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Dynamics of Disordered Harmonic Lattices. I. Normal-Mode Frequency Spectra for Randomly Disordered Isotopic Binary Lattices*†

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Results of computer calculations of normal-mode frequency spectra of certain binary isotopically disordered harmonic lattices are presented. Linear chains, and square, triangular, simple-cubic, and body-centered cubic lattices are discussed. Interesting features of the results include dramatic changes in the nature of the spectra as the mass ratio of the two components or their relative concentration is varied. Discussions are given of the physical interpretation of the special frequencies of the linear chain and of a possible extension to higher dimensions.

INTRODUCTION

A THEORETICAL understanding of the spectra of disordered lattices has been much pursued in recent years, but so far has been largely elusive.[1] Without exception, the spectra which have been calculated have either borne little resemblance to reality or have themselves been basically results of computer experiments. Much ingenuity has been displayed in setting up schemes according to which the computer can efficiently and accurately get desired numbers. Much more is needed to achieve a deeper understanding of the vibrations of disordered systems. It remains a challenging task to bring this subject from the domain of the numerical analyst into the realm of the theoretical physicist.

In the present series of papers, our aim is not to deepen the theoretical understanding of the properties of disordered lattices. Most of our results, too, are generated by computer experiments. We hope to accomplish two things. First, we wish to present a more complete and detailed exposition of precisely what the properties of disordered lattices are. Some of the early attempts at calculating disordered-lattice spectra were not recognized to be unsuccessful simply because the nature of the correct answer was not known. Our first aim is then to enrich the field of data and to broaden the testing ground for future analytic attempts at understanding disordered lattices.

Secondly, we plan to use our results, and extensions of them, to compute certain observables directly, such as some thermodynamic properties, transport coefficients, neutron scattering, and Mössbauer factors for disordered lattices. Although we are limited to fairly small arrays in the three-dimensional case, we believe the results to be nevertheless significant, because other methods are still much less accurate.

Theoretical pursuit of the disordered-lattice spectrum began in 1953, with Dyson's work on glasslike linear chains.[2] His method was subsequently elaborated and simplified, but it proved to be unsuitable for lattices of 2 or 3 dimensions.[3] Other approaches were subsequently invented and exploited—such as the moment-trace method, the Green's-function expansions in powers of the concentration, and the transfer-matrix method. But it was not until the exact numerical calculations of Dean were done for a finite linear chain that the actual nature of the spectra was appreciated.[4] For moderately low concentration of light impurities, for example, the spectrum is very jagged. Its irregularity explains the extreme difficulties people had in calculating it analytically.

The disordered lattice has, in fact, a normal-mode frequency spectrum which is nonanalytic in the mass defect. This is clear from the fact that the localized modes (an example of which is the single mode of frequency higher than the continuum of phonons when an isolated light impurity is present) appear suddenly out of the continuum as the impurity mass is reduced. It is also nonanalytic in the frequency and in the concentration. This was shown by Lifshitz,[5] who derived by simple probabilistic arguments what the dependence of the spectrum on frequency and concentration should be in the neighborhood of a band edge. In retrospect, therefore, it is not surprising that analytic attempts to calculate these spectra have failed.

Our plan is to present in Sec. I the model on which most of our calculations are based. This uses nearest-neighbor harmonic central and noncentral forces which allow x, y, and z motions to be separated. In Sec. II the method of calculation of the normal-mode spectra is discussed. Like Dean, we use the method of counting the changes in sign of a Sturm sequence to generate the spectra. The next section is specialized to the one-dimensional case and includes presentation of the spectra for various cases, discussion of the special fre-

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† Part of this work is included in a thesis submitted by one of us (D.N.P.) in partial fulfillment of the requirements for the Ph.D. degree at the University of Missouri at Rolla.

[1] An up-to-date and extensive bibliography of theoretical and experimental work on disordered lattices is contained in an article by A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 273.

[2] F. J. Dyson, Phys. Rev. **92**, 1331 (1953).

[3] R. Englman, Nuovo Cimento **10**, 615 (1958); R. Bellman, Phys. Rev. **101**, 19 (1956).

[4] P. Dean, Proc. Phys. Soc. (London) **73**, 413 (1959); Proc. Roy. Soc. (London) **A254**, 507 (1960); **A260**, 263 (1961).

[5] I. M. Lifshitz, Advan. Phys. **13**, 483 (1964).

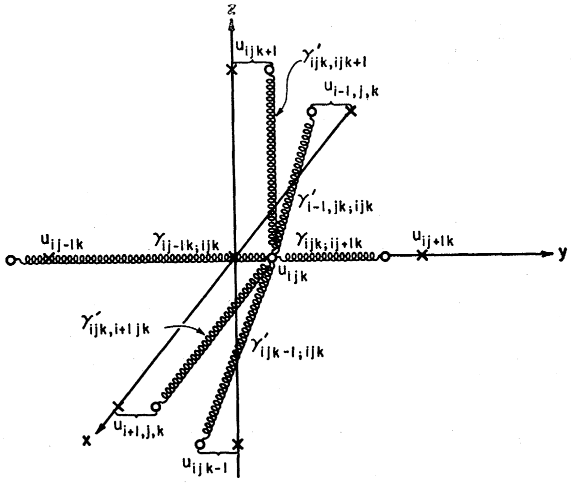

FIG. 1. Labeling scheme for the simple-cubic case. Forces are always along the direction of the displacement. Those exerted by atoms located along the line of displacement are central forces, with force constants γ. The others are noncentral forces with constants γ'. Displacements in this example are in the y direction. The x, y, and z displacements in this model are all independent.

quencies of Borland, Hori, and Matsuda,[6] and other comments on the nature of the results. An extension of the Sturm sequence method, again similar to Dean's, is used in Sec. IV to calculate the normal-mode spectra of the separable models of the square and simple cubic lattices. Results for certain nonseparable models—namely the triangular and body-centered cubic lattices—are given in Sec. V. The final section consists of a summary and discussion of the significant results.

