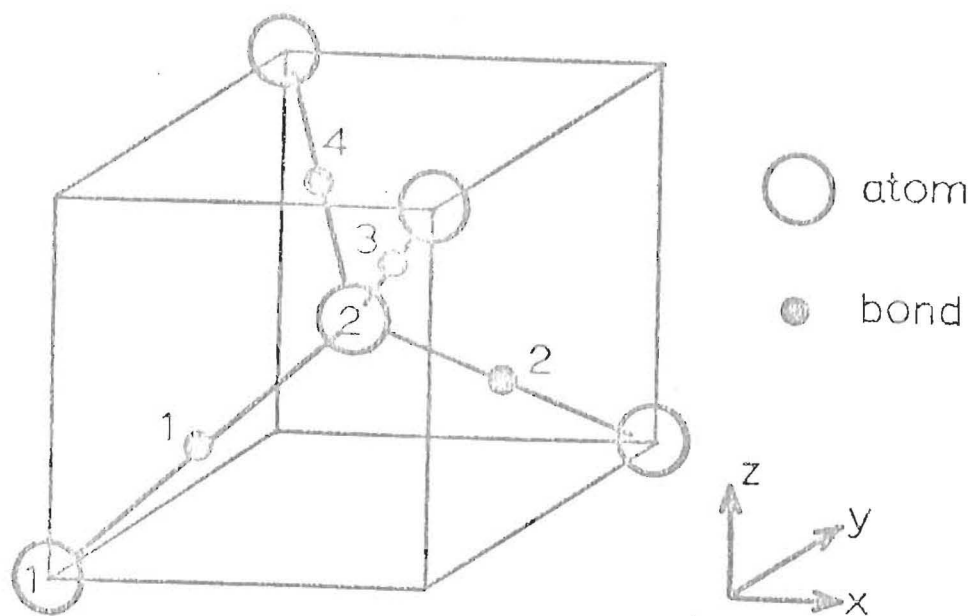


Figure 5.2 The unit cell of the diamond-cubic structure illustrating the basis of two atoms and four bonds.

Kronecker delta.

For the case of two 'atomic' species, the dynamical matrix equations can be written

$$\begin{aligned} \underline{\underline{A}} \underline{a} + \underline{\underline{C}} \underline{b} &= M \omega^2 \underline{a} \\ \underline{\underline{C}}^{\dagger} \underline{a} + \underline{\underline{B}} \underline{b} &= m \omega^2 \underline{b} \end{aligned} \quad (5.2.3)$$

where $\underline{\underline{A}}$, $\underline{\underline{B}}$, $\underline{\underline{C}}$ denote atom-atom, BC-BC, atom-BC dynamical matrices, $\underline{a}$, $\underline{b}$ denote atom, BC displacements and M , m denote atom, BC masses respectively. The matrices are derived in the usual manner. In the adiabatic approximation the BC mass is zero so the dynamical matrix put into the secular equation 1.2.6 is given by

$$\underline{\underline{D}} = \underline{\underline{A}} - \underline{\underline{C}} \underline{\underline{B}}^{-1} \underline{\underline{C}}^{\dagger} \quad (5.2.4)$$

Since the unit cell of the diamond structure contains two atoms and four BC's, as shown in Figure 5.2, the dimensions of the matrices are $\underline{\underline{A}}(6 \times 6)$, $\underline{\underline{B}}(12 \times 12)$, $\underline{\underline{C}}(6 \times 12)$. The values of these matrices at the point $\underline{k}=(k_x, k_y, k_z)$ in the FCC zone are given in Appendix 5.2.

The four parameters of the SR BCM cannot be determined by fitting the Raman frequency and the three elastic constants since α and γ enter the expressions for these quantities in the same linear combination (Weber 1977). They were obtained by least-squares fitting the experimentally measured phonon frequencies (Nilsson and Nelin 1971) at the following points;

$$\begin{array}{lll} \Gamma(0.0, 0.0, 0.0) & & \\ (0.5, 0.0, 0.0) & (0.3, 0.3, 0.0) & (0.3, 0.3, 0.3) \\ X(1.0, 0.0, 0.0) & (0.6, 0.6, 0.0) & L(0.5, 0.5, 0.5) \end{array}$$

in units of $2\pi/a$, where a is lattice constant defined in Figure 1.2.

Extra weight was placed on the TA frequencies to ensure the correct force constant ratios required to reproduce them well. The parameters are

$$\alpha=0.1416 \quad \beta=0.3441 \quad \gamma=0.0057 \quad \delta=0.1544 \quad (5.2.5)$$

in units of 10^5 Nm^{-1} . The smallness of γ emphasises the mechanism of TA flattening in Weber's model. The dispersion curves along the (100), (110) and (111) directions of the zone obtained with these parameters are compared with the experimental points in Figure 5.3; the SR BCM compares very well with the full model (see Weber 1977).

One further modification is required before the BCM can be used in our Recursion calculation. Equation 5.2.4 shows that $\underline{B}$ must be inverted to derive the final dynamical matrix $\underline{D}$, a prohibitive step for a calculation appropriate to a CRN because of the size of this matrix. The inversion can be avoided by allowing the BC's to have a small but finite mass. As long as $m/M < 0.1$, the lower six phonon branches are unaffected. In this case the Fourier transformed dynamical matrix is given by

$$\underline{D} = \begin{vmatrix} \frac{1}{M} \underline{A} & \frac{1}{(mM)^{1/2}} \underline{C} \\ \frac{1}{(mM)^{1/2}} \underline{C}^+ & \frac{1}{m} \underline{B} \end{vmatrix} \quad (5.2.6)$$

The dynamical matrix used in the Recursion calculation is constructed in the usual manner from the cluster coordinates, assuming all bond lengths to be unchanged and the equilibrium positions of the BC's to remain mid-way between the atoms. The modifications to the method involve treating the BC's as a second atomic species, more than doubling the original number of sites. The local DOVS are of course only calculated for atoms. Figure 5.4 compares the result of our Recursion calculation for a spherical 248-atom cluster with the diamond-cubic structure with the result obtained by integration over the Brillouin zone. The correct positions,

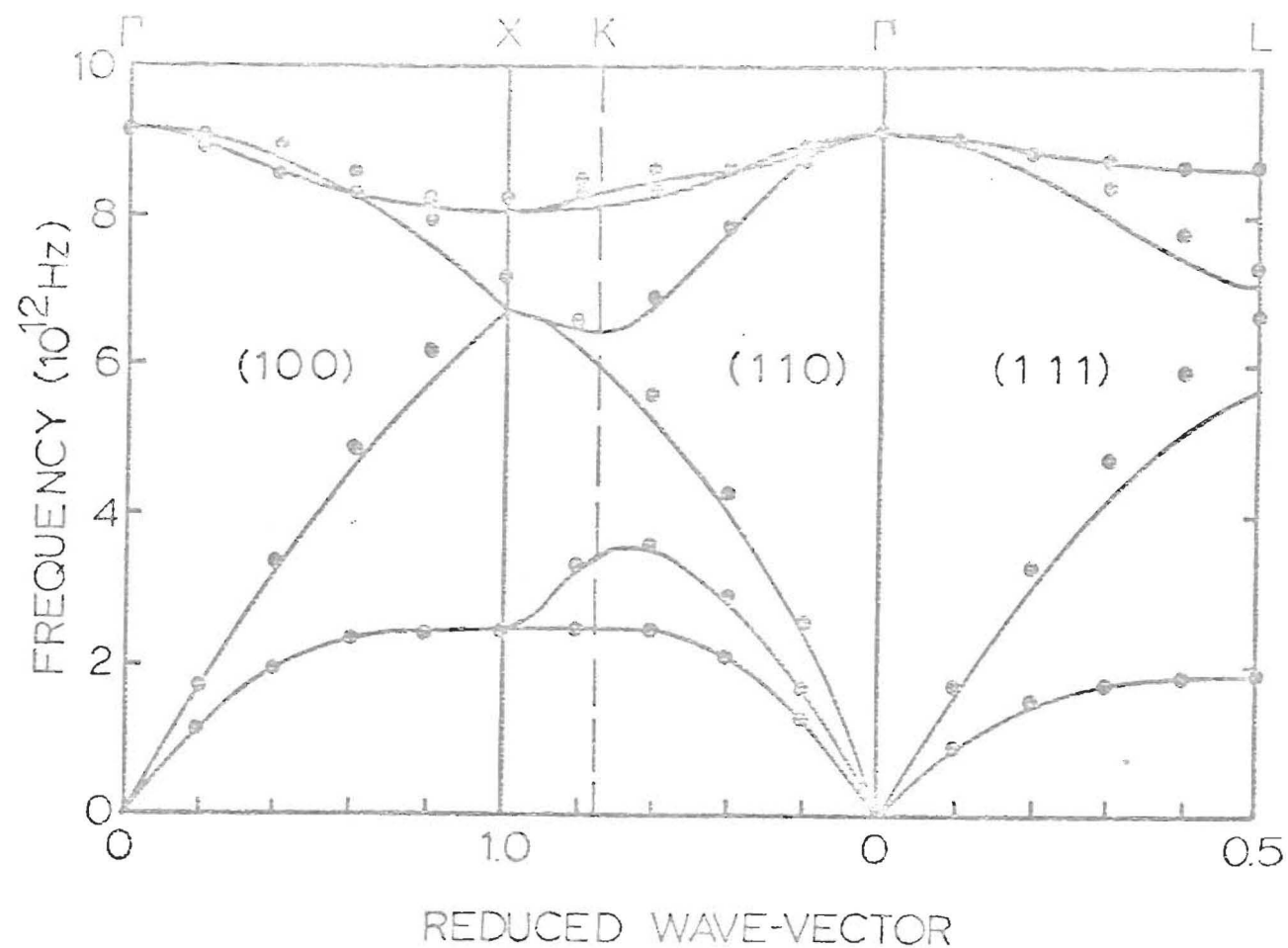


Figure 5.3 Comparison of the SR BCM phonon dispersion curves (solid lines) along the symmetry axes of the FCC Brillouin zone of c-Ge with the experimental points obtained by Nilsson and Welin(1971).

weights and general shapes of the features in the reciprocal space result are well reproduced. The continued fraction expansions are calculated to 100 levels; although this may seem large, note that the cluster contains about 600 sites and two-thirds of the spectrum (the 'bond' bands) remains unused. The inadequacy of calculations to fewer levels is emphasised by the plot to 50 levels shown in Figure 5.5. The ratio $m/M=0.01$ was chosen to ensure a wide enough band gap between the 'atom' and 'bond' modes to prevent any interference between them, even when broadened in the CRN results. A smaller ratio would increase the number of levels needed for adequate resolution (and hence the computation time) even further.

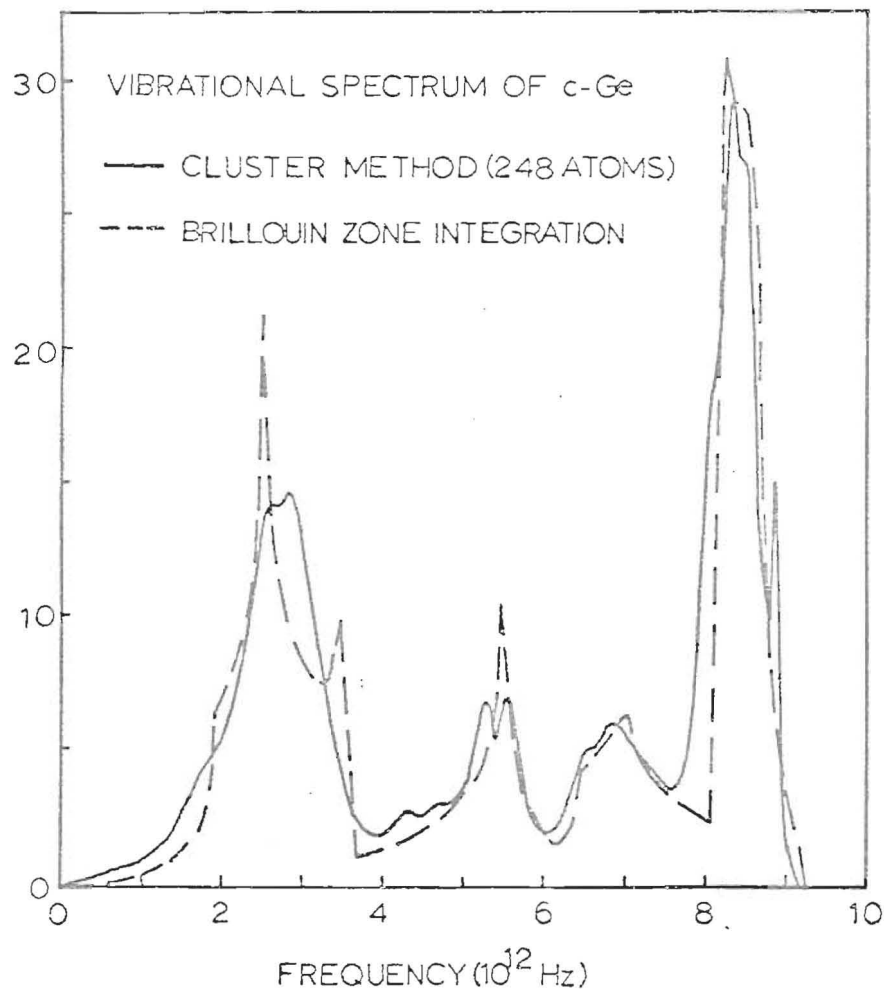


Figure 5.4 Comparison of c-Ge DOVS calculated by the Recursion method (100 levels) and integration over the Brillouin zone.

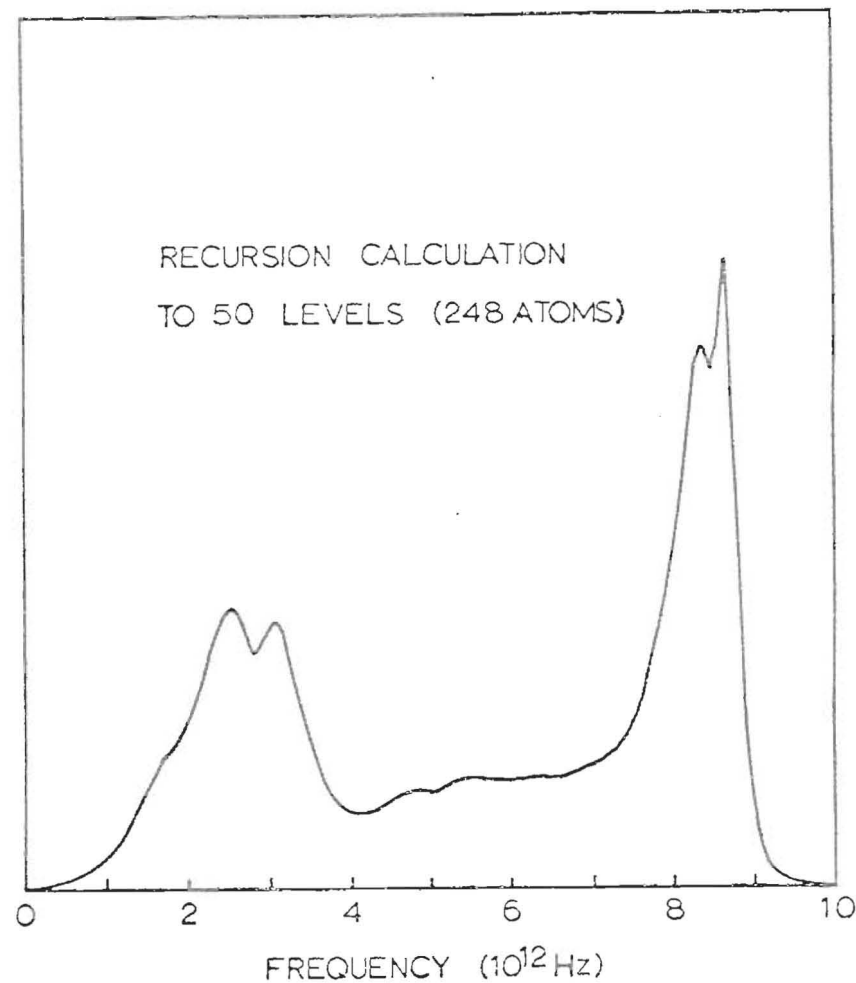


Figure 5.5 The DOVS for c-Ge obtained from the Recursion method accurate to 50 levels, illustrating the lack of convergence.

5.5 RESULTS

The results of the first application of our SR BCM to the series of CRN's of Table 5.1 are shown in Figure 5.6. The diamond-cubic structure result is repeated for comparison with those for the Steinhardt model, the original C-T model and the series C-T B to C-T F. There are no significant differences between the averages over 5 and 10 central sites of the network; these results are all 10 atom averages to 100 levels. The models are in order of increasing rms bond angle distortion.