I. DESCRIPTION OF THE MODEL

We use a model in which the atoms of the crystal lattice are represented by point masses connected to their nearest neighbors by central and noncentral springs. In the n-dimensional simple cubic lattice this choice affords the simplification that the motions in each cartesian direction are independent. This separation reduces the number of coupled variables in the n-dimensional lattice of N atoms from nN to N.

The equation of motion for an atom in the interior of an n-dimensional simple cubic lattice is then, in the harmonic approximation,

$$\begin{aligned} m_{i_1,i_2,\cdots}\ddot{u}_{i_1,i_2,\cdots} = {} & \gamma_{i_1,i_2,\cdots;i_1+1,i_2,\cdots}(u_{i_1+1,i_2,\cdots}-u_{i_1,i_2,\cdots}) \\ & +\gamma_{i_1-1,i_2,\cdots;i_1,i_2,\cdots}(u_{i_1-1,i_2,\cdots}-u_{i_1,i_2,\cdots}) \\ & +\gamma'_{i_1,i_2,\cdots;i_1,i_2+1,\cdots}(u_{i_1,i_2+1,\cdots}-u_{i_1,i_2,\cdots}) \\ & +\gamma'_{i_1,i_2-1,\cdots;i_1,i_2,\cdots}(u_{i_1,i_2-1,\cdots}-u_{i_1,i_2,\cdots}) \\ & +\cdots, \end{aligned} \tag{1}$$

where $m_{i_1,i_2,\cdots,i_n}$ is the mass of the atom, γ and γ' are the central and noncentral force constants, and $u_{i_1,i_2,\cdots}$ is the displacement of the $(i_1,i_2,\cdots,i_n)$th atom from equilibrium in a direction parallel to one of the cube edges. Figure 1 shows an example of the indexing for $n=3$. The displacements u in this case are all in the y direction.

The set of Eqs. (1) is, in matrix notation,

$$[\mathbf{M}_n-\omega^2\mathbf{I}_n]\mathbf{u}=0, \tag{2}$$

where $\mathbf{M}_n$ is the dynamical matrix of the n-dimensional (n-D) simple cubic lattice. This matrix can, from Eq. (1), be seen to have a block tridiagonal form,

$$\mathbf{M}_n=\begin{bmatrix} \mathbf{A}_1 & \mathbf{B}_2 & & & 0 \\ \mathbf{B}_2^T & \mathbf{A}_2 & \mathbf{B}_3 & & \\ & \mathbf{B}_3^T & \mathbf{A}_3 & \mathbf{B}_4 & \\ & & \ddots & \ddots & \ddots \\ 0 & & & \mathbf{B}_{i_n}^T & \mathbf{A}_{i_n} \end{bmatrix}, \tag{3}$$

where $\mathbf{B}_i^T$ is the transpose of $\mathbf{B}_i$. These blocks are in turn made up of block matrices if $n\geq 2$, etc.

Most lattices cannot be described by an n-D simple cubic model, and consequently, the problem becomes more difficult. As a simple example of a nonseparable lattice consider the triangular lattice shown in Fig. 2. The equation of motion for the (i,j)th atom with central and noncentral force constants between nearest neighbors only is

$$\begin{aligned} m_{ij}\begin{pmatrix}\ddot{x}_{ij}\\ \ddot{y}_{ij}\end{pmatrix} = {} & \begin{pmatrix}\gamma_{ij;i+1j} & 0\\ 0 & \gamma_{ij;i+1j}'\end{pmatrix}\left[\begin{pmatrix}x_{i+1j}\\ y_{i+1j}\end{pmatrix}-\begin{pmatrix}x_{ij}\\ y_{ij}\end{pmatrix}\right]+\text{other central term} \\ & +\frac{1}{4}\begin{pmatrix}\gamma_{ij;ij+1}+3\gamma_{ij;ij+1}' & \sqrt{3}(\gamma_{ij;ij+1}-\gamma_{ij;ij+1}')\\ \sqrt{3}(\gamma_{ij;ij+1}-\gamma_{ij;ij+1}') & \gamma_{ij;ij+1}+3\gamma_{ij;ij+1}'\end{pmatrix}\times\left[\begin{pmatrix}x_{ij+1}\\ y_{ij+1}\end{pmatrix}-\begin{pmatrix}x_{ij}\\ y_{ij}\end{pmatrix}\right]+\text{other noncentral terms}. \end{aligned} \tag{4}$$

The x and y coordinates in Eq. (4) are coupled; therefore, in the triangular lattice one must work with $2N$ variables. Most real solids are either body-centered cubic, face-centered cubic, or hexagonal close-packed lattices. The equations of motion for none of these lattices are separable; consequently their frequency spectra are more difficult to calculate than the simple cubic spectrum.

II. METHOD OF CALCULATION

Consider now the problem of finding the spectrum of eigenvalues of Eq. (2). It is sufficient first to determine the integrated frequency spectrum $M(\omega^2)$ which

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[6] R. E. Borland, Proc. Phys. Soc. (London) 83, 1027 (1964); H. Matsuda, Progr. Theoret. Phys. (Kyoto) 31, 161 (1964); J. Hori, *ibid.* 31, 940 (1964).

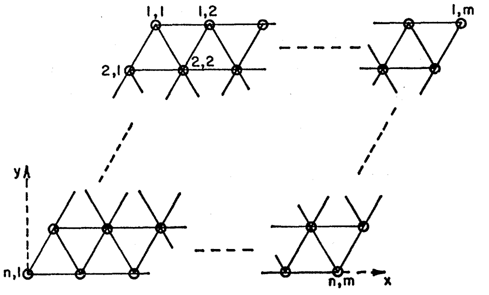

FIG. 2. Site-labeling scheme for the triangular lattice.

gives the number of frequencies of the system less than its argument. Thus the number of frequencies less than some ω^2 is just $\eta(M_n-\omega^2 I)$ where the symbol $\eta(\ )$ denotes the number of negative eigenvalues of the argument matrix and I is the unit matrix. Once the integrated spectrum has been determined, the frequency spectrum $D(\omega^2)$ can be obtained by differentiation,

$$D(\omega^2)=dM(\omega^2)/d\omega^2, \tag{5}$$

and consequently, the number of normal modes which lie between ω^2 and $\omega^2+d\omega^2$ is $D(\omega^2)d\omega^2$.

The integrated spectrum can be determined by a method used by Dean and Bacon,[7] based on elementary determinant theory. Using the notation used by Dean and Bacon, we let

$$\mathbf{L}^{(1)}=l_{ij}^{(1)}=\mathbf{M}_n-\omega^2\mathbf{I}, \tag{6}$$

where $\mathbf{M}$ is the dynamical matrix for any lattice of N atoms considered. The $N\times N$ symmetric matrix $\mathbf{L}^{(1)}$ can be partitioned as follows:

$$\mathbf{L}^{(1)}=\left[\begin{array}{c|c} \mathbf{X}_i & \mathbf{Y}_1 \\ \hline \mathbf{Y}_1^T & \mathbf{Z}_1 \end{array}\right], \tag{7}$$

where the submatrix $\mathbf{X}_1$ is of order unity and $\mathbf{Z}_1$ is of order $N-1$. In other words, $\mathbf{X}_1=l_{11}^{(1)}$, and $\mathbf{Y}_1$ is a row matrix with the column matrix $\mathbf{Y}_1^T$ its transpose. Now the determinant of $\mathbf{L}^{(1)}$ can be written

$$\det\mathbf{L}^{(1)}=\det\mathbf{X}_1\det\mathbf{L}^{(2)}, \tag{8}$$

where

$$\mathbf{L}^{(2)}=\mathbf{Z}_1-\mathbf{Y}_1^T\mathbf{X}_1^{-1}\mathbf{Y}_1, \tag{9}$$

after reducing all but the first element of the first column of $\det\mathbf{L}^{(1)}$ to zero by subtraction of appropriate multiples of the first row from succeeding ones. Therefore, we can write

$$\eta(\mathbf{L}^{(1)})=\eta(\mathbf{X}_1)+\eta(\mathbf{L}^{(2)}), \tag{10}$$

and by repeating the reduction on $\mathbf{L}^{(2)}$ and its successors $\mathbf{L}^{(3)}, \mathbf{L}^{(4)}\cdots$, we obtain

$$\eta(\mathbf{L}^{(1)})=\sum_{i=1}^{N}\eta(\mathbf{X}_i), \tag{11}$$

enabling us to find the number of eigenvalues smaller than ω^2 by counting the number of negative terms in the sequence $l_{11}^{(1)}, l_{11}^{(2)}, l_{11}^{(3)}, \cdots, l_{11}^{(N)}$.

The procedure for spectrum calculations is then to compute the sequences of matrices $\mathbf{L}^{(1)}, \mathbf{L}^{(2)}, \cdots, \mathbf{L}^{(N)}$ and to note the signs of the upper left elements of these matrices. The generating relation for the sequence is just the generalization of Eq. (9),

$$\mathbf{L}^{(j+1)}=\mathbf{Z}_j-\mathbf{Y}_j^T\mathbf{Y}_j/l_{11}^{(j)}\quad(j=1,2,\cdots,N-1). \tag{12}$$

This technique is formally identical to the reduction process of Gaussian elimination. An error analysis has been made by Wilkinson,[8] and the method of Gaussian elimination is accurate in all cases except where one of the upper left elements ($l_{11}^{(j)}$) becomes very small. In the reduction of the dynamical matrix this never happens.

Equation (11) has been used to calculate frequency spectra for lattices of one, two, and three dimensions. The calculations were executed on the IBM 7030 digital computer, utilizing source programs written in FORTRAN IV.