The most obvious features of the results are the broadening of the TA- and TO-like peaks with the angular distortions and a smoothing of the details of the LA+LO-like region. There is no LA-LO dip in any of the CRN results except that for the Steinhardt model, which has unrealistically small angular distortions. On the other hand, a definite TA-LA-like dip is preserved. The simultaneous broadening of the TO- and TA-like peaks can be traced to the equivalent distortions of the atom-atom and BC-atom-BC angles respectively, by the same argument presented in Chapter 2 for the broadening of the TO-like peak in the case of central forces only. Surprisingly, there is no topological dependence of the spectra, a completely opposite result to that obtained for the Born model in Chapter 2. The lack of topological dependence is emphasised by the position of the Steinhardt CRN result in Figure 5.6; it contains the largest concentration of 5-membered rings yet fits into the sequence between the diamond-cubic and original C-T structures. It appears that atomic motions due to forces of shorter range than the distances across the rings in these structures are sensitive to the orders of those rings. On the other hand, in the BCM the BC-mediated forces are of significantly longer range than such distances, thus no ring-order dependence arises. The wider implications of this result are discussed in Chapter 8.

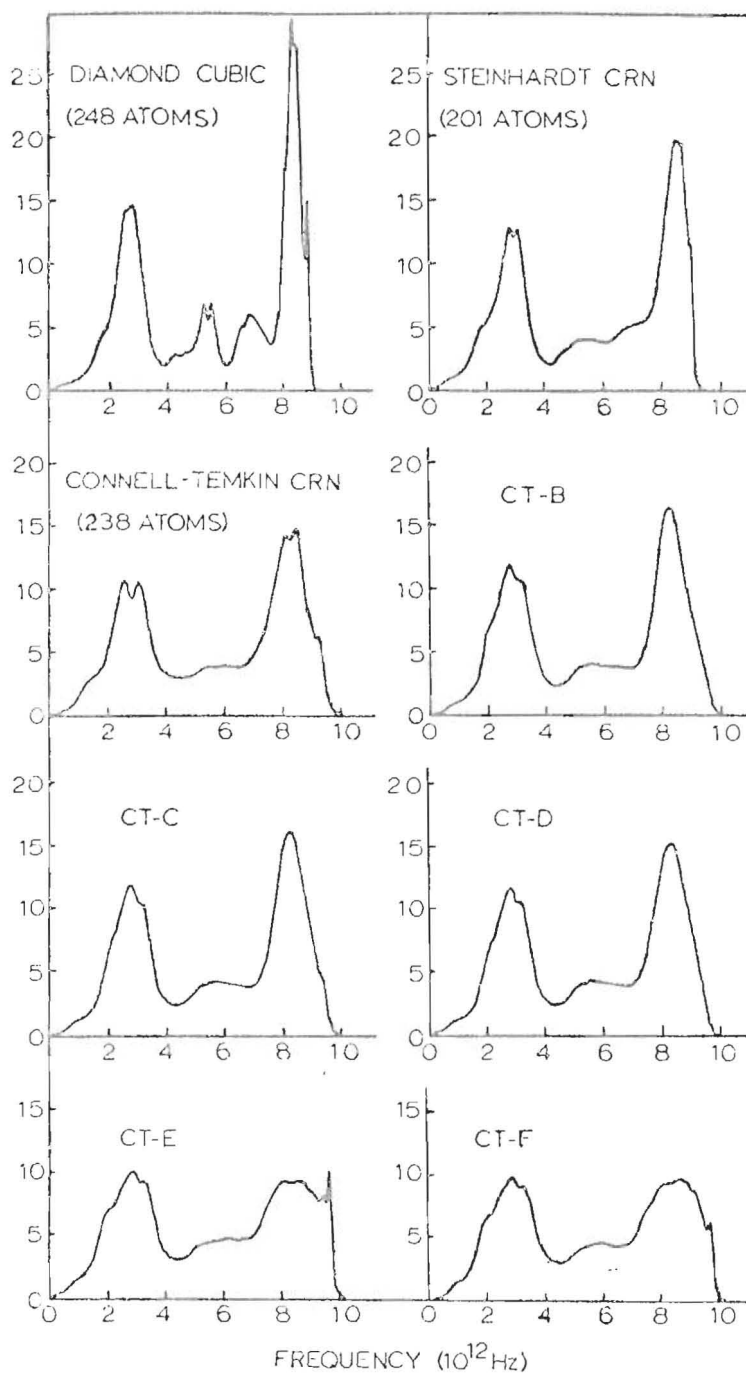


Figure 5.6 DOVS for the series of CRN's of Table 5.1 calculated by the Recursion method using the force constants of equation 5.2.5.

A careful examination of these results reveals that the TA shift to lower frequencies has not been reproduced in the CRN spectra. The SR BCM does, however, provide a simple means of reproducing this shift; by reducing the central atom-BC force constant γ to $0.0025 \times 10^5 \text{ Nm}^{-1}$ the centre of gravity of the TA-like peak is reduced by about 15%, as shown in Figure 5.7. These results are now ready for comparison with experimental data. A discussion of the seemingly arbitrary reduction of γ to fit the known data is given subsequently.

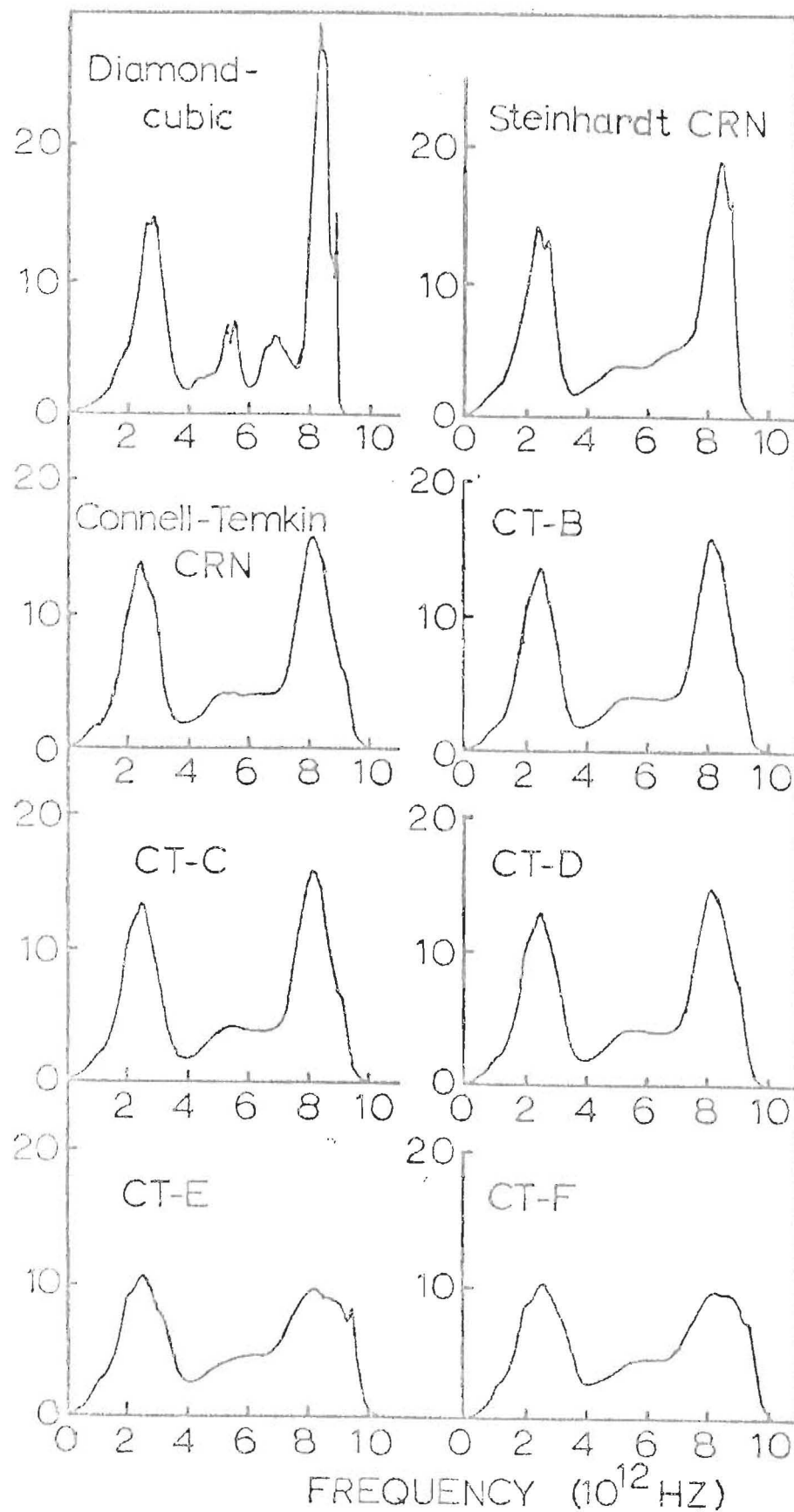


Figure 5.7 The same as Figure 5.6 but with the force constant γ reduced to shift the CRN TA-like peaks to lower frequencies.

5.4 COMPARISON WITH EXPERIMENT

No direct measurement of the full vibrational spectrum of a-Ge by inelastic neutron scattering has yet been made, so no structural data can be deduced from the results of Figure 5.7. Our apparent 'success' in comparing in detail the calculated DOVS of Chapter 2 with the IR and Raman spectra of a-Si and a-Ge prevents us from repeating the process here. All that can be said at this stage is that the RDF comparisons of Beeman and Bobbs (1975) and the results of electronic structure calculations (see Chapter 6) suggest that the structure of a-Ge is an intermediate of the C-T D and C-T E models.

We can, however, learn something of the Raman coupling to the DOVS in a-Ge without making any assumptions as to the detailed nature of the displacement induced polarisability in the solid (c.f. Alben et al 1975). Assuming the breakdown of all selection rules so that light is scattered from all normal modes, Shuker and Gammon (1970) gave the following expression for the Stokes intensity for first-order scattering;

$$I(\omega) = \sum_b C_b(\omega) \left[1 + n(\omega, T) \right] \frac{1}{\omega} g_b(\omega) \quad (5.4.1)$$

where C_b is the coupling for phonon branch b , $n(\omega, T)$ is the Einstein-Bose function and $g_b(\omega)$ is the density of states for branch b . In Figure 5.8a we present the reduced Raman spectrum

$$I_R(\omega) = \omega I(\omega) / \left[1 + n(\omega, T) \right] = \sum_b C_b g_b(\omega) \quad (5.4.2)$$

obtained by Lannin (1973), which the theory indicates to be simply related to the densities $g_b(\omega)$ by the coupling constants C_b . This picture is supported by the plot of the coupling

$$C(\omega) = g(\omega) / I_R(\omega) \quad (5.4.3)$$

shown in Figure 5.8b. The broken line is $g(\omega)$ for the C-T D model, from which $C(\omega)$ was deduced. $C(\omega)$ divides into four regions, each roughly centred on the vertical lines indicating the corresponding type of vibration in the crystal. The result is therefore consistent with different degrees of coupling to modes of different character and indicates that the crystalline mode character is rather well preserved in the amorphous phase. The spike at the upper edge of $C(\omega)$ arises from the broader bandwidth of the Raman data and is therefore probably due to background intensity and/or second order scattering. Neither the experimental nor theoretical curves are sufficiently reliable at lower frequencies to support comment on the validity of ω^2 behaviour of $C(\omega)$ in the Debye-like region (see King et al 1974).

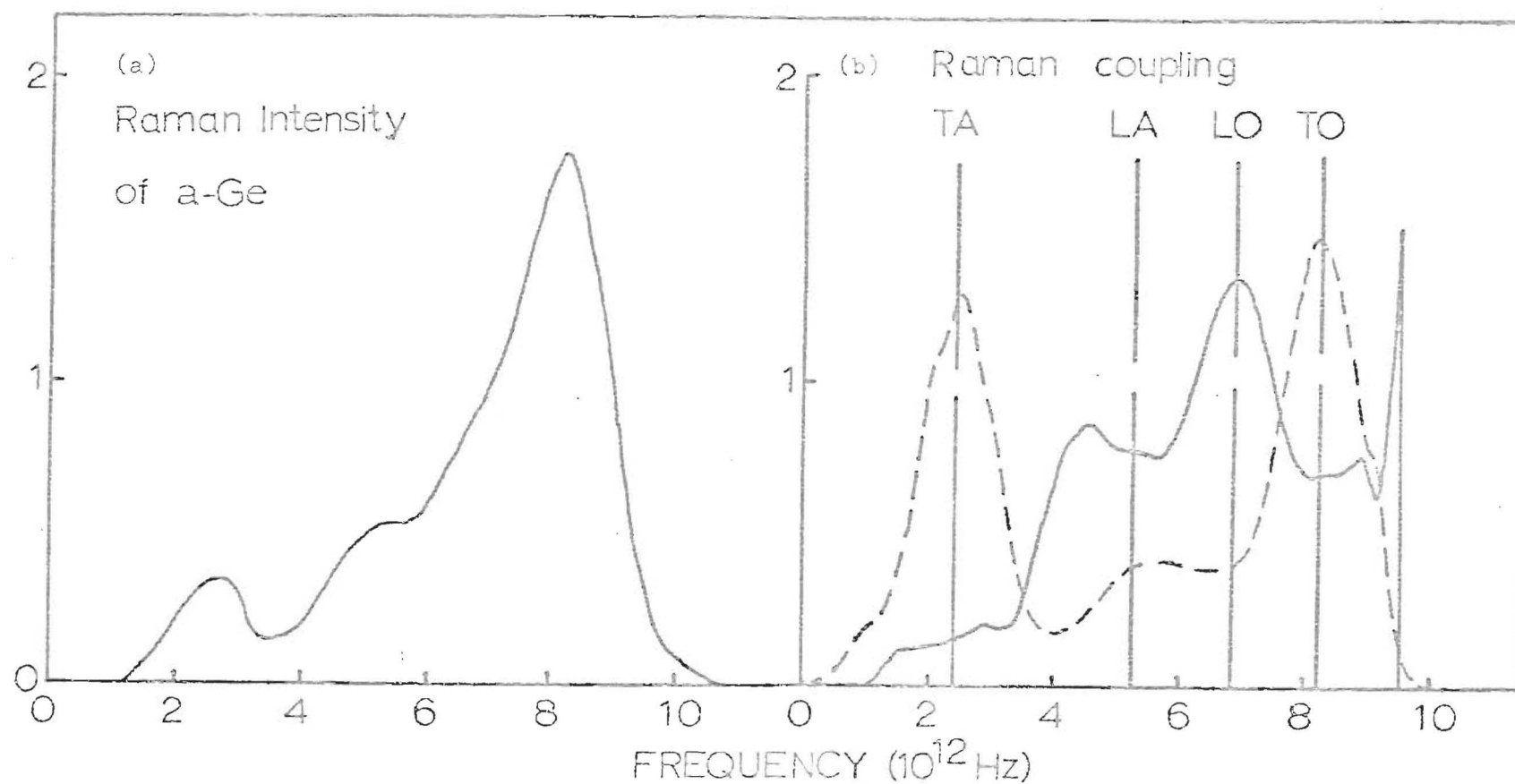


Figure 5.8 a) The experimental Raman intensity of a-Ge (after Lannin 1973).

b) The Raman coupling $C(\omega)$ as a function of frequency (full line) compared to the DOVS for the C-T D model of a-Ge (broken line) from which it was derived.

5.5 BOND-CHARGES IN AMORPHOUS Ge

Consider now the efficacy of reducing the atom-BC force constant to reproduce the experimentally observed shift of the TA-like peak in a-Ge. In Weber's full BCM the flat TA branches have frequencies which are effectively proportional to the magnitude of the bond-charge Z_b . Fitting the experimental data produces values of Z_b in reasonable agreement with Phillips' theory for both Group IV and III-V semiconductors (Weber 1977, Rustagi and Weber 1976). But why should Z_b decrease by about 15% in the amorphous phase?

It is important to recognise that Z_b is an effective point charge representing the distribution of charge built up in the region of lower potential between nearest neighbour atoms. In terms of orbital overlap, the bond-charge is defined as the charge density in excess of the atomic charge densities. In c-Ge, pairs of sp^3 orbitals point towards each other as in Figure 5.9a but due to the angular distortions in a-Ge, if perfect sp^3 hybridisation is retained, the overlap will be reduced and the bond-charge will be more diffuse, as illustrated in Figure 5.9b. To maximise the bonding energy, however, the orbitals will tend to point towards each other, yet exchange repulsion tends to maintain the tetrahedral angles. d-hybridisation is necessary to construct four orbitals pointing towards the neighbours of each atom in systems with angular distortions as large as in a-Ge. We may expect the exchange repulsion, however, to promote a general spreading out of the bond-charge.