III. ONE-DIMENSIONAL APPLICATION

1. Calculational Results

In the linear chain many simplifications can be made which speed the calculation. Since the dynamical matrix is a tridiagonal matrix of simple elements, the calculation is reduced to counting the number of sign changes in a very simple sequence. It is for this reason that very long chains can be calculated to study convergence. For example, the time required to calculate the spectrum of a chain of 100 000 atoms at 100 frequencies is approximately 10 min on the IBM 7030 computer.

The spectrum of the monatomic chain can be calculated analytically and has the well-known U-shaped form given by $D(\nu)=\pi^{-1}[4-(\nu-2)^2]^{-1/2}$ for values of $0<\nu<4$, where $\nu=\omega^2$ and $D(\nu)$ is the frequency spectrum. Figure 3 shows a series of computed spectra, starting with the regular monatomic chain [Fig. 3(a)]. When light impurities are introduced into the chain at random positions, modes are shifted up out of the continuum of the host lattice spectrum. For the mass ratio of 3:1 which is illustrated here, the spectrum at higher frequencies is not at all smooth, and as the concentration of light impurities is increased, the spectrum near the upper band edge of the host mass continuum becomes depleted while numerous spikes reflecting

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[7] P. Dean and M. D. Bacon, Proc. Roy. Soc. (London) A283, 64 (1965).

[8] J. H. Wilkinson, *Rounding Errors in Algebraic Processes* (Her Majesty's Stationery Office, London, 1963), Chap. 3.

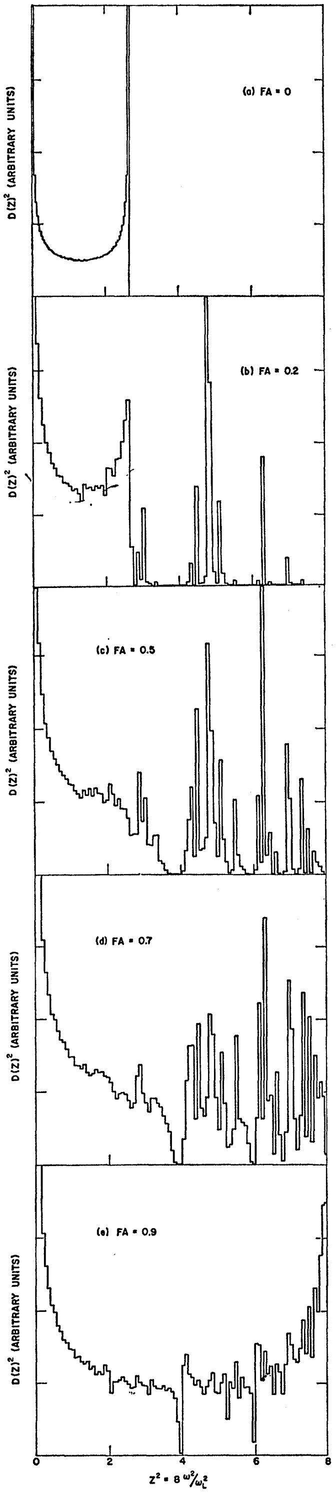


FIG. 3. Frequency spectra for the 100 000-atom linear chain for a random arrangement of light masses of concentration *FA* and heavy masses 3 times as heavy.

localized modes appear at higher frequencies. This is shown for a light atom concentration of 0.2 in Fig. 3(b). The upper band edges assume a shape like that predicted by Lifshitz in his work on the spectra of disordered lattices.[5]

As the concentration of lighter atoms is increased, the erosion of the monatomic host continuum, especially near the upper end, continues; while the peaks at higher frequencies continue to increase in size and do not smooth out into a continuum. This increase in the

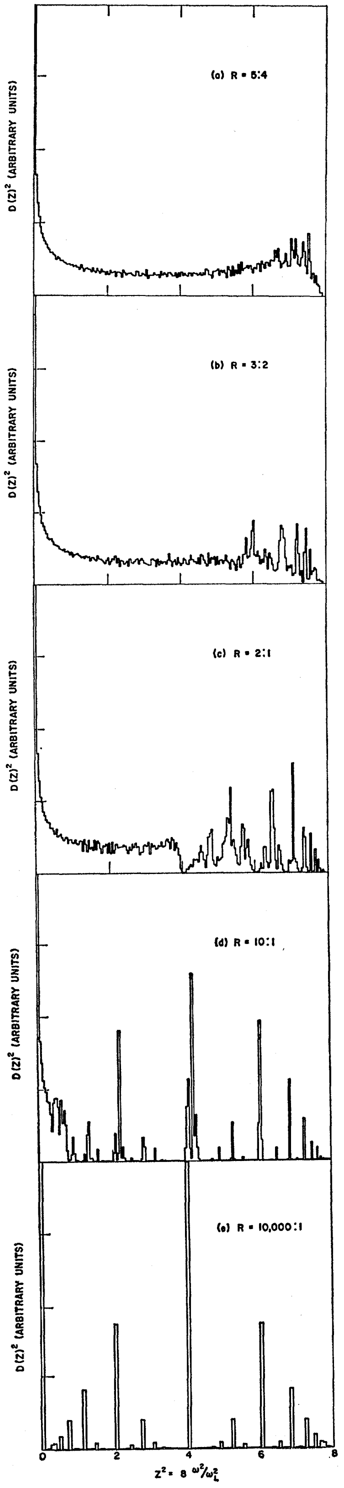
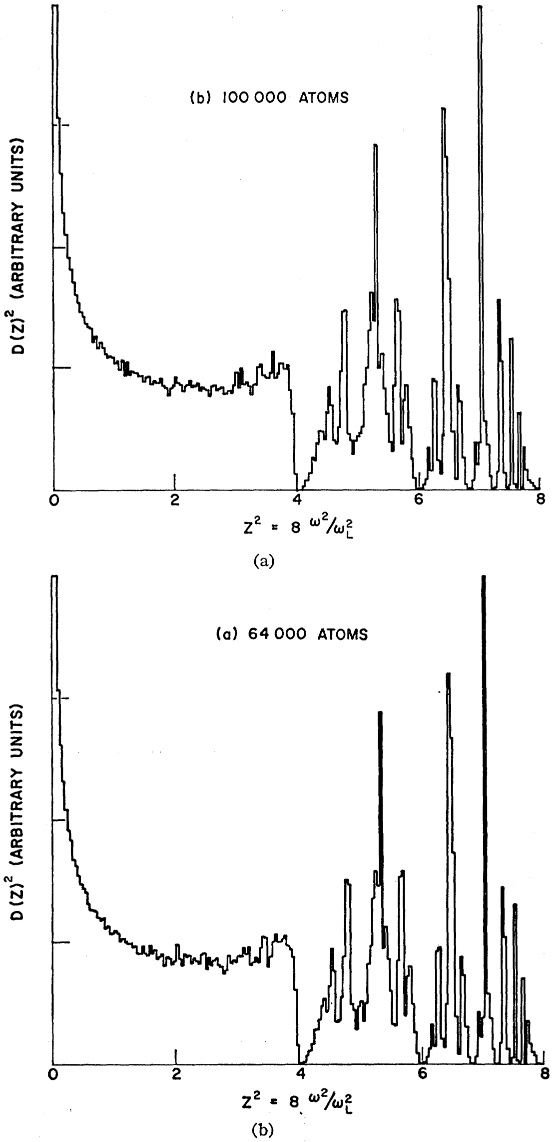


FIG. 4. Frequency spectra for the 8000-atom linear chain for a random arrangement with equal proportions of two masses whose ratio is *R*.



(a)

(b)

FIG. 5. Frequency spectra of two independent, randomly disordered linear chains with mass ratio 2:1. It is clear that little of the structure at high frequencies is due to a statistical error which would disappear for an infinite chain. Below the heavy-mass continuum cutoff, though, most of the unevenness is of statistical origin.

peaked structure is apparent from Figs. 3(c) and 3(d). In Fig. 3(e) the concentration of the light atoms has been increased to 0.9, and it is apparent that the spectrum is approaching the spectrum of the monatomic light chain. The chains shown in Fig. 3 each consisted of 100 000 atoms.

The effect of varying the mass ratio is shown in Fig. 4. The concentration of both atomic species in these chains is 0.5 and their lengths are 8000 atoms. Figures 4(a) and 4(b) show the spectra for mass ratios of 5:4 and 3:2. They are qualitatively different from the spectra for higher mass ratios.

In Fig. 4(e) we show the spectrum of the binary chain with one of the masses very large. The mass ratio is 10 000:1 and the light atoms are dynamically isolated from each other. The spikes occur at normal-mode frequencies of isolated chains (islands) and their heights are proportional to the number of islands in the chain with that normal-mode frequency. Figure 5 shows the frequency spectra of two independent random chains of different lengths. The mass ratio used in these chains is 2:1, and the impurity concentration is 0.5 in both. Figures 5(a) and 5(b) show the spectra for chains of lengths 64 000 and 100 000 atoms, respectively. It can be seen that the structures are almost identical at the higher frequencies. One can further study the effect of size by observing that the spectrum of a chain of 8000 atoms as shown in Fig. 4(c) has similar quantitative features. One can therefore be quite sure that the major irregularities of the spectra are not due to poor statistics or to the finite chain length, but will persist substantially unchanged from those shown in Fig. 5 in an infinite chain. Many of the peaks, as Dean and Bacon[9] showed, and as we will elaborate in a subsequent paper, can be identified with modes of islands of light impurities.

2. Special Frequencies

Exact, analytic, nontrivial results about the spectra of disordered lattices are very meager. The only ones, in fact, which actually yield values of the integrated spectrum are related to the special or forbidden frequencies of Borland, Matsuda, and Hori.[6] The most general statement[10] so far enunciated of the special frequency theorem for a one-dimensional chain may be understood as follows.

The spectrum of a randomly disordered linear chain in which the heavy masses have infinite mass may be derived trivially, and a good approximation to it is shown in Fig. 4(e). With considerable differences in degeneracy the normal-mode frequencies are given, for an infinite chain, by

$$\omega^2(q) = (4\gamma/m)\sin^2(\pi q/2), \qquad (13)$$

where $q = k/l$ is a rational number, with integers $k < l$. Now, if the heavy masses are decreased, then, by one of Rayleigh's theorems, all the frequencies will increase.[11] The special frequency theorem says that as long as the mass ratio satisfies the inequality

$$\frac{M}{m} > 1 + \cot\frac{\pi}{2l}\tan\frac{(l-k)\pi}{2l}, \qquad (14)$$

then no frequency will cross $\omega^2(k/l)$ given by Eq. (13),

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[9] P. Dean and M. D. Bacon, Proc. Phys. Soc. (London) **81**, 642 (1963).