A more diffuse bond-charge as a result of angular distortions in the amorphous phase is consistent with a smaller effective charge Z_b in the corresponding dynamical model. We therefore expect the observed weaker bonding in the metastable amorphous phase and the occurrence of a semiconductor-metal phase transition at a lower pressure compared to that of c-Ge (Minomura et al 1974), since a smaller Z_b provides less stability

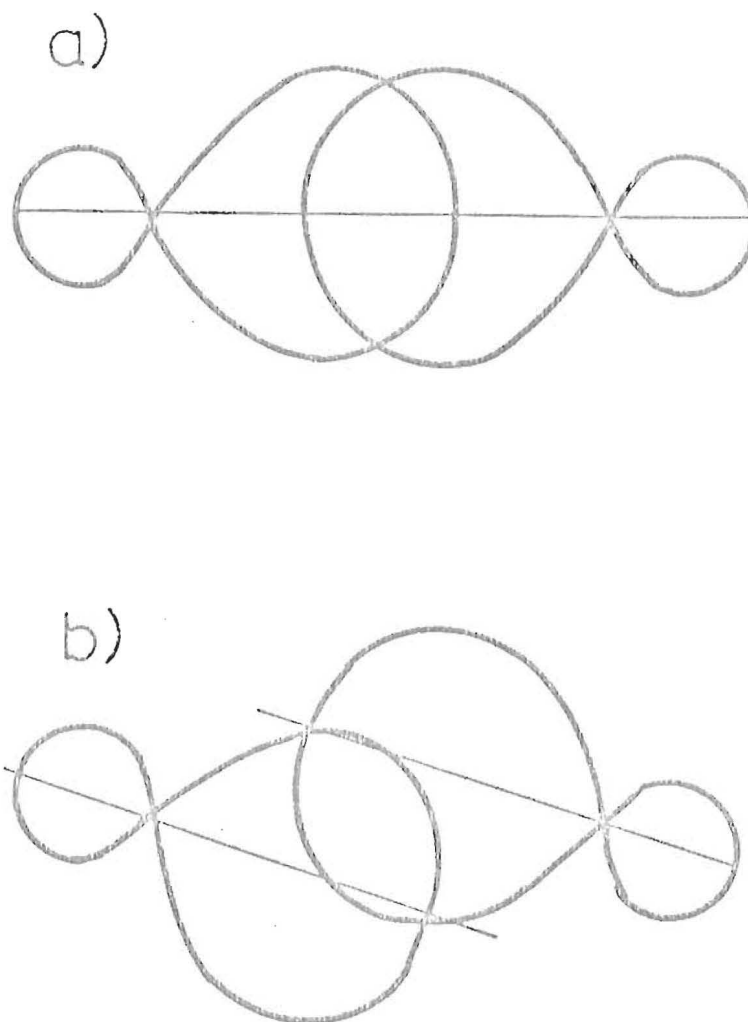


Figure 5.9 a) Schematic diagram of sp^3 orbital overlap in crystalline germanium.
b) Reduction in overlap caused by angular distortions.

against shear. It is not unreasonable that this should be 15% effect in the bond bending mode frequencies, but there is no obvious calculation that would verify our belief that angular distortions are the only cause of the TA shift. In any event, it is very doubtful that the insight gained by reliable charge-density calculations for, say, the diamond-cubic and ST-12 Ge structures would merit the effort involved. For this reason in particular, no such calculation was performed.

5.6 EXCESS SPECIFIC HEAT IN GLASSY SOLIDS

An excess specific heat relative to their crystalline counterparts at temperatures of about 10K seems to be a property common to a great many glassy solids. For example, excess specific heats have been observed in each of the elemental amorphous semiconductors Ge (King et al 1974), As (Wu and Luo 1973) and Se (Berton and Lasjaunais 1973). In the Debye approximation of a parabolic DOVS, the specific heat C is proportional to T^3 at low temperatures i.e. the Debye regime. Thus a peak in the experimental plot of C/T^3 against T identifies a pronounced peak in the vibrational spectrum. For instance the TA peak for c-Ge at about 22K reduces to one at about 18K for a-Ge.

Since we have attributed the excess specific heat in a-Ge to angular distortions and in a-Se to increased inter-molecular separations, these two mechanisms may form the basis of a qualitative explanation of this effect as a natural consequence of structural disorder. The loss of long-range order will promote angular distortions in systems of higher coordination like a-Ge and increased molecular separations in systems of lower coordination like a-Se. A system such as a-As, however, may be expected to exhibit the effect for both reasons; in Chapter 3 we saw that a-As exhibits a 10° rms angular distortion and increased inter-layer separations. To determine which has the greater effect on the low-temperature specific heat, we require a more complete description of the vibrational behaviour of rhombohedral As. In spite of this, our simple qualitative mechanisms for the excess specific heat in a-Ge and a-Se provide a reasonable basis for asserting that whenever this effect occurs, it is a logical consequence of structural disorder.

6.1 INTRODUCTION

In this chapter we present, by way of completeness, calculations of the valence band densities of states (VB DOS) appropriate to the series of CRN models of a-Si/a-Ge of Table 5.1. Previous calculations by Kelly and Bullett (1976a) have already shown that network topology is the main determinant of the shape of the VB DOS and suggested that the typical structure of a-Si/a-Ge is that of the Polk model with fewer odd-membered rings. Our results enable us to define better the typical structure of a-Si/a-Ge and present some interesting implications for the consideration of topological disorder in other such systems.

Experimental data on the VB DOS of crystalline and amorphous Si and Ge have been provided by XPS (Ley, Kowalczyk, Pollak and Shirley 1972, Eastman, Freeouf and Erbudak 1974) and optical measurements (Pierce and Spicer 1972). The data of Ley et al are reproduced in Figure 6.1. Within the one-electron approximation, the photo-emission intensity at energy E due to photons of energy $\hbar\omega$ may be approximated by

$$I(E) \propto n^i(E) n^f(\hbar\omega - E) \sigma(\hbar\omega, E) \quad (6.1.1)$$

where n^i denotes density of initial states, n^f denotes density of final states (including that of the photo-electron) and σ denotes the emission cross-section. For large $\hbar\omega$ the final states are featureless free-electron-like bands, so $I(E)$ reflects the VB DOS modulated only by the photo-emission cross-section. Thus the peak heights all differ in Figure 6.1 by virtue of the differing cross-sections for 3s, 3p, 4s and 4p electrons. Despite this, the results show that the gross features of the VB DOS are the same for both phases. As in the phonon case, this can be attributed to

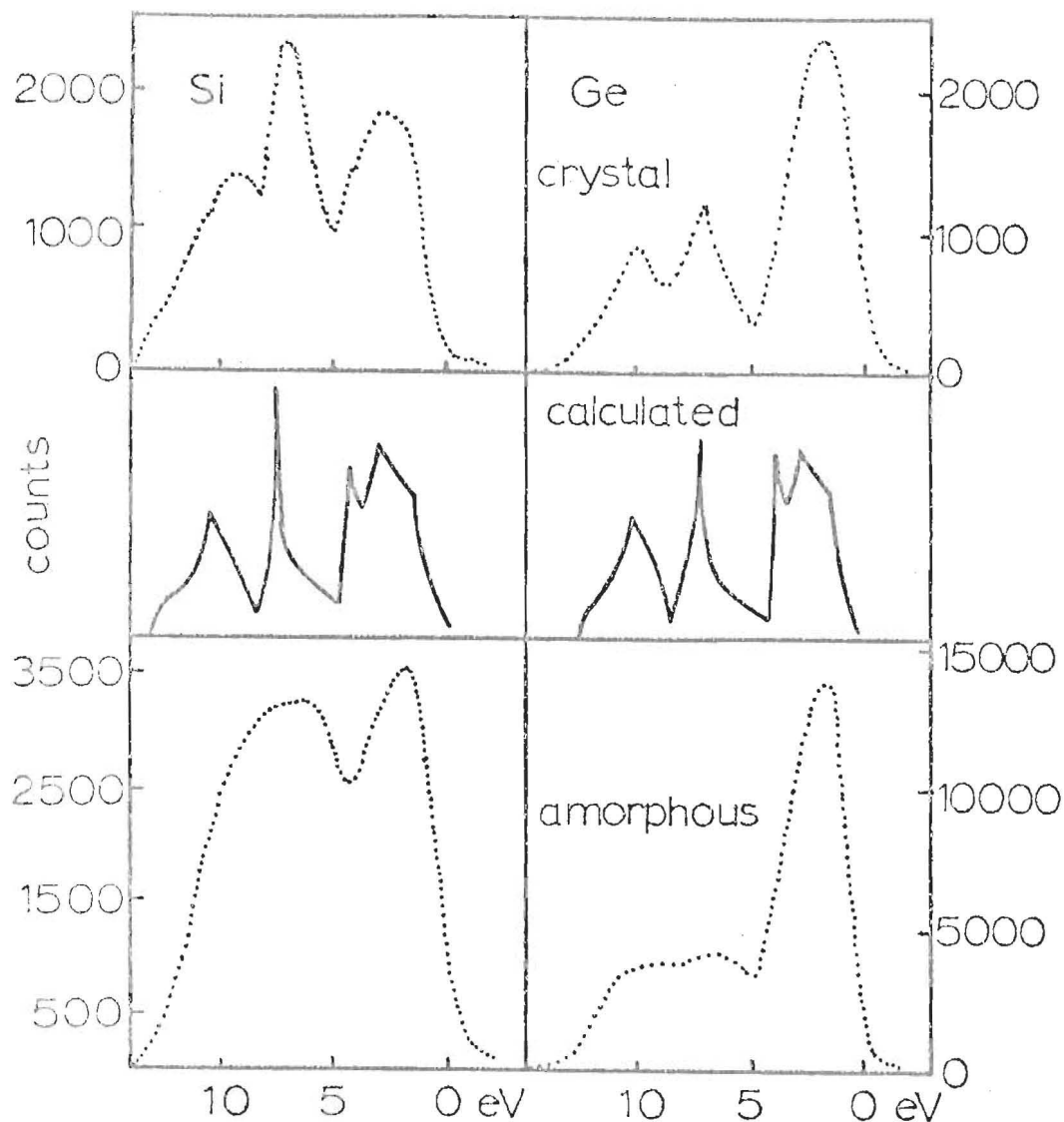


Figure 6.1 Valence band XPS data for crystalline and amorphous Si and Ge (after Ley et al 1972).

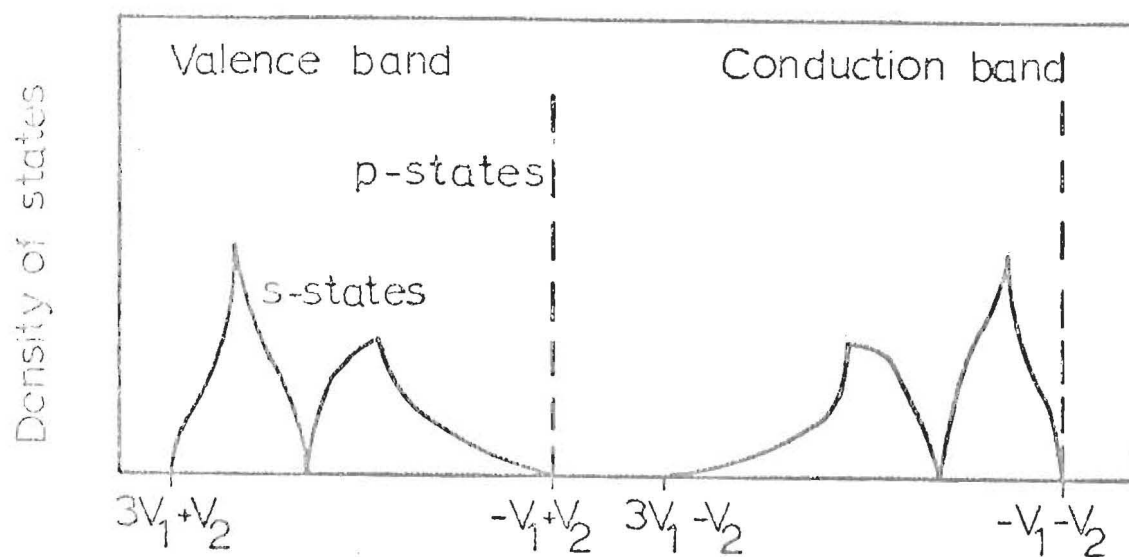


Figure 6.2 Electronic density of states for Si/Ge calculated using the Weaire-Thorpe tight-binding Hamiltonian.

the retention of the crystalline short-range order in the amorphous phase. The VB DOS of crystalline Si and Ge as calculated by Joannopoulos and Cohen (1973) using the Empirical Pseudopotential Method (EPM) are also included in Figure 6.1 for reference. In detail, the differences between the crystalline and amorphous phases are;

1. The p-peak at the top of the VB is preserved but skewed over towards E_F with a perceptibly reduced half-width.
2. A detectable minimum between s-like and p-like states is retained.
3. The low-lying s-states are smoothed considerably, but a small dip is detectable.

A very fruitful theoretical approach to these phenomena is the simple tight-binding theory of Weaire et al (Weaire and Thorpe 1971, Thorpe and Weaire 1971, Weaire, Thorpe and Heine 1972, Thorpe, Weaire and Alben 1973). Their Hamiltonian includes non-zero, structure-independent matrix elements only between sp^3 orbitals associated with the same atom i (V_1) or the same bond j (V_2) i.e.

$$H = \sum_i V_1 |i\rangle\langle i| + \sum_j V_2 |j\rangle\langle j| \quad (6.1.2)$$

The energy level spectrum for the diamond-cubic structure calculated using this Hamiltonian with $|V_2|/|V_1| > 2$ is presented in Figure 6.2. This simple model gives a reasonable description of the valence band of crystalline Si/Ge (see Figure 6.1) but interactions out to much further neighbours would be required for an adequate description of the more extended conduction states. The utility of the approach lies in its analytic tractability. For example, Weaire and Thorpe have shown that the bounds on the valence and conduction bands shown in Figure 6.2 hold for any four-fold coordinated structure, thus explaining the existence of a band-gap in amorphous Si/Ge. They have also quantitatively related

the s-state parts of the valence and conduction bands to the simple s-band Hamiltonian discussed in Chapter 2, thereby linking both the vibrational and electronic properties to the structure of the solid. We therefore expect a significant filling of the s-state dip in the amorphous phase VB DOS to arise from the presence of odd-membered rings, as discussed in the DOVS case for a-Ge in Chapter 2. Weaire and Thorpe have also proved that the p-state ϕ -functions at the tops of the bands in Figure 6.2 depend only on four-fold coordination, hence explaining the preservation of the VB p-peak in the amorphous phase. To see this for the VB case, consider how many orthogonal pure p-bonding wavefunctions can be constructed; without matching conditions, there are $3N$ orthogonal p-states in all (3 per atom) but the requirement of perfect bonding everywhere leads to the $2N$ constraints that the coefficients of the orbitals along any path are equal in magnitude with the sign sequence ...+-+--+... i.e. one matching condition per bond and two bonds per atom. Thus there are at least $3N-2N=N$ pure p-bonding functions. They form a p-state ϕ -function containing one state per atom at the top of the VB. For the conduction band case, pure antibonding p-states are considered.

Complementary to the work of Weaire et al are the EPM calculations of the electron densities of states of polymorphs of Si and Ge reported by Joannopoulos and Cohen (1973). Correlating differences in the electronic properties of the different polymorphs with their structural characteristics, leads by analogy to interpretation of the electronic features of the amorphous phase. These authors made use of the transferability of the pseudopotential form factor to calculate electron densities of states for both Si and Ge atoms on the diamond-cubic, wurtzite, BC-8 and ST-12 lattices. They found a smoothing of the VB s-states by the

* Note that some arbitrariness occurs in the interpolation of form factor data for an atom in different structures, as discussed for Ge by Aymerich and Smith (1973); however this is unlikely to effect the general conclusions presented here.

odd rings present in the ST-12 structure and that the conduction band DOS is smoothed in the more disordered structures, in agreement with the optical data for the amorphous phase. Although the VB p-peak is preserved in all of the spectra, it is skewed slightly to higher energies for those structures with eclipsed second neighbour bonds (i.e. wurtzite and ST-12). Now, the broadening of the p-state δ -function in the Weaire-Thorpe model is produced by second neighbour interactions (see for example Kelly and Bullett 1976a) and is therefore sensitive to the dihedral angle distribution. Thus, it appears that a larger concentration of eclipsed bonds, associated with odd rings in the ST-12 structure and random networks, leads to an increase in the number of p-states at higher energies. No convincing explanation of this has yet been given; we may naively expect the metastability of the amorphous phase to be mirrored by an increase in the average energy of the p-states, which localise electrons in the bonds, since it is the bond-charges which provide the stability of the structure against shear. There may be some subtle connection between this behaviour and the TA-shift of a-Ge discussed in Chapter 5 since both phenomena are intimately connected with the bonding electrons.