[10] J. Hori and M. Fukushima, J. Phys. Soc. Japan **19**, 296 (1964).

[11] Lord Rayleigh, *Theory of Sound* (Dover Publications, Inc., New York, 1945), Vol. 1.

and the integrated spectrum up to that point remains the same as that for the infinite mass ratio. If, for example, $k=l-1$, then the inequality says $M/m>2$, which is the case Borland considered. The maximum frequency of a chain of length $l-1$ with rigid boundaries is $\omega^2(l-1/l)$. For mass ratios smaller than 2 there are no special frequencies. This is consistent with the observed fact (see Fig. 4) that the spectra for smaller mass ratios abruptly become smooth. To within the uncertainty caused by our finite mesh size, all our linear-chain spectrum calculations are consistent with these special frequencies. That is, the integrated spectra are, at the relevant special frequencies, equal to the integrated spectra for the infinite-mass-ratio case, and the spectra themselves vanish at those points.

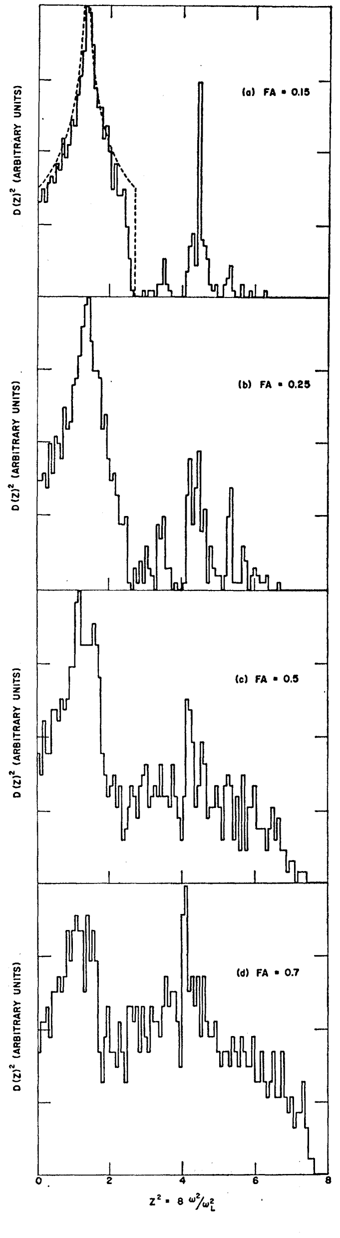

FIG. 6. Frequency spectra of 30×30 atom square lattices, randomly disordered with a fraction *FA* of light masses, the remainder being 3 times as heavy. The dashed line in (a) is the analytically calculated spectrum for the infinite pure heavy lattice.

It is appropriate to observe here that Borland's arguments for the case $k=l-1$ can as well be applied to an arbitrarily ordered chain as to a randomly disordered one. Therefore if one knows the order of a chain, hence the spectrum for infinite mass ratio, then all the frequencies given by Eq. (13) with $k=l-1$ are special as long as $M/m>2$, and the integrated spectrum at these points remains the same as that for $M/m=\infty$. We may conjecture that the same is true for all $k<l$. This too is consistent with our numerical results. It may in particular be easily verified that the optical band edges of the ordered diatomic chain $\cdots ABAB\cdots$ are special frequencies as long as the mass ratio satisfies Eq. (14). The shape of the frequency spectrum in the neighborhood of the special frequencies depends on the frequency of occurrence of certain successions of light and heavy chains and on the mass ratio. In particular, notice the striking difference between the shape of the $M/m=2$ spectrum at the lowest special frequency and that for $M/m=3$ [Figs. 4(c) and 3(c)].

IV. TWO- AND THREE-DIMENSIONAL LATTICES

1. Square Lattices

Consider now the square lattice. The motions of the atoms in either the x or y directions are described by Eq. (2) with $n=2$. The fact that the x and y coordinates are independent means that our computer can, in the same time and with the same memory, handle a lattice with about twice as many atoms as it otherwise could. The spectra presented here are for lattices of 30×30 atoms.

A comparison of the effects on the spectrum of the addition of various concentrations of light atoms into a square lattice of heavy atoms is shown in Fig. 6. The characteristic shape of the continuum of the heavy-atom lattice appears in Fig. 6(a) along with the analytic spectrum of the monatomic host lattice. In these lattices the central and noncentral force constants were equal; thus the singularities of the monatomic spectrum appear as a single logarithmic singularity.[12] A jagged structure again appears at higher values of the frequency. These peaks can be identified with localized modes of various configurations of light impurities. In the transition from the light impurity concentration (*FA*) of 0.25 to 0.5 a marked change in the spectrum occurs. The spectrum becomes relatively smooth without the isolated bands or peaks. At a concentration of approximately 0.5 the probability of an island of light atoms of infinite extent being formed in an infinite lattice becomes unity. It is at this point that the spectrum becomes relatively

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[12] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 3, Suppl.