In the next section we describe our calculations and how much they depend on the previous work of Kelly and Bullett. The VBDOS results for our series of CRN's using two parameter sets are presented in Section 6.3 and discussed in Section 6.4.

6.2 CALCULATIONS

A convenient way of generating the valence bands of a tetrahedrally coordinated semiconductor is by consideration of a tight-binding basis of bonding orbitals along the $(1\ 1\ 1)$, $(\bar{1}\ \bar{1}\ 1)$, $(\bar{1}\ 1\ \bar{1})$ and $(1\ \bar{1}\ \bar{1})$ directions. Consider the more general case of the zincblende structure i.e. the diamond-cubic structure of Figure 1.2 but with different atomic species on the two sublattices. The secular equation 1.3.3 is set up as outlined in Section 1.2 by computing the sums 1.3.4 for matrix elements between first neighbour bonds with common A and B atoms ($V1A$, $V1B$), second neighbour bonds with dihedral angle 60° ($V2$) and second neighbour bonds with dihedral angle 180° ($V3$). Setting the energy of the isolated bond to zero produces the Hamiltonian matrix

$$H = \begin{vmatrix} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{12}^* & H_{22} & H_{23} & H_{24} \\ H_{13}^* & H_{23}^* & H_{33} & H_{34} \\ H_{14}^* & H_{24}^* & H_{34}^* & H_{44} \end{vmatrix} \quad (6.2.1)$$

where $H_{11} = \langle 111 | \hat{H} | 111 \rangle$
 $H_{12} = \langle 111 | \hat{H} | \bar{1}\bar{1}1 \rangle \quad \text{etc}$

Thus,

$$H_{11} = 2\sqrt{3} \left[\cos(\alpha+\beta) + \cos(\beta+\gamma) + \cos(\gamma+\alpha) \right]$$

$$H_{22} = 2\sqrt{3} \left[\cos(\alpha+\beta) + \cos(\beta-\gamma) + \cos(\gamma-\alpha) \right]$$

$$H_{33} = 2\sqrt{3} \left[\cos(\alpha-\beta) + \cos(\beta+\gamma) + \cos(\gamma-\alpha) \right]$$

$$H_{44} = 2\sqrt{3} \left[\cos(\alpha-\beta) + \cos(\beta-\gamma) + \cos(\gamma+\alpha) \right]$$

$$H_{12} = (V1B+V1A)\cos\left(\frac{1}{2}\alpha+\frac{1}{2}\beta\right) + i(V1B-V1A)\sin\left(\frac{1}{2}\alpha+\frac{1}{2}\beta\right) + 2V2\left[\cos\left(-\frac{1}{2}\alpha+\frac{1}{2}\beta+\gamma\right) + \cos\left(\frac{1}{2}\alpha-\frac{1}{2}\beta+\gamma\right)\right]$$

$$(6.2.2)$$

$$H_{13} = (V_{1B} + V_{1A}) \cos\left(\frac{1}{2}x + \frac{1}{2}z\right) + i(V_{1B} - V_{1A}) \sin\left(\frac{1}{2}x + \frac{1}{2}z\right) + 2V_2 \left[\cos\left(\frac{1}{2}x + y - \frac{1}{2}z\right) + \cos\left(-\frac{1}{2}x + y + \frac{1}{2}z\right) \right]$$

$$H_{14} = (V_{1B} + V_{1A}) \cos\left(\frac{1}{2}y + \frac{1}{2}z\right) + i(V_{1B} - V_{1A}) \sin\left(\frac{1}{2}y + \frac{1}{2}z\right) + 2V_2 \left[\cos\left(x - \frac{1}{2}y + \frac{1}{2}z\right) + \cos\left(x + \frac{1}{2}y - \frac{1}{2}z\right) \right]$$

$$H_{23} = (V_{1A} + V_{1B}) \cos\left(\frac{1}{2}y - \frac{1}{2}z\right) + i(V_{1A} - V_{1B}) \sin\left(\frac{1}{2}y - \frac{1}{2}z\right) + 2V_2 \left[\cos\left(x + \frac{1}{2}y + \frac{1}{2}z\right) + \cos\left(x - \frac{1}{2}y - \frac{1}{2}z\right) \right]$$

$$H_{24} = (V_{1A} + V_{1B}) \cos\left(\frac{1}{2}x - \frac{1}{2}z\right) + i(V_{1A} - V_{1B}) \sin\left(\frac{1}{2}x - \frac{1}{2}z\right) + 2V_2 \left[\cos\left(\frac{1}{2}x + y + \frac{1}{2}z\right) + \cos\left(-\frac{1}{2}x + y - \frac{1}{2}z\right) \right]$$

$$H_{34} = (V_{1A} + V_{1B}) \cos\left(\frac{1}{2}x - \frac{1}{2}y\right) + i(V_{1A} - V_{1B}) \sin\left(\frac{1}{2}x - \frac{1}{2}y\right) + 2V_2 \left[\cos\left(\frac{1}{2}x + \frac{1}{2}y + z\right) + \cos\left(-\frac{1}{2}x + \frac{1}{2}y + z\right) \right]$$

where $x = ak_x$ etc. and $\underline{k} = (k_x, k_y, k_z)$ denotes a point in the FCC Brillouin zone shown in Figure 2.2a. This Hamiltonian is the same as that used by Shevchik et al (1974). Diagonalising the matrix 6.2.1 analytically at the Γ , X and L points of the zone gives useful expressions for the valence band energy levels and degeneracies in terms of the matrix elements V_{1A} , V_{1B} , V_2 and V_3 . In the notation of Figure 6.3c,

$$\Gamma_{15} = - (V_{1A} + V_{1B} + 4V_2) + 6V_3$$

$$\Gamma_1 = 3(V_{1A} + V_{1B} + 4V_2) + 6V_3$$

$$X_5 = - (V_{1A} + V_{1B}) - 4V_2 - 2V_3$$

$$X_3 = - V_{1A} + 3V_{1B} - 4V_2 - 2V_3$$

$$X_1 = 3V_{1A} - V_{1B} - 4V_2 - 2V_3$$

(6.2.3)

$$L_3 = - (V_{1A} + V_{1B}) + 2V_3$$

$$L_2 = (V_{1A} + V_{1B}) - 2V_3 - \left[(V_{1A} + V_{1B} + 4V_3)^2 + 3(V_{1A} - V_{1B})^2 \right]^{1/2}$$

$$L_1 = (V_{1A} + V_{1B}) - 2V_3 + \left[(V_{1A} + V_{1B} + 4V_3)^2 + 3(V_{1A} - V_{1B})^2 \right]^{1/2}$$

For Si and Ge the matrix elements V_{1A} and V_{1B} are equal and the energy level notation goes over to that of Figures 6.3a and 6.3b.

Figure 6.3a illustrates the valence band structure for Si calculated with the matrix elements deduced by Bullett (1974) from first principles. The matrix elements are obtained by integration using bonding orbital

wavefunctions derived from normalised bonding combinations of sp^3 orbitals and the approximation that an electron feels the free-atom potential of the nearest atom with all others fully screened. Although this probably leads to over-correlation of the electrons, the validity of the approach has been exhaustively tested by Bullett (1974). The simplicity of the approach is invaluable in determining how the matrix elements vary with the angular orientations of the orbitals (see below). Bullett's parameters for Si are

$$V1A=V1B=-1.2\text{eV} \quad V2=-0.28\text{eV} \quad V3=+0.17\text{eV} \quad (6.2.4)$$

The VBDOS of Figure 6.3a compares well with the EPM result for the diamond-cubic structure calculated by Joannopoulos and Cohen and included in Figure 6.1, except that the L_1 peak is rather too close to the top of the band. This is remedied in the band structure shown in Figure 6.3b where the matrix elements have been adjusted to ensure a more realistic L_1 peak position using the equations 6.2.3. In this case the matrix elements are

$$V1A=V1B=-1.3\text{eV} \quad V2=-0.16\text{eV} \quad V3=+0.38\text{eV} \quad (6.2.5)$$

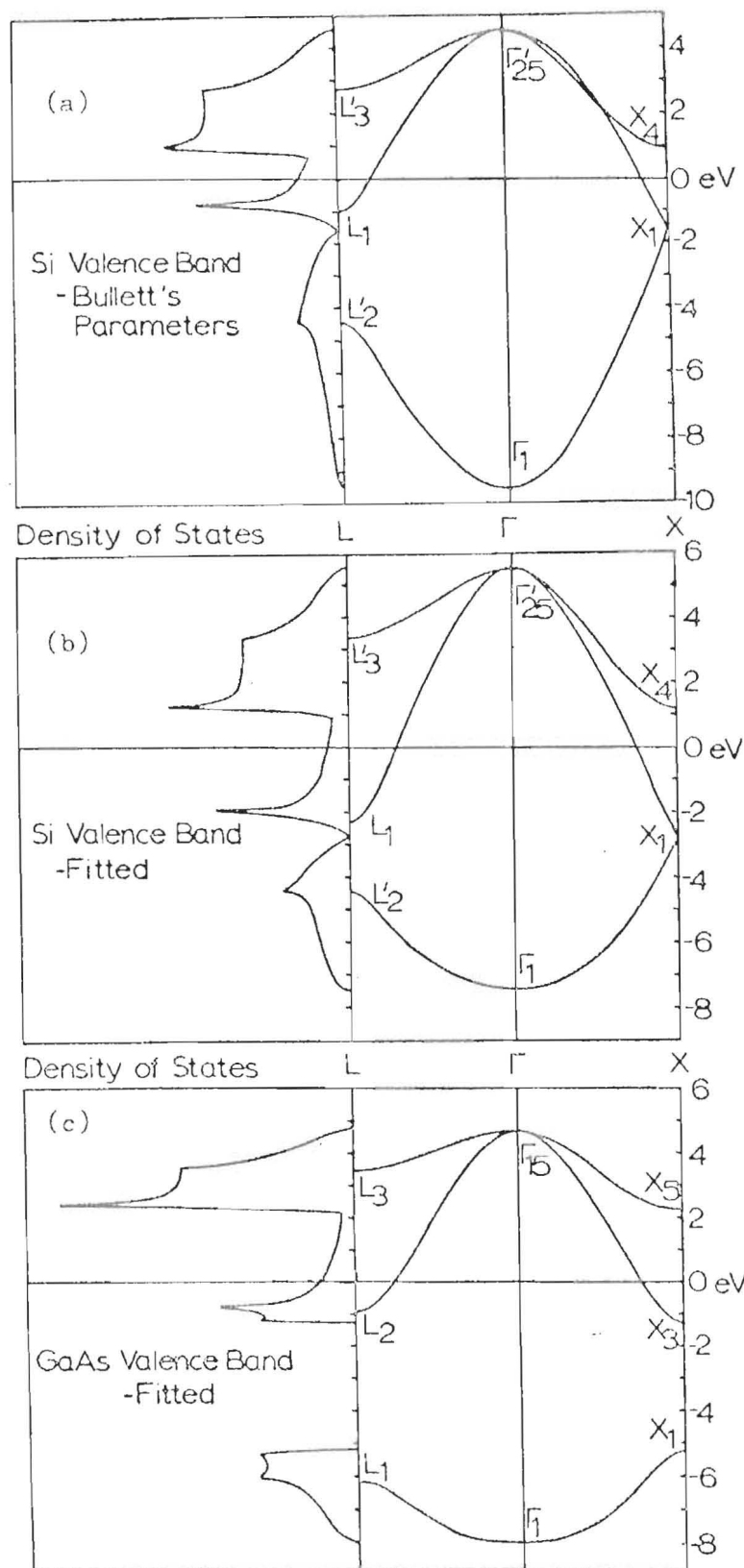
Figure 6.3c shows the VB structure of GaAs fitted, using equations 6.2.3, to the results of an EPM calculation by Cohen and Bergstresser (1966). The parameters are

$$\begin{aligned} V1A &= -2.0\text{eV} & V2 &= -0.10\text{eV} & V3 &= +0.20\text{eV} & (6.2.6) \\ V1B &= -1.0\text{eV} \end{aligned}$$

We include this result to facilitate later discussion in relation to the VBDOS of amorphous III-V compounds, as typified by a-GaAs.

For the VBDOS Recursion calculations we make use of the matrix element interpolation formulae derived by Bullett (1974). Assuming negligible bond length deviations in a-Si/a-Ge, the matrix elements between first and second neighbour bonds were calculated as functions of bond angles (θ) and dihedral angles (ϕ) respectively. The interpolation

Figure 6.3 a) Valence band-structure for Si from Bullett's parameters.



b) Valence band-structure for Si from fitted parameters.

c) Valence band-structure for GaAs from fitted parameters.

formulae for Si are

$$\begin{aligned} V_1 &= -1.2 + 0.0124\theta \quad \text{eV} \\ V_2 &= -0.13 - 0.30\cos\phi \quad \text{eV} \end{aligned} \quad (6.2.7)$$

with θ and ϕ measured in degrees. Assuming the same functional dependence of the matrix elements, we have deduced a second set of formulae which reproduce equation 6.2.5 in the c-Si case; these are

$$\begin{aligned} V_1 &= -1.3 + 0.0134\theta \quad \text{eV} \\ V_2 &= +0.02 - 0.36\cos\phi \quad \text{eV} \end{aligned} \quad (6.2.8)$$

Using these formulae and the angular deviations and dihedral angles derived from the CRN coordinates, we deduce the corresponding Hamiltonian matrix from which the VBDOS is generated using the Recursion method in the usual manner. (See Appendix 1.3).

6.3 RECURSION RESULTS

The results of the VBDOS calculations using Bullett's interpolation formulae appropriate to the diamond-cubic structure and the series of CRN's listed in Table 5.1 are shown in Figure 6.4. The Brillouin zone integration result is repeated for comparison with the diamond-cubic Recursion result, indicating the reliability of the latter and which features can be attributed to cluster-size and numerical effects. The DOS was calculated to 15 levels of the continued fraction to obtain adequate resolution of the L_1 peak. Although the comparison is not as successful as in some of our previous applications, we feel that useful information can still be extracted. Each of the CRN results is an average over 10 central bonds, there being negligible differences between averages over 5 and 10 such bonds.

Unlike the vibrational spectra presented in Chapter 5, the form of the VBDOS for the CRN's are almost completely determined by their topological structures. This is emphasised by the arrangement of the models in order of increasing odd-membered ring concentrations. Consider the Steinhardt model; although it has by far the smallest rms angular distortion, it fits in at the end of the series due to its high concentration of odd rings. The fundamental importance of network topology is also emphasised by the results of some investigative calculations performed by Kelly and Bullett (1976a). They set all $\Delta\theta=0^\circ$, $V_2(\phi)=V_2(60^\circ)$ for $0^\circ \leq \phi < 90^\circ$ and $V_2(\phi)=V_2(180^\circ)$ for $90^\circ \leq \phi < 180^\circ$ and still obtained the same basic results for the Polk and Connell-Temkin CRN's. The observed topological dependences of the s- and p-like states are in excellent agreement with the arguments and results discussed in Section 6.1.

In Figure 6.5 the VBDOS calculated using the modified interpolation formulae of equation 6.2.8 are presented. The improved description of the L_1 peak position in the crystalline case carries over to modify the

details of the CRN results. The results of both sets of calculations are discussed in the following section.