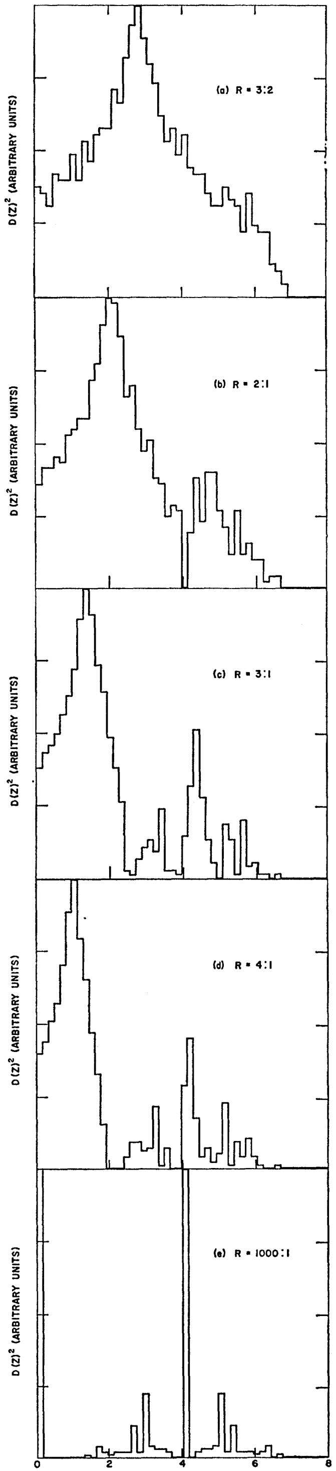

FIG. 7. Frequency spectra of a 30×30 atom square lattice which is a randomly disordered mixture of 75% heavy masses and 25% light masses with mass ratio *R*. Special frequencies seem to begin to appear at $R=2$. The low-frequency behavior of the spectra is determined largely by the harmonic mean mass up to the frequency of the big peak, whose position is inversely proportional to the harmonic mean mass.

smooth. This concentration is called the critical percolation concentration.[13] Beyond this critical concentration an inversion of the roles of host and impurity occurs, and one has effectively a host light lattice with a concentration of heavy impurities of $1-FA$. The spectrum shown in Fig. 6(d) is that of a light lattice doped with heavier atoms and exhibits a low-frequency resonance-mode peak.[14] The mass ratio of the lattices considered in Fig. 6 was 3:1.

Figure 7 shows the behavior of the spectrum as the mass ratio is increased from 3:2 to 1000:1. The concentration of light impurities is 0.25. For a further comparison the spectrum shown in Fig. 6(d) can be included in this study since it has the same concentration of random impurities with a mass ratio of 3:1.

These spectra make plausible the conjecture that there are special frequencies in the square lattice. The spectrum vanishes at $\omega^2=\frac{1}{2}\omega_L{}^2$ in each part of Fig. 7, except 7(a), and the integrated spectra at this point are all equal. Other points where all the integrated spectra coincide (at least for mass ratios greater than 3:1 and small light atom concentration) are $\omega^2=\frac{5}{8}\omega_L{}^2$, corresponding to the uppermost modes of an isolated pair of light atoms, and $\omega^2=\frac{1}{8}(4+\sqrt{2})$, corresponding to the modes of the triple atom defect in an infinitely heavy square lattice ($\omega^2=\frac{1}{2}\omega_L{}^2$ is, of course, the frequency of a single isolated impurity in a very heavy lattice). Figure 8 shows these integrated spectra for several mass ratios. The multiple crossing points could be special frequencies; they are points at which the spectra of Fig. 7 vanish. We therefore believe it rea-

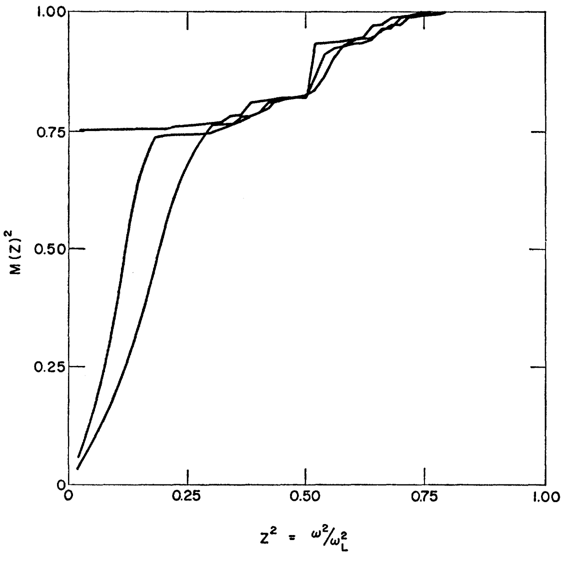

FIG. 8. Integrated spectra for three 30×30 atom square lattices, randomly disordered 25–75% mixtures of light and heavy atoms with mass ratios 3, 5, and 1000. The points at which the curves cross (to within the uncertainty engendered by the finite calculational mesh on the abscissa) can be special frequencies, as discussed in the text. The abscissa here is the square of the frequency, scaled so that the maximum frequency of an infinite pure light lattice is unity.