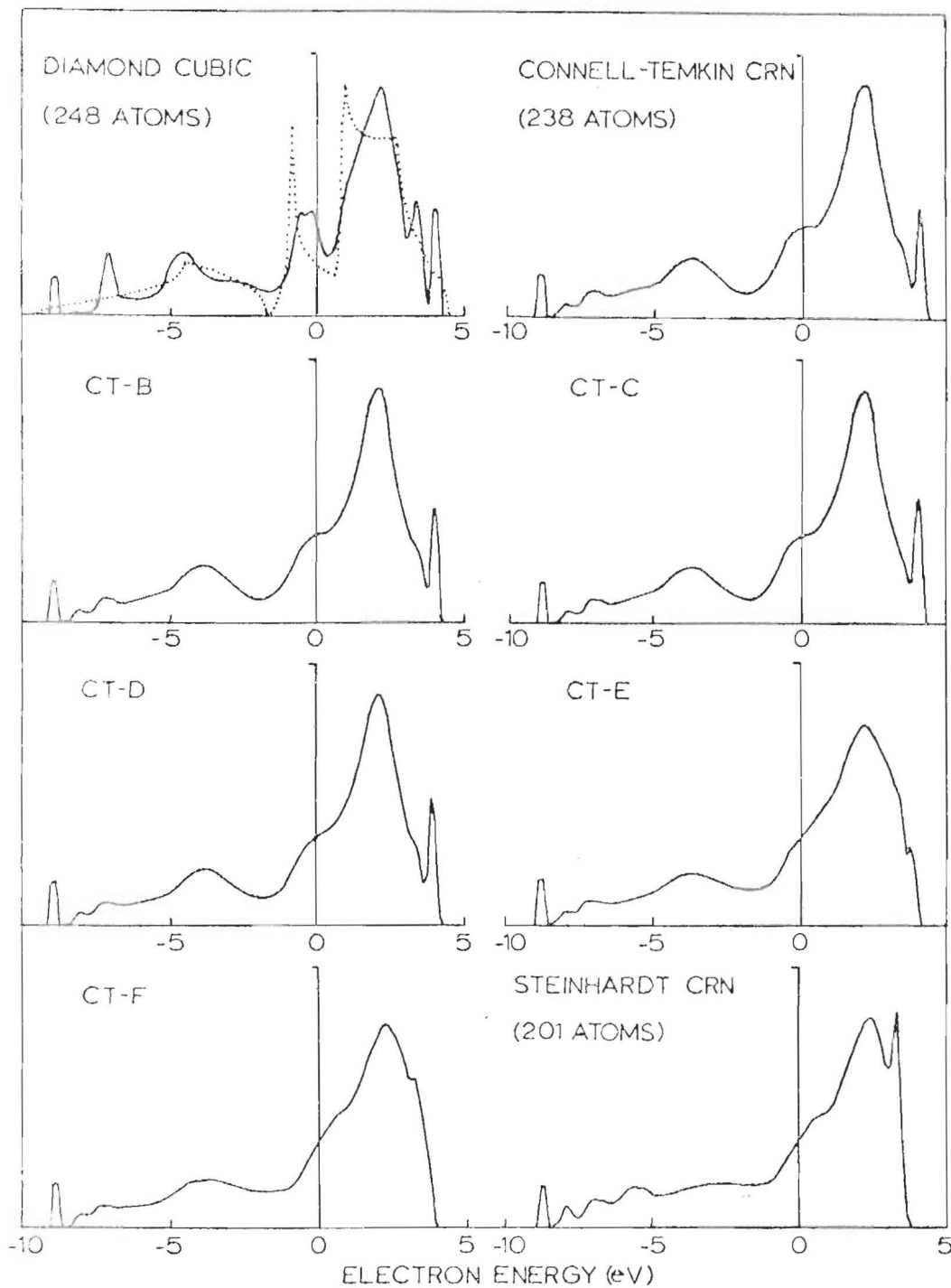


Figure 6.4 VBDOS for the CRN's of Table 5.1 calculated using Bullett's interpolation scheme; the broken line is the diamond-cubic result obtained by Brillouin zone integration.

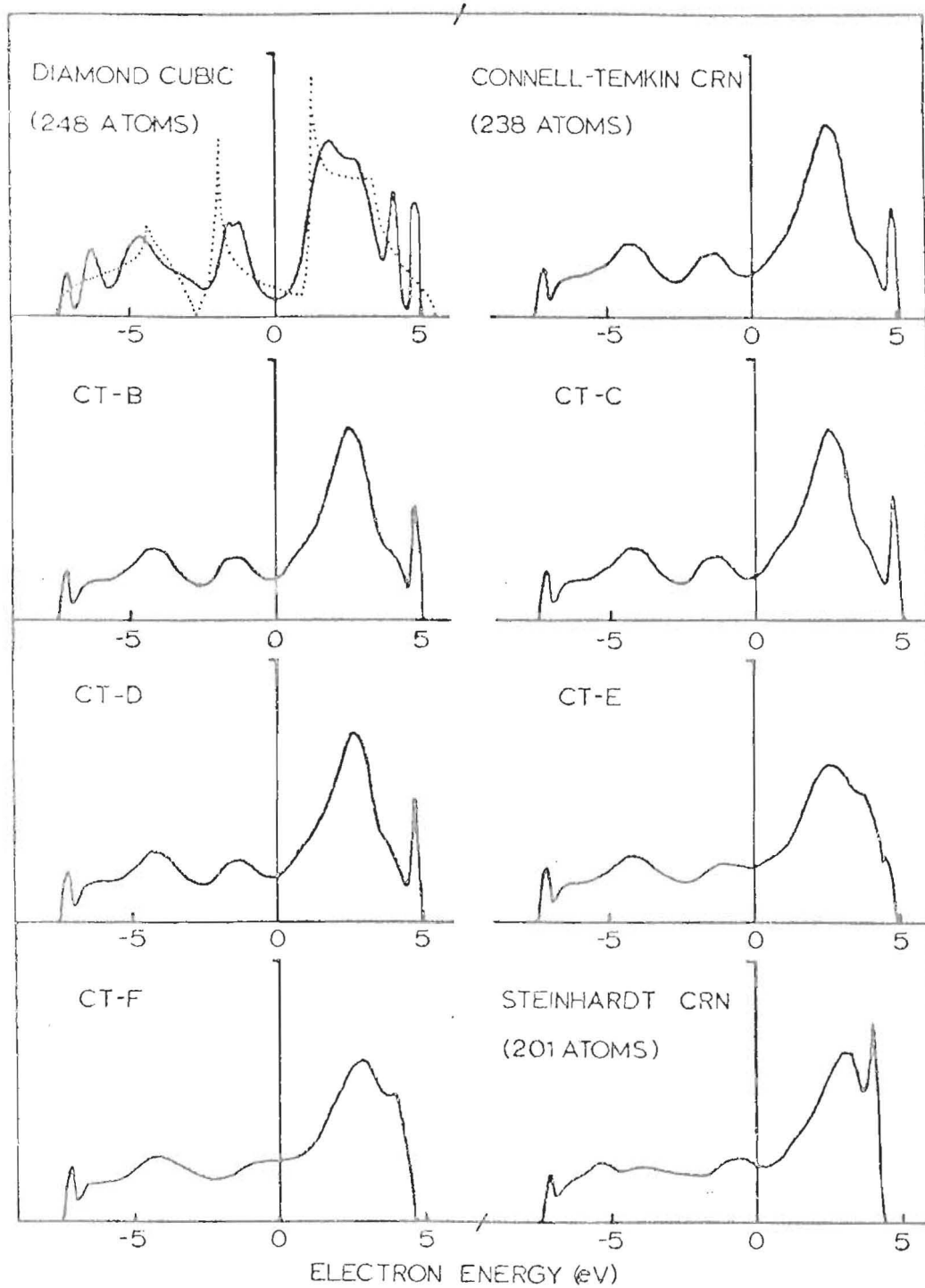


Figure 6.5 The same result as in Figure 6.4 but calculated using the adjusted interpolation scheme for the matrix elements (see text).

6.4 DISCUSSION

In this section the results of the Recursion calculations shown in Figures 6.4 and 6.5 are discussed in terms of the typical topological structures of a-Si/a-Ge and amorphous III-V compounds, as typified by a-GeAs. Some interesting general points also arise out of the discussion.

Considering the XPS data of Figure 6.1 and the results for the Connell-Temkin and Steinhardt models in Figure 6.4 reveals why Kelly and Bullett reached the conclusion that the typical structure of a-Si/a-Ge is that of the Steinhardt (or Polk) model but with fewer odd rings. Comparing the data with the results for the series of CRN's of Table 5.1 enables us to estimate more closely the typical number of odd rings present. Looking through the VB DOS for an almost filled s-state dip and a slightly skewed and narrowed p-peak leads us to conclude that the typical structure of a-Si/a-Ge lies between those of the C-T D and E models. Referring to Table 5.1 therefore reveals quantitative bounds on the ring statistics of a-Ge. Perhaps a more appropriate definition of topology than the average numbers of n-membered rings passing through an atom is the wrong bond^{*} concentration; for a-Ge we estimate therefore a wrong bond concentration f of 5 or 6 %.

We would expect further calculations aimed at improving this estimate of f to be hampered by the imperfections of our Hamiltonian. Indeed, the noticeable dip between s- and p-like states in the XPS data is absent in the CRN results of Figure 6.4 because the L_1 peak in the crystalline case is too close to the VB maximum. (See Figure 6.3a). This deficiency is removed by the adjustment of Bullett's parameters to give better

* A 'wrong bond' is defined as a bond between like atoms when we try to form the CRN from two atomic species such that each atom is bonded to four neighbours of the other species.

agreement with the EPM results for the diamond-cubic case. The VB DOS calculated with the modified interpolation formulae are shown in Figure 6.5 where it is noticeable that an s-p-like minimum is evident in both the C-T D and E results. Given the retention of this small dip in the CRN results, we may expect it to be amplified to the extent shown in the XPS data due to the different scattering cross-sections for s and p electrons.

The results of Figures 6.4 and 6.5 also illustrate that a surprisingly large number of odd rings are required before the resulting VB DOS is noticeably different from that of a purely even-membered ring structure. There is very little qualitative difference between the results for the original C-T and the C-T D models, yet the latter already contains a significant proportion of wrong bonds ($f=4.2\%$). This result may be of use in considerations of the topological dependence of electronic structure in other disordered systems. For example, Shevchik (1977) has measured the densities of states of crystalline and amorphous As and suggests one of his results may be evidence of a purely even-ringed structure. Our results indicate that, should this result apply to an amorphous sample, a significant proportion of odd rings may in fact be present, but in insufficient quantity to noticeably effect the electronic energy level structure.

Despite our systematic approach to the inter-dependence of topological and electronic structure, have we learned anything worthwhile about a-Ge? Certainly the wrong bond fraction consistent with the model calculation and the XPS data is known more closely, but no significant improvement over the contribution of Kelly and Bullett has been achieved. Indeed, from comparing the RDF's of theirs and the Polk model with the experimental data, Connell and Temkin (1974) suggested that the real structure is an average of the two. We are fortunate in having the series of CRN's generated by Beeman and Bobbs (1975) as a basis for calculations relevant

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to a-Si/a-Ge. No such series exist for other systems such as a-As or any of the oxide glasses; but do we really need them? Comparing our results with those of Kelly and Bullett illustrates the law of diminishing returns. It seems that identifying the topological structure of an amorphous solid by comparison of detailed electronic structure calculations with XPS/UPS and optical data is very fruitful. However, calculations for only two or three models of very different topologies should be sufficient to identify a typical topological structure. We therefore hope our results will lead to some labour saving in the modelling studies of other disordered systems.

Do our results bear any relevance to the structure of amorphous III-V compounds? The band structure of c-GaAs shown in Figure 6.3c is noticeably different from that of c-Ge in that a gap exists between the L_2 and L_1 peaks as a result of the non-equivalence of the matrix elements V_{1A} and V_{1B} (see Equation 6.2.3). XPS data on the valence bands of amorphous III-V compounds reported by Shevchik et al (1974) reveal two important differences from the results for a-Si/a-Ge. The deep s-like dip is retained and the p-peak is less skewed over to higher energies. Thus, the topological implications of previous work and the results of our more realistic model calculations are consistent with a negligible fraction of wrong bonds in amorphous III-V compounds. The s-state dip is retained by virtue of the splitting present in the crystal and the simple s-band argument of Joannopoulos and Cohen (1973). The reduced modification of the p-peak is consistent with there being fewer eclipsed second neighbour bonds, as expected in an even-membered ring structure (Connell and Temkin 1974). Full network Recursion calculations for a-GaAs are certainly feasible, given Bullett's technique for calculating matrix elements, but the results are unlikely to reveal anything that has not already been inferred. (See also Joannopoulos and Cohen 1976).

CHAPTER SEVEN OPTICAL PHONONS IN TIN DICHALCOGENIDES

7.1 INTRODUCTION

In this somewhat parenthetical chapter we describe the use of simple force constant models, of the type so far applied to amorphous semiconductors, in determining which forces are chiefly responsible for the observed optical phonon anisotropies in the layer compounds SnS_2 and SnSe_2 . The Raman- and IR-active zone-centre modes of these materials have been found to exhibit very different frequencies for atomic motions parallel and perpendicular to the layers (Smith et al 1977, Lucovsky et al 1976). This may be naively attributed to strong ionic/covalent bonding within the layers, which interact only weakly via Van der Waal's forces. A more fundamental understanding of this behaviour, however, would be preferred.

Since no measurement of the phonon dispersion in either SnS_2 or SnSe_2 has yet been reported, we are restricted as to the number of force constants that can be used to describe the lattice dynamics and subsequently evaluated by fitting to experimental data. The task we set ourselves, therefore, is to obtain a satisfactory least-squares fit to four optically-active zone-centre modes using a maximum of three short-range force constants. In this way some indication of the more important forces in these materials can be obtained.

In the next section the structure and polytypism of the tin dichalcogenides is described. Our calculations and conclusions are presented subsequently.

7.2 STRUCTURE AND POLYTYPES

SnS_2 and SnSe_2 occur in the cadmium iodide structure; Figure 7.1a illustrates the two-dimensional ligand-metal-ligand (L-M-L) sandwich structure in which the M atoms are octahedrally coordinated to six nearest-neighbour L atoms. The hexagonal lattice and a single unit cell containing three basis atoms are depicted in Figure 7.1b. Throughout the following, the L-M-L sandwiches are assumed to be stacked so that there is only one sandwich per unit cell - this is known as the 2H structure. Thus the basis and lattice of 2H- CdI_2 are completely defined by Figure 7.1 and it follows that the corresponding Brillouin zone is the same as that used for trigonal Se and Te (see Figure 4.4).

If the L-M-L sandwiches are stacked so that more than one sandwich lies within the unit cell, various polytypes of SnS_2 and SnSe_2 result. These higher polytypes are interesting in that they exhibit optically-active rigid-layer shear modes with characteristically low frequencies, reflecting the weak inter-sandwich interactions. The structures and rigid-layer modes of the 4H and 6H polytypes of $\text{SnS}_2/\text{SnSe}_2$, which have two and three sandwiches per unit cell respectively, have been discussed by Smith et al (1977). Our simple treatment of the 2H structure naturally precludes any discussion of these modes, our present interest lies more with the important intra-sandwich forces.

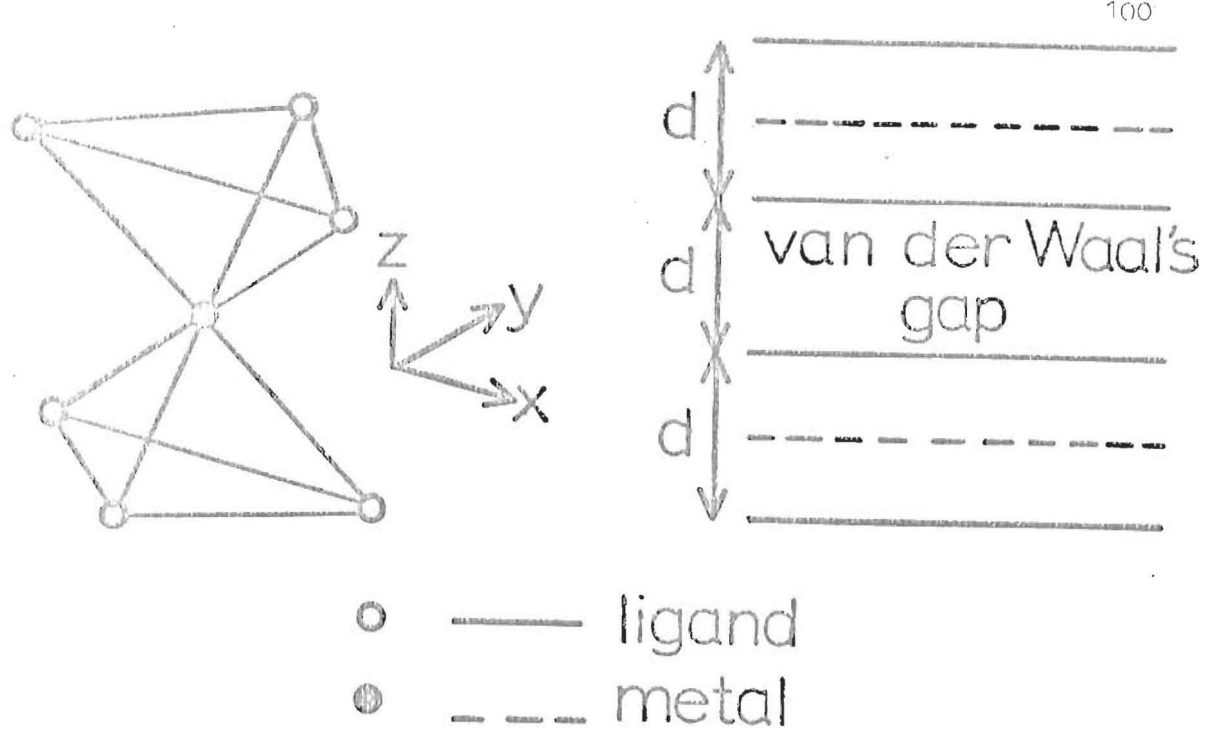


Figure 7.1 a) The octahedral coordination and sandwich structure of the CdI_2 crystal.

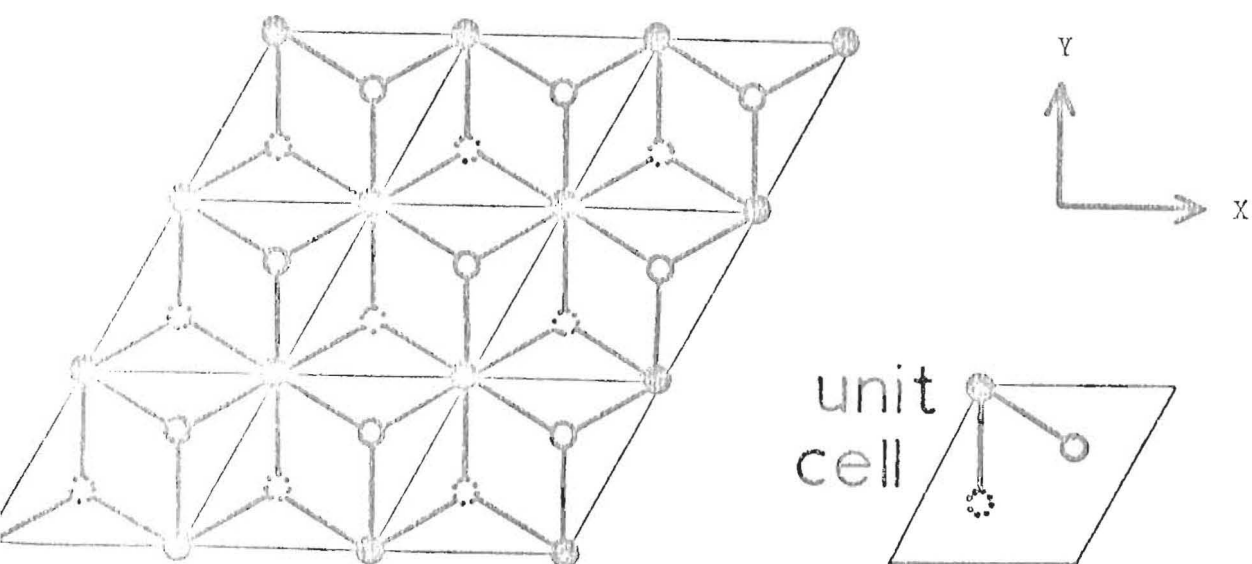


Figure 7.1 b) The hexagonal lattice and three-atom basis of the CdI_2 crystal.

7.3 OPTICAL ACTIVITY

The three-atom basis of the 2H-CdI_2 structure gives rise to nine vibrational modes at any point in the zone. At the zone-centre there are three doubly-degenerate modes in the basal plane (denoted E) and three non-degenerate modes parallel to the c-axis (denoted A). These modes decompose into the irreducible representations (Lucovsky et al)

$$\Gamma = A_{1g} + E_g + 2A_{2u} + 2E_u \quad (7.3.1)$$

They are separated into acoustical, Raman-active optical and IR-active optical modes by their transformation properties; for instance Raman-active (IR-active) modes are symmetric (anti-symmetric) under inversion. The results of the analysis provide the following assignments; E_g and A_{1g} are Raman-active, E_u and A_{2u} are IR-active. The results of the Group Theory are indispensable in correctly assigning the experimentally observed frequencies to the corresponding vibrations but they are not critical to this discussion. Once the dynamical matrix is constructed and diagonalised at the zone-centre, the eigenvectors, effective masses and degeneracies of the modes leave no doubts as to which eigenfrequencies to compare with the experimental data (see below). Experimentally, of course, the mode assignments are made by observation of their depolarisation behaviour.

7.4 CALCULATIONS

Using force constants defined as suggested by Keating, several combinations of forces between the metal and ligand atoms were tried before making the final choice. The potential expressions were set up as in previous applications and the corresponding dynamical matrices were derived. Since we required to fit only zone-centre modes, once a combination of forces was chosen it was possible to assess whether or not it reproduced the observed anisotropies without the need for detailed calculation.

First attempts involved intra-sandwich forces only; using M-M, M-L and L-L central forces produced a poor fit, as did using a M-L central force with both L-M-L and M-L-M bond bending forces. The latter model, however, became no worse on omitting the L-M-L bond bending contribution, thus allowing us to choose the third force to act between the sandwiches. Choosing the inter-sandwich force to be a L-L central force significantly improved the fit to the zone-centre modes.

The potential expression for the final model is

$$\begin{aligned}
 V = & \frac{1}{2} \sum_M \left[4\alpha \sum_L \left\{ \chi_{ML} (u_M - u_L) \right\}^2 \right] \\
 & + \frac{1}{2} \sum_L \left[4\alpha \sum_M \left\{ \chi_{LM} (u_L - u_M) \right\}^2 + 4\beta \sum_{L'} \left\{ \chi_{LL'} (u_L - u_{L'}) \right\}^2 \right] \\
 & + \frac{1}{2} \sum_L \left[\gamma \sum_{M, M'} \left\{ \chi_{LM} (u_L - u_{M'}) + \chi_{LM'} (u_L - u_M) \right\}^2 \right]
 \end{aligned} \tag{7.4.1}$$

where α is the intra-sandwich M-L central force, β is the inter-sandwich L-L central force and γ is the intra-sandwich M-L-M bond bending force. The dynamical matrix corresponding to a general point $\underline{k}$ in the hexagonal

Brillouin zone is given in Appendix 7.4. The effective masses and degeneracies of the non-zero zone-centre mode frequencies make the following zone-centre mode assignments for the CdI_2 structure obvious;

$$\begin{aligned}\omega^2(\bar{E}_g) &= \frac{1}{m} (8\alpha + 8\beta + \gamma) & \text{Raman} & & (x2) \\ \omega^2(A_{1g}) &= \frac{1}{m} (8\alpha + 32\beta + 4\gamma) & \text{Raman} & & (x1) \\ \omega^2(\bar{E}_u) &= \left[\frac{2}{M} + \frac{1}{m} \right] (8\alpha + \gamma) & \text{IR} & & (x2) \\ \omega^2(A_{2u}) &= \left[\frac{2}{M} + \frac{1}{m} \right] (8\alpha + 4\gamma) & \text{IR} & & (x1)\end{aligned}\tag{7.4.2}$$

where M is the metal atom mass and m is the ligand atom mass.

The results of the least-squares fits to the experimental data for SnS_2 and SnSe_2 are presented in Table 7.1, where they are compared with the measured Raman and IR frequencies for the 2H forms. The corresponding eigenvectors are depicted in terms of the L-M-L 'molecule' displacements. The Raman modes parallel and perpendicular to the basal plane clearly display inversion symmetry and why the metal atom mass does not enter the corresponding frequency expression. The IR active modes are clearly of dipolar character. All of the experimental frequencies are fitted with less than 8% error, the fit being noticeably better for the selenide. It is the quality of fit obtained with the present model which suggests that some of the most important forces in these materials have been isolated. The values of the force constants obtained are

$$\begin{array}{lllll}\text{SnS}_2 & & & & \\ \alpha=0.3725 & \beta=0.181 & \gamma=2.72 & (\text{Nm}^{-1}) & (7.4.3)\end{array}$$

$$\begin{array}{lllll}\text{SnSe}_2 & & & & \\ \alpha=0.2275 & \beta=0.154 & \gamma=2.43 & (\text{Nm}^{-1}) & (7.4.4)\end{array}$$

Symmetry	Activity	Displacements	Frequencies (cm ⁻¹)			
			SnS ₂		SnSe ₂	
			Theory	Expt.	Theory	Expt.
E _g	Raman		194.6	205 ^a	107.9	113.5 ^a
A _{1g}	Raman		322.6	315 ^a	187.0	187.5 ^a
E _u	IR		215.7	205 ^b	145.6	144 ^b
A _{2u}	IR		336.2	340 ^b	239.8	241 ^b

a) Smith et al (1977)

b) Lucovsky et al (1976)

Table 7.1 Comparison of experimental and fitted optically-active zone-centre mode frequencies in SnS₂ and SnSe₂.

The phonon dispersion for SnS_2 along the principle symmetry directions of the hexagonal zone are presented in Figure 7.2; the results for SnSe_2 differ only in that the bands are less well separated into regions of acoustic and optic character. The zero-frequency mode at the K-point corresponds to a shearing motion of adjacent sandwiches; since only central inter-sandwich forces are used in the final model, there are no restoring forces for such vibrations. The results show reasonable general agreement with the available experimental data on the dispersion in CdI_2 reported by Dorner, Ghosh and Harbeke (1976), which does not include any optic mode branches. The DOVS for SnS_2 and SnSe_2 calculated by sampling 4120 points in the irreducible zone and smoothing the resultant histograms are shown in Figure 7.3. Since the model parameters were fitted at the zone-centre only, it is unlikely that these spectra will bear more than a general resemblance to the corresponding DOVS for the real materials.

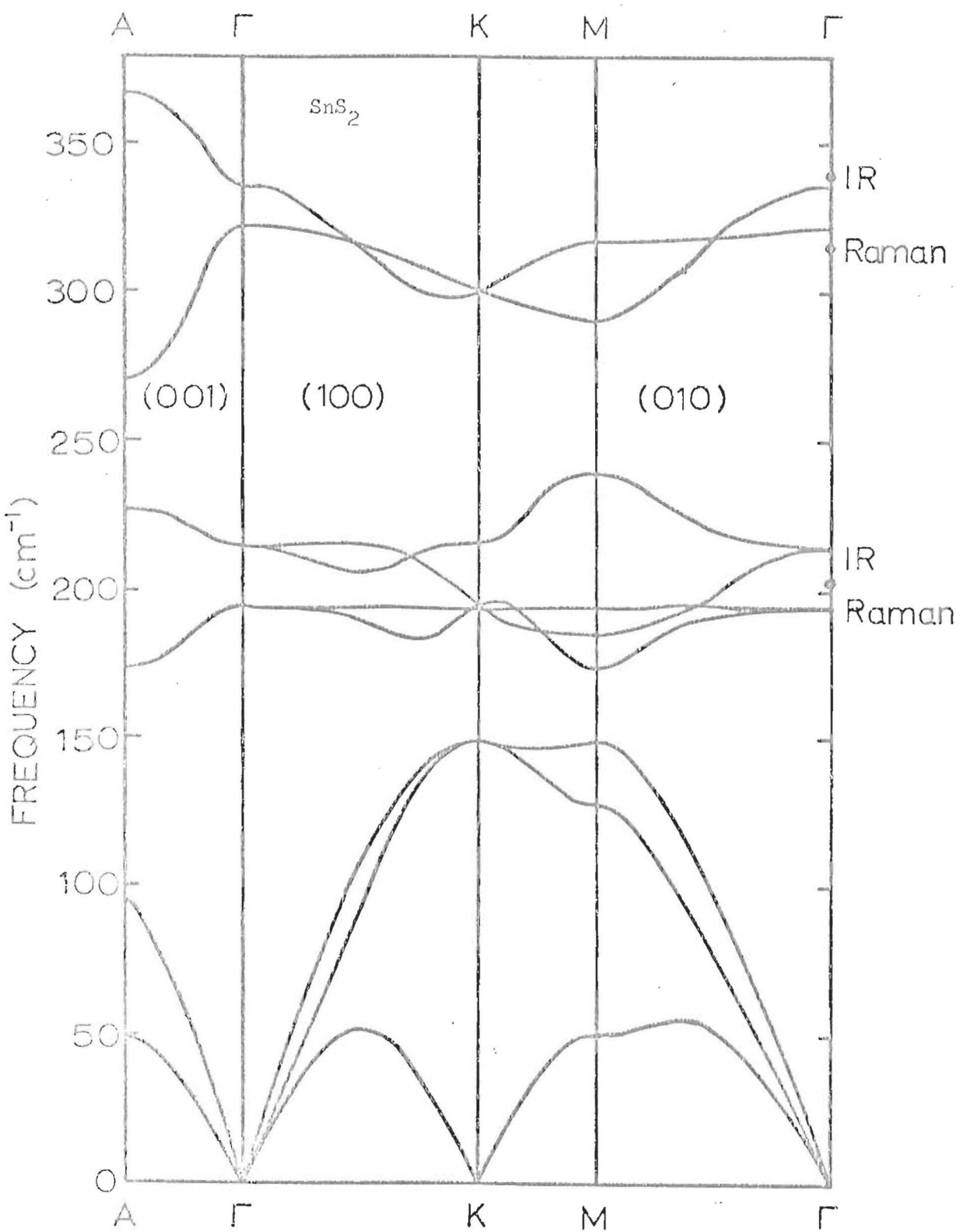


Figure 7.2 Phonon dispersion along some principal symmetry directions of the hexagonal zone for SnS_2 ; the frequencies of the IR- and Raman-active zone-centre modes are also indicated.

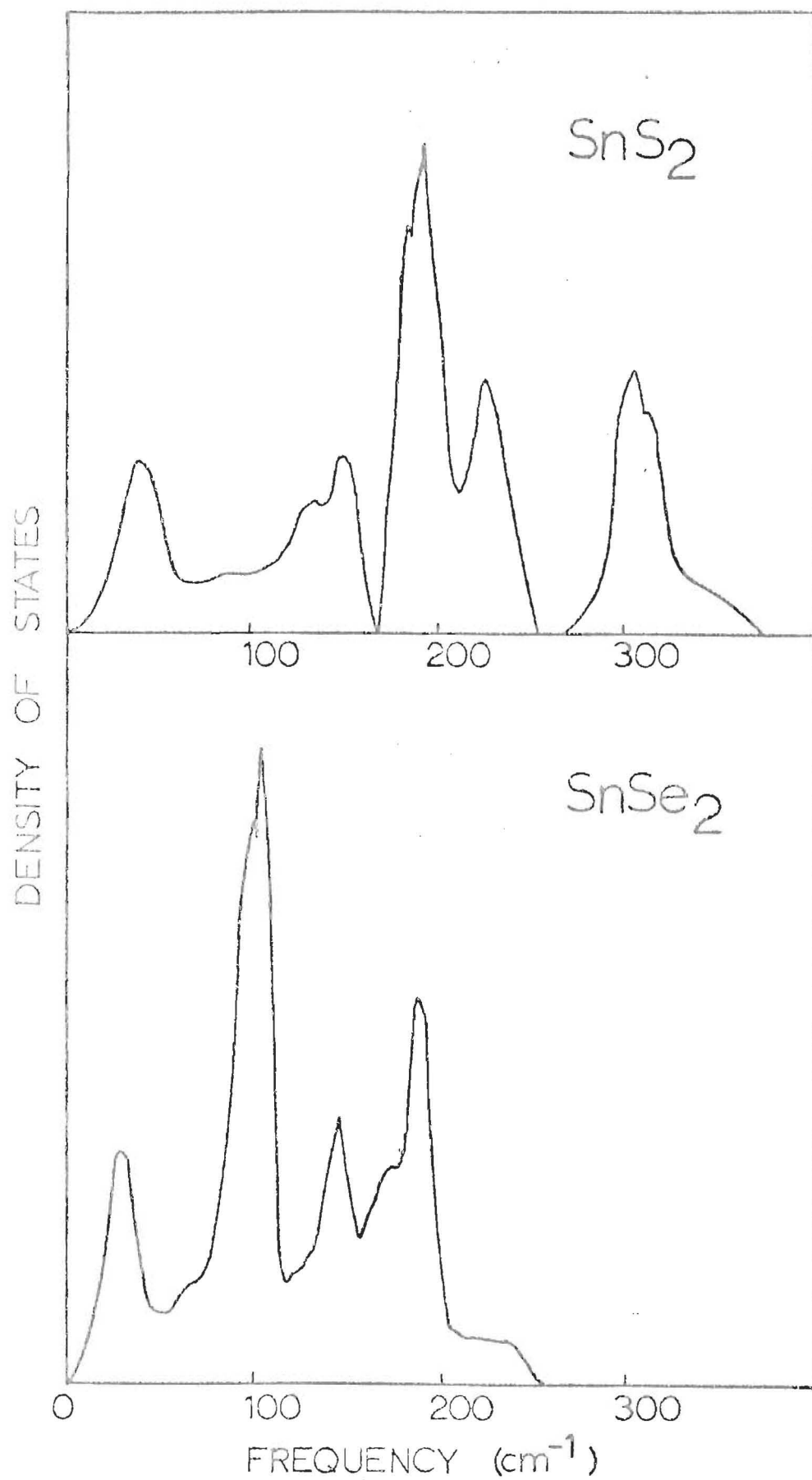


Figure 7.3 Vibrational spectra for SnS_2 and SnSe_2 calculated by sampling over the irreducible part of the Brillouin zone.

7.4 DISCUSSION

The observation that the final dynamical model gives poorer results for SnS_2 than SnSe_2 is consistent with the suggestion of Lucovsky et al (1976) that Coulomb forces are important in the lattice dynamics of these materials. We may naively expect the Coulomb interaction to be more important in the sulphide than the selenide due to its greater ionicity. Considering short-range forces together with effective charges on the metal and ligand atoms would no doubt improve the fit to experiment but such a calculation lies outside our approach. The trend of smaller force constants for the selenide, as revealed by our fitting procedure, is consistent with the stronger bonding expected in the sulphide.

Having fitted the zone-centre modes of the tin dichalcogenides, can we now identify which forces are responsible for the observed phonon anisotropies in these materials? We may expect the M-L central force to determine the gross features of the dispersion but it does not contribute to the differences in frequency between the modes parallel and perpendicular to the basal plane. Equations 7.4.2 indicate that the M-L-M bond bending forces produce the anisotropy whereas the L-L inter-sandwich forces contribute to the difference between the Raman and IR frequencies, acting in the opposite sense to the differing effective masses for the vibrations. The greater importance of the M-L-M bond bending forces compared to the corresponding L-M-L force can be qualitatively justified by considering the bond-charges of the M-L bonds. These will be nearer the more electronegative ligands, producing comparatively large restoring forces when the M-L-M bond angles are modified.

A more sophisticated calculation of the vibrational properties of these materials awaits the experimental measurement of their phonon dispersion relations.

CHAPTER EIGHT CONCLUSION

8.1 SUMMARY

We have seen how the vibrational spectra of model structures appropriate to disordered solids such as a-Ge, a-As and a-Se can be calculated using the Recursion method. Calculations using simple force constant schemes revealed dependence of the DOVS on topological disorder, angular distortions and inter-molecular separations. The results provided information on the structures and characteristic vibrational properties of these materials and the predictions of earlier workers were verified and extended. Comparison of the calculated spectra with experimental data also indicated that the effects of force constant variations and anharmonicity are negligible if only intra-molecular forces are considered. The most important effects arise from variations in the directions of the inter-atomic forces, the connectivity and the inter-molecular distances. The principal result is a smoothing of the corresponding crystalline density of states, the general form of the DOVS being preserved in the disordered phase along with the characteristic local order. Similar short-range force constant models also proved useful in identifying those forces chiefly responsible for the observed anisotropies in the optically-active zone-centre modes of the layer compounds SnS_2 and SnSe_2 .

In Chapters 5 and 6 we considered rather more realistic models of both the vibrational and electronic behaviour of a-Ge. Figures 5.7 and 6.5 respectively show how the modifications to the crystalline DOVS are determined by the angular distortions of the model structure whereas the modifications to the crystalline VB DOS are determined by the topology of the CRN. This very important distinction can be naively attributed to the vector nature of interatomic forces compared to the scalar nature

of Hamiltonian matrix elements. The differences between the results of the Born and BCM dynamical model calculations for a-Ge have important consequences for further applications of the method. It appears that in future we must be very cautious in interpreting the results of simple model calculations of the vibrational spectra of disordered solids.

8.2 VALIDITY OF OUR APPROACH

The comparisons of our Recursion results with those of reciprocal space calculations have generally been rather good, see for example Figure 5.4. The standard of agreement can be improved by increasing the number of moments of the vibrational spectra calculated exactly, in other words calculating more levels of the continued fraction expansion in larger clusters. The computational effort, however, increases in proportion to both the number of levels and the cluster size. Our experience suggests that CRN models of about 500 atoms are likely to give the best results for the computational effort required.

Our policy of neglecting force constant variations with changes in bond lengths and angles has been successful so far, however we would expect this to become a major problem in some future applications. For example, more reliable calculations of the DOVS appropriate to a-As and a-Se will require realistic modelling of the variations of inter-molecular forces with varying layer and chain separations respectively.

Long-range Coulomb forces cannot be incorporated into our scheme. In Weber's BCM for c-Ge, however, the important Coulomb forces can be absorbed into the short-range forces and so the model can be incorporated into our calculation. This may or may not carry over into the realistic models of the phonon dispersion in other such crystals. The dangers of making do with simple dynamical models have been highlighted by our calculations for a-Ge.

In summary then, our approach has been successful so far; it remains to be seen whether or not it can be satisfactorily applied to more complex systems such as a-As or a-Se with equal success.

8.3 FURTHER WORK

Our calculations of the vibrational spectra of disordered solids are entirely dependant on the availability of suitable dynamical and structural models. A suitable dynamical model consists of only short-range interactions and gives a reliable description of the phonon dispersion in the corresponding crystalline material; simple Born-like schemes are to be avoided, as illustrated by our experience with a-Ge. Thus, more detailed calculations for structural models of a-As and a-Se should be preceded by the development of dynamical models as successful for rhombohedral As and trigonal Se as the adiabatic BCM has been for Group IV and III-V crystals. It is frustrating that the phonon dispersion of rhombohedral As has not been measured, although results for Sb (Sharp and Warming 1971) and Bi (Macfarlane 1971) have appeared in the literature. In contrast, the dispersion in trigonal Se and Te has been measured yet no dynamical model has been devised to reproduce the more subtle features of the vibrational behaviour. We would expect a successful model to reflect the distortions from the simple cubic structure in the Group VI elements (S-Se-Te-Po) and to incorporate the effects of the lone-pair orbitals, which seem to have significant bearing on the properties of the lighter elements of the Group (see Robertson 1976). Only when such models are available can definitive calculations of the vibrational spectra appropriate to the amorphous forms be attempted using the Recursion method.

Amorphous compounds and alloy systems present further problems in that their crystalline counterparts may not exist and appropriate dynamical models are far less likely to have been developed. From our experience with a-Ge, Recursion DOVS calculations with Born-like forces may well be very misleading. In such cases it seems that the 'molecular' approach of Lucovsky et al (see Lucovsky and Martin 1972, Lucovsky and Knights

1974, Nemanich, Solin and Lucovsky 1977) will prove the most economical. This approach involves the consideration of the normal modes of typical structural units or 'molecules', such as Ge_5 and GeSe_4 molecules in the cases of a-Ge and a- GeSe_2 respectively. Assuming the DOVS to be a broadened normal mode spectrum of the appropriate molecule(s) provides insight into the typical normal mode character within the DOVS and is equally applicable to elemental, compound and alloy systems.

As for experimental data, more vibrational spectra need to be measured directly by inelastic neutron scattering experiments. These experiments are very difficult to perform in that the results are complicated by multiple scattering effects. At large transfer wave-vectors, however, the scattering spectrum corresponds to the DOVS without the complications of matrix element effects present in IR and Raman spectra (see Axe et al 1974, Alben et al 1975). Results for a-Ge and a-Se may be available soon. IR and Raman spectra are simpler to measure and are correspondingly more plentiful. However they are complicated by the frequency-dependence of the radiation/vibration coupling, so the development of a suitable dynamical model must precede that of a reliable description of the coupling mechanisms. IR and Raman spectra are discussed further in Section 8.4.

Although reliable vibrational spectra of amorphous solids are at present difficult to both calculate and measure, this is not the case for electronic densities of states. Electronic spectra can be comparatively easily measured by UPS/XPS and optical means and reliably calculated for different structures using the tight-binding approach (see Chapter 6 and Robertson 1975a). Our experience therefore suggests that more structural information can be deduced from the comparison of electronic calculations with experimental data, particularly in view of the topological dependence of the VBDOS seen in Chapter 6.

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8.4 IR AND RAMAN SPECTRA

Although no calculations of IR and Raman spectra have been presented in this thesis, such calculations are possible with the Recursion method. In this final section we outline the required modifications to the DOVS calculation and briefly discuss the viability of the calculation of IR and Raman spectra.

To evaluate the vibrational spectrum of a cluster projected onto the displacement of atom i in the direction α , we have used the identity 1.4.1 to compute the local DOVS defined by

$$N(\lambda) = \sum_n \langle n | V \rangle^2 \delta(\lambda - \lambda_n) \quad (8.4.1)$$

where λ_n and $|n\rangle$ are the eigenvalue and eigenvector of the n th normal mode respectively and $|V\rangle$ is the initial vector of the tridiagonal basis ($=|i\alpha\rangle$ in the notation of Section 1.4). IR and Raman spectra can also be generated by choosing the starting vector $|V\rangle$ in the appropriate manner.

The first-order IR spectrum is generated by choosing $|V\rangle$ such that

$$V_{i\alpha} = \sum_{\gamma} \epsilon_{\gamma} e_{i\alpha}^{\gamma} \quad (8.4.2)$$

where $\underline{\epsilon}$ is the polarisation vector of the light and $\underline{e}_{i\alpha}$ is the dipole moment associated with the displacement of atom i in direction α . Thus $\langle n | V \rangle^2$ gives the relative contribution of each mode to the IR spectrum and $IR(\lambda) \propto N(\lambda)$. Choosing a model of the IR coupling determines the dependence of the dipole moment on the atomic motions. Ideally this should be derived from the electron density response to the atom motions, but such a calculation is prohibitive. Simple models of the IR activity must be devised; for example Alben et al (1975) and Beeman and Alben

(1977) have assumed IR coupling to the dipole arising from the motion of charge from compressed to extended bonds.

To generate a first-order Raman spectrum $|V\rangle$ is chosen to be the vector of displacement induced polarisability;

$$V_{i\alpha} = \sum_{r,s} \epsilon_i^r \epsilon_i^s D_{i\alpha}^{rs} \quad (8.4.3)$$

where $\underline{\epsilon}_i$ and $\underline{\epsilon}_i$ are the polarisation vectors of the incident and scattered light and $\underline{D}_{i\alpha}$ is the change in the polarisability tensor due to a displacement of i along α . Thus the Raman intensity is proportional to $N(\lambda)$. (See Boeman and Alben 1977). Again the form of the induced polarisability tensor $\underline{D}_{i\alpha}$ is model dependant; Alben et al used a combination of contributions from individual bonds in their CRN calculations.

Thus, calculations of IR and Raman spectra are in principle possible with the Recursion method but suitable models for both the dynamics and the coupling mechanisms must be developed. Calculations for a-Ge, a-As and a-Se presented by Alben and co-workers for simple dynamical and IR and Raman coupling schemes have been reasonably successful but they must be very carefully interpreted in view of the results presented in this thesis. Perhaps a more economical approach in view of the complexities of the problem is that of deriving the coupling as a function of frequency by comparison of the experimental IR or Raman data with the DOVS obtained either by experiment (see Lannin 1976) or by calculation (see Chapter 5).

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APPENDIX 1.4

In this Appendix we present a flow-diagram of the Recursion method computer calculations. Specifications and listings of FORTRAN programs and subroutines designed for general use can be obtained from C.M.M. Nex, TCM Group, Cavendish Laboratory.

STAGE 1

```

INPUT=> Cluster coordinates & Neighbour map
      :
      : Compute blocks of Dynamical matrix;
      :           index in interaction map
      :
      : Set up initial vector of tridiagonal basis
      :
      : Compute continued fraction coefficients using
      :           Recursion algorithm
      :
OUTPUT=> Continued fraction coefficients

```

STAGE 2

```

INPUT=> N sets of continued fraction coefficients
      :
OUTPUT=> Compute resultant set of coefficients

```

STAGE 3

```

INPUT=> Resultant set of coefficients
      :
      : Compute DOVS on grid of 100-200 points
      :
OUTPUT=> Tabulate and/or plot DOVS

```


The non-zero elements of the lower triangle of the Hermitian matrix

D at the point $\underline{k}=(k_x, k_y, k_z)$ for the trigonal Se structure are listed below. The real and imaginary parts of D_{ij} are $DR(i, j)$ and $DI(i, j)$

respectively. The force constants are denoted by a, b, c and d ; the cell dimensions are A, B and C ; B is the radius of the chain spiral; $KX = \frac{1}{2}Ak_x$,

$$KY = \frac{1}{2} \sqrt{3} A k_x, \quad KZ = C k_z.$$

```

P1=1/(r1*r1)      P2=1/(r2*r2)      P3=1/(r1*r2)      RT=SQR(3)
CS1=COS(KA+BY)     CS2=COS(KX+BY)     CS3=COS(KX+BY)
S1=SI(KX+BY)        S2=SI(KX+BY)        S3=SI(KX+BY)

AT01=1-AT01-3*LOCK
AR(1,1)=a*r1*3*(a*r1+b*r1+g*r1*9*b*a+c*r2*(2*a*a-72*a*b+72*b*b)
+4*a*r1*45/2*a*b+c*r3*(-12*a*a+c27*a*b)+a*r2*(6*a*a-21*a*b+45/2*b*b)
+4*a*r3*(a*(3/2*a-A)*CS1+3/2*a*(3*a-A)*(CS2+CS3))
AR(2,1)=a*r3*(C1*1/2*a*(3*a-A)*CS3-CS2)
AI(2,1)=a*r3*(51*1/2*a*a*(S3-S2))
AR(2,2)=a*r1*12*a*b+b*r1*6*a*b+c*r2*(12*a*a-24*a*b+24*b*b)
+4*a*r1*27/2*a*b+4*a*r3*3*a*b+c*r2*(6*a*a-15*a*b+27/2*b*b)
+4*a*r3*(3*a*b*CS1+3/2*a*(b-A)*(CS3+CS2))
AR(3,1)=a*r3*((b*c-A*(c/6)*(CS3-CS2))
AI(3,1)=a*r3*(-A*c/6*(S3-S2))
AR(3,2)=a*r1*2/RT*a*b+b*r1*2/RT*a*b+c*r2*(16/RT*a*b-c/RT*a*c)
+4*a*r1*1/2*a*c+4*a*r2/RT*a*b+c*r2*(-2/RT*a*a+c*RT*a*b)
+4*a*r3*(2/RT*a*b*(S1+16/6*c*(2a-A)*(CS3+CS2))
AI(3,2)=a*r3*(-RT/6*a*(S3+S2))
AR(3,3)=a*r1*16/9*c*c+c*r1*2/9*c*c+c*r2*32/9*c*c+(a*r1*4/3*c*c
+4*a*r3*4/9*c*c+c*r2*4/3*c*c+c*r3*(2/9*c*c*(CS1+CS3+(S2+CS3))

AT02=1-AT02-3*LOCK
AR(4,4)=a*r1*19*a*b+b*r1*27/4*a*b+c*r2*(14*a*a-56*a*b+36*b*b)
+4*a*r1*63/4*a*b+c*r3*(-3*a*a+9*a*b)+a*r2*(6*a*a-33/2*a*b+63/4*b*b)
+4*a*r3*(3*a*(3/2*a-A)*CS1+3/2*a*(3*a-A)*CS2)
AR(5,4)=a*r1*a*b*(c*(c-1)+3/4*a*b+c*r2*(-2*a*b*a+12*a*b*b-12*a*b*c)
+4*a*r1*9/4*a*b*(a*(3*a-A)*CS1+3/2*a*(3*a-A)*CS2)
+4*a*r3*(1/2*a*(A-3*a)*CS1-1/2*a*RT*a*b*CS3+3/2*a*b*(A-b)*CS2)
AI(5,4)=a*r3*(-1/2*a*b*(S3+S2))
AR(5,5)=a*r1*30*a*b+b*r1*33/4*a*b+c*r2*(18*a*a-60*a*b+60*b*b)
+4*a*r1*9/4*a*b+c*r3*(-9*a*a+21*a*b)+a*r2*(6*a*a-39/2*a*b+81/4*b*b)
+4*a*r3*(3/2*a*(A-3*a)*CS1+3/2*a*(2*a-A)*CS3+3/2*a*(5*a-3*a)*CS2)
AR(6,4)=a*r1*4*a*b*(b*b+c*c+c*r2*(a*a*c-b*b*c)-a*r1*5/2*a*b*c
-a*r3*(c*c+c*r2*(c*(-3/2*a*b*c)+4*a*r3*(7*a*c/3-b*c)*CS1+4*a*c/6*CS3-b*c*c)
AI(6,4)=a*r3*(-4*a*c/3*S1+4*a*c/6*S3)
AR(6,5)=a*r1*4/RT*a*b+c*r1*1/RT*a*b+c*r2*(4/RT*a*b-c/RT*a*c)
-a*r2*1/2*a*b*(A-16/RT*a*b+c*r2*(A*c/RT-1/2*a*b*b*c)
+4*a*r3*(A*c/RT*(CS1-CS2)+RT/6*c*(A-4*a)*CS3)
AI(6,5)=a*r3*(RT/6*a*(A-S3))
AR(6,6)=a*r1*16/9*c*c+(a*r1*2/9*c*c+c*r2*32/9*c*c+(a*r1*4/3*c*c
+4*a*r3*4/9*c*c+c*r2*4/3*c*c+c*r3*(2/9*c*c*(CS1+CS3+(S2+CS2))

```

ATDMS-AIDMS FLECK

$$AR(7,7) = a * R1 * 1 * R * R + b * R1 * 27/4 * R * R + c * R2 * (14 * A * A - 36 * A * R + 36 * R * R) + d * R1 * 63/4 * R * R$$

$$+ d * R3 * (-3 * A * R + 6 * R * R) + d * R2 * (6 * A * A - 33/2 * A * R + 53/4 * R * R)$$

$$+ d * R3 * (3 * R * (3/2 * R - A) * CS1 + 3/2 * R * (3 * R - A) * CS3)$$

$$AR(6,7) = a * R1 * 6 * R1 * 2 * R * R + b * R1 * 3/4 * R1 * R * R + c * R2 * (2 * R1 * A * A - 12 * R1 * A * R + 12 * R1 * R * R)$$

$$+ d * R1 * 9/2 * R * T * R * R + d * R3 * (-3 * R1 * A * R + 6 * R1 * R * R) + d * R2 * (-3/2 * R1 * A * R + 9/4 * R1 * R * R)$$

$$+ d * R3 * (1/2 * R1 * R * (3 * R - A) * CS1 + 3/2 * R1 * R * (R - A) * CS3 + 1/2 * R1 * A * R * CS2)$$

$$AI(8,7) = d * R3 * (1/2 * R1 * A * R * (S1 + S2))$$

$$AR(5,8) = a * R1 * 3 * R * R + b * R1 * 33/4 * R * R + c * R2 * (1 * R * A * A - 6 * R * A * R + 6 * R * R * R)$$

$$+ d * R1 * 1 * R1/4 * R * R + d * R3 * (-4 * A * R + 21 * R * R) + d * R2 * (1 * A * A - 39/2 * A * R + R1/4 * R * R)$$

$$+ d * R3 * (3/2 * R * R * CS1 + 3/2 * R * (R * R - 3 * A) * CS3 + 3 * R * (2 * R - A) * CS3)$$

$$AR(9,7) = a * R1 * 4 * R * C - b * R1 * R * C + c * R2 * (-4 * A * C + 5 * R * C) + d * R1 * 5/2 * R * C$$

$$+ d * R3 * 4 * R * C + d * R2 * (-A * C + 3/2 * R * C) + d * R3 * ((-R * C - A * C/3) * CS1 + 3 * R * C * CS3 - A * C/6 * CS2)$$

$$AI(9,7) = d * R3 * (A * C/3 * S1 - A * C/6 * S2)$$

$$AR(9,8) = -a * R1 * 4/3 * R * C + b * R1 * 1/3 * R * C + c * R2 * (-8/3 * R * R * C + 4/3 * R * A * C)$$

$$- d * R1 * 1/2 * R * T * R * C - d * R3/3 * R * R * C + d * R2 * (A * C/RT - 1/2 * R1 * R * C)$$

$$AI(9,8) = d * R3 * (R1/6 * A * C + S1/2)$$

$$AR(9,9) = a * R1 * 16/9 * R * C * C + b * R1 * 1/2 * R * C * C + c * R2 * 32/9 * R * C * C + d * R1 * 4/3 * R * C * C$$

$$+ d * R3 * 4/9 * R * C * C + d * R2 * 4/3 * R * C * C + d * R3 * (2/9 * R * C * C * (CS1 + CS2 + CS3 + CS3))$$

125

127

APPENDIX 5.2

The matrices $\underline{A}$ (6x6), $\underline{B}$ (12x12) and $\underline{C}$ (6x12) of the SR BCM eigenproblem are listed below. The real and imaginary parts are AR/AI, BR/BI and CR/CI respectively; since $\underline{A}$ and $\underline{B}$ are Hermitian only their lower triangles are given, $\underline{C}$ is given in full. Only non-zero elements are given. The force constants are denoted by a,b,c and d; $KX=2ak_x$, $KY=2ak_y$, $KZ=2ak_z$.

```

CXY=COS(KX+PY)
SXY=SIN(KX+PY)
CYZ=COS(KY+KZ)
SYZ=SIN(KY+KZ)
CZX=COS(KZ+KX)
SZX=SIN(KZ+KX)

```

```

A100=AI00: INTERACTION MATRIX AR/AI
P=(2/3)*(4*a+b+4*c+d+2*d)
A1(1,1)=P      AR(2,2)=P      AR(3,3)=P
A1(4,4)=P      AR(5,5)=P      AR(6,6)=P
Q=-(2/3)*(4*a-d)
R=-(1/3)*(8*a+d)
A1(4,1)=P*(1+(XY+CYZ+LZX))
A1(4,1)=P*(SXY+SYZ+SZX)
A1(4,2)=Q*(1+LXY-CYZ-LZX)
A1(4,2)=Q*(SXY-SYZ-SZX)
A1(4,3)=Q*(1-CXY-CYZ-CZX)
A1(4,3)=Q*(-SXY-SYZ-SZX)
A1(5,1)=A1(4,2)
A1(5,2)=A1(4,1)
A1(5,3)=A1(4,1)
A1(5,3)=Q*(1-CXY+CYZ-CZX)
A1(5,3)=Q*(-SXY+SYZ-SZX)
A1(6,1)=A1(4,3)
A1(6,1)=A1(4,3)
A1(6,2)=A1(5,3)
A1(6,2)=A1(5,3)
A1(6,3)=A1(4,1)
A1(6,3)=A1(4,1)

```

```

C100=CI00: INTERACTION MATRIX BR/BI
P=(1/3)*(4*b+2*a+16*c+8*d)
Q=(1/3)*(-4*b+2*a+16*c-4*d)
A100=AI00: BLOCK
P=(1,1)=P      BR(2,2)=P      BR(3,3)=P
P=(2,1)=0      BR(3,2)=0      BR(6,6)=P
P=(3,1)=0      BR(5,5)=P      BR(6,6)=P
P=(4,4)=P      BR(6,5)=0      BR(6,6)=P
P=(5,4)=0      BR(8,8)=P      BR(9,9)=P
P=(6,4)=0      BR(9,8)=0      BR(12,12)=P
P=(7,7)=P      BR(11,11)=P
P=(8,7)=0      BR(12,11)=0
P=(9,8)=0      BR(12,11)=0
P=(10,10)=0
P=(11,10)=0      BR(12,11)=0
P=(12,10)=0      BR(12,11)=0

```


$$\begin{aligned} BR(4,3) &= P \\ BR(5,3) &= P \\ BR(6,3) &= P \\ BR(7,3) &= P \\ BR(8,3) &= P \\ BR(9,3) &= P \\ BR(7,3) &= -P \\ BR(8,3) &= -P \\ BR(9,3) &= -P \\ BR(7,3) &= -P \\ BR(8,3) &= -P \\ BR(9,3) &= -P \\ BR(10,3) &= -P \\ BR(11,3) &= -P \\ BR(12,3) &= -P \\ BR(10,3) &= -P \\ BR(11,3) &= -P \\ BR(12,3) &= -P \\ BR(7,6) &= P \\ BR(8,6) &= P \\ BR(9,6) &= -P \\ BR(7,6) &= P \\ BR(8,6) &= P \\ BR(9,6) &= -P \\ BR(10,6) &= P \\ BR(11,6) &= P \\ BR(12,6) &= -P \\ BR(10,6) &= P \\ BR(11,6) &= P \\ BR(12,6) &= -P \\ BR(10,6) &= P \\ BR(11,6) &= -P \\ BR(12,6) &= P \\ BR(10,6) &= P \\ BR(11,6) &= -P \\ BR(12,6) &= P \end{aligned}$$
$$\begin{aligned} CR(1,2) &= 0 \\ CP(2,2) &= P \\ CR(3,2) &= 0 \\ CR(4,2) &= 0 \\ CR(5,2) &= P \\ CR(6,2) &= 0 \end{aligned}$$
$$\begin{aligned} C_2(1, 5) &= 0 \\ C_2(2, 5) &= 0 \\ C_2(3, 5) &= 1 \\ C_1(1, 5) &= 1 \\ C_1(2, 5) &= 1 \\ C_1(3, 5) &= 0 \end{aligned}$$
$$\begin{aligned} CR(4,5) &= U \\ CR(5,5) &= P \\ CR(6,5) &= - \end{aligned}$$

```
CP(1,8)=-
CR(2,8)=P
CR(3,8)=-
CI(1,8)=R
CI(2,8)=-
CI(3,8)=C
```

$$\begin{aligned} CR(4, 8) &= - \\ CR(5, 6) &= P \\ CR(6, 6) &= - \end{aligned}$$
$$\begin{aligned} C(1,11) &= \\ C(2,11) &= \\ C(3,11) &= \\ C(1,11) &= \\ C(2,11) &= \\ C(3,11) &= \end{aligned}$$
$$\begin{aligned} C^P(4, 11) &= \\ C^P(5, 11) &= \\ C^P(6, 11) &= \end{aligned}$$
$$\begin{aligned} CR(1,3) &= 0 \\ CR(2,3) &= 0 \\ CR(3,3) &= P \\ CR(4,3) &= 0 \\ CR(5,3) &= 1 \\ CR(6,3) &= H \end{aligned}$$

$CF(1, b) = -$
 $CF(2, b) = -$
 $CF(3, b) = b$
 $CI(1, b) = 0$
 $CI(2, b) = 0$
 $CI(3, b) =$

$$\begin{aligned} CF(4, a) &= - \\ CF(5, b) &= - \\ CF(6, c) &= 5 \end{aligned}$$

$CF(1,9) = 0$
 $CF(2,9) = 1$
 $CF(3,9) = 1$
 $CI(1,9) = 1$
 $CI(2,9) = 1$
 $CI(3,9) = 1$

$$\begin{aligned} C(4, 9) &= 0 \\ C(5, 9) &= - \\ C(6, 9) &= 1 \end{aligned}$$
$$\begin{aligned} C_1(1, 12) &= \\ C_1(2, 12) &= \\ C_1(3, 12) &= \\ C_1(1, 12) &= \\ C_1(2, 12) &= \\ C_1(3, 12) &= \end{aligned}$$
$$\begin{aligned} C_F(4, 12) &= \\ C_F(5, 12) &= \\ C_F(6, 12) &= \end{aligned}$$

APPENDIX 7.4

The non-zero elements of the lower triangle of the Hermitian matrix $\underline{D}$ for the 2H-CdI_2 structure are listed below in the usual manner. The force constants are a, b and c ; AMASS and BMASS are the metal and ligand atom masses respectively; $KX = \frac{1}{2}Ak_x$, $KY = \frac{1}{2}\sqrt{3}Ak_x$, $KZ = Ck_z$.

```

AL=1/AMASS
BL=1/BMASS
CL=0.011(AM*BM)
CS1=CL*(BX+BX)
SS1=SL*(BX+BX)
CS2=CL*(BX-BY)
SS2=SL*(BX-BY)
CS3=CL*(BX+BY)
SS3=SL*(BX+BY)
L12=1/SL*CL(2)
L13=1/SL*CL(3)
L16=1/SL*CL(6)

A11=1-A11C1 BLOCK
D(1,1)=AL*(16*a+2*c*(2-CS1))
D(2,1)=AL*(2*BL*3*c*(CS2-CS3))
D(2,2)=AL*(16*a+2/3*c*(3+CS1-2*CS2-2*CS3))
D(3,1)=AL*(2*BL*6*c*(CS2-CS3))
D(3,2)=AL*(2/3*BL*2*c*(-2*CS1+CS2+CS3))
D(3,3)=AL*(16*a+4/3*c*(3+CS1+CS2+CS3))

A11=2-A11C2 BLOCK
D(4,4)=BL*(8*a+4*b+c)
D(5,4)=BL*(4,4)
D(6,4)=BL*(6*a+16*b+4*c)

A11=3-A11C3 BLOCK
D(7,7)=BL*(4,4)
D(8,8)=BL*(4,4)
D(9,9)=BL*(6,6)

A11=2-A11C4 BLOCK
D(4,1)=CL*(-4*a*(CS2+CS3)-c)
D(4,2)=CL*(-4*a*(SS2-SS3))
D(4,3)=CL*(14*a-c)*BL*3*(CS2-CS3)
D(4,4)=CL*(4*a-c)*BL*3*(SS2+SS3)
D(4,5)=CL*(-(8*a+c)*BL*6*(CS2-CS3))
D(4,6)=CL*(-(8*a+c)*BL*6*(SS2+SS3))
D(5,1)=BL*(4,2)
D(5,2)=BL*(4,2)
D(5,3)=CL*(-(16*a-c)/3-(4*a+2*c)/3*(CS2+CS3))
D(5,4)=CL*(-(14*a+2*c)/3*(SS2-SS3))
D(5,5)=CL*(-(8*a+c)/3*(2-CS2-CS3))
D(5,6)=CL*(-(8*a+c)/3*(SS2-SS3))
D(6,1)=CL*(-(8*a-2*c)*BL*(CS2-CS3))
D(6,2)=CL*(-(8*a-2*c)*BL*(SS2+SS3))
D(6,3)=CL*(-(8*a-2*c)/3*BL*2*(2-CS2-CS3))
D(6,4)=CL*(-(8*a-2*c)/3*BL*2*(SS2-SS3))
D(6,5)=CL*(-(8*a+4*c)/3*(1+CS2+CS3))
D(6,6)=CL*(-(8*a+4*c)/3*(SS2-SS3))

```

AT003-AT041 BLOCK

```

DP(7,1)=CP*(4*a*(1+CS1)-c*CS2)
D1(7,1)=CV*(4*a*SN1-c*SN2)
DP(7,2)=CP*(4*a-c)*K13*(1-CS1)
D1(7,2)=CV*(-(4*a-c)*K13*SN1)
DP(7,3)=CP*(-(4*a+c)*K13*(1-CS1))
D1(7,3)=CV*(-(4*a+c)*K13*SN1)
DP(7,4)=DP(7,2)
D1(7,4)=D1(7,2)
DP(8,2)=CP*(-(4*a+2*c)/3*(1+CS1)-(16*a-c)/3*CS2)
D1(8,2)=CV*(-(4*a+2*c)/3*SN1-(16*a-c)/3*SN2)
DP(8,3)=CP*(8*a+c)/3*K12*(1+CS1-2*CS2)
D1(8,3)=CV*(8*a+c)/3*K12*(SN1-2*SN2)
DP(9,1)=CP*(-(8*a-2*c)*K16*(1-CS1))
D1(9,1)=CV*(-(8*a-2*c)*K16*SN1)
DP(9,2)=CP*(8*a-2*c)/3*K12*(1+CS1-2*CS2)
D1(9,2)=CV*(8*a-2*c)/3*K12*(SN1-2*SN2)
DP(9,3)=CP*(-(8*a+4*c)/3*(1+CS1+CS2))
D1(9,3)=CV*(-(8*a+4*c)/3*(SN1+SN2))

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AT003-AT002 BLOCK

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CS1=1/3*(X/Z)
SN1=5/12*(X/Z)
CS2=1/3*(X+Y+Z)
SN2=1/3*(X+Y+Z)
CS3=1/3*(X+Y+Z)
SN3=1/3*(X+Y+Z)
DP(7,4)=CP*(-2*a*(CS1+CS2))
D1(7,4)=CV*(-2*a*(SN1+SN2))
DP(7,5)=CP*(-2*a*K13*(CS1-CS2))
D1(7,5)=CV*(-2*a*K13*(SN1-SN2))
DP(7,6)=CP*(8*a*K12*(CS1-CS2))
D1(7,6)=CV*(8*a*K12*(SN1-SN2))
DP(8,4)=DP(7,5)
D1(8,4)=D1(7,5)
DP(8,5)=CP*(-2/3*a*(CS1+CS2+4*CS3))
D1(8,5)=CV*(-2/3*a*(SN1+SN2+4*SN3))
DP(8,6)=CP*(8/3*a*K12*(CS1+CS2-2*CS3))
D1(8,6)=CV*(8/3*a*K12*(SN1+SN2-2*SN3))
DP(9,4)=DP(7,6)
D1(9,4)=D1(7,6)
DP(9,5)=DP(8,4)
D1(9,5)=D1(8,4)
DP(9,6)=DP(8,6)
D1(9,6)=D1(8,6)
DP(9,7)=CP*(-16/3*a*(CS1+CS2+CS3))
D1(9,7)=CV*(-16/3*a*(SN1+SN2+SN3))

```