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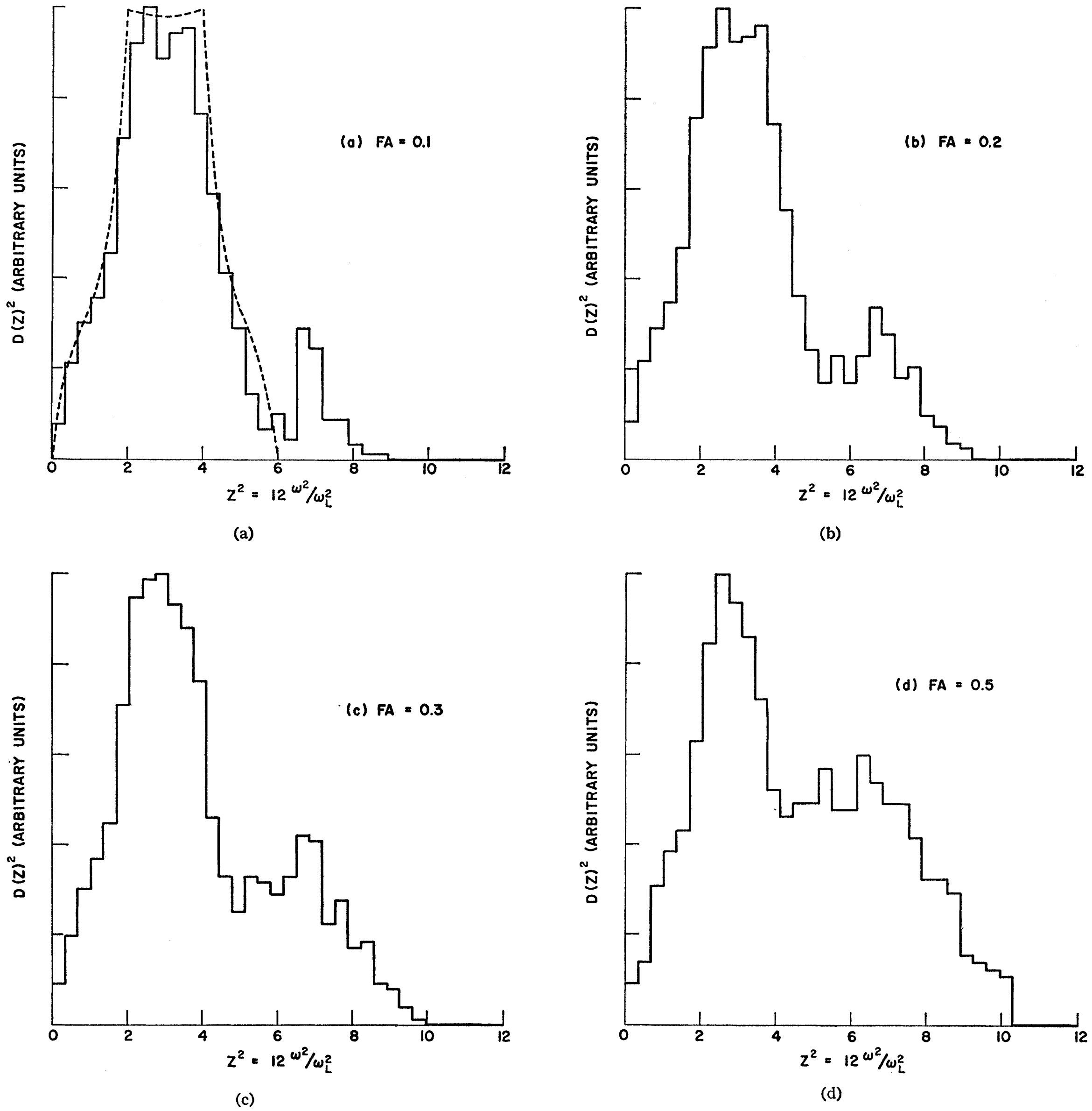
[13] M E. Fisher, J. Math. Phys. **2**, 620 (1961).

[14] R. Brout and W. M. Visscher, Phys. Rev. Letters **9**, 54 (1962); Y. Kagan and Y. A. Iosilevskii, Zh. Eksperim. i Teor. Fiz. **42**, 259 (1962) [English transl.: Soviet Phys.—JETP **15**, 182 (1962)].



(a) (b) (c) (d)

FIG. 9. Frequency spectra for a 6×6×25 atom randomly disordered simple-cubic lattice with a mass ratio of 2 and light-atom concentration given by *FA*. The dashed line is the exact spectrum for an infinite lattice with $FA=0$.

sonable to conclude that there are indeed special frequencies in the square lattice and that their origin and nature are straightforward generalizations of those of the special frequencies of the linear chain.

The boundary conditions were such that the two shorter sides (or opposite sides in a square array) were fixed and the other two were restricted by helical constraints. That is, an atom on one edge was connected to an atom on the opposite edge one row removed by a noncentral spring. The spectra for several lattices of varying shapes but constant number of atoms were calculated to give an estimate of the effect of the boundaries on the structure of the spectrum. The changes in the spectra between lattices of 8×112, 16×56, and 30×30 were quantitatively small and qualitatively negligible.

2. Simple Cubic Lattices

After the calculation of the one- and two-dimensional frequency spectra for isotopically disordered binary lattices, one can almost predict what general features the three-dimensional simple cubic lattice will have. Indeed, the spectrum of the simple cubic lattice of two masses in random order exhibits the continuum spectrum of the monatomic host lattice with impurity modes superimposed. If the impurities are lighter than the host these modes appear above the continuum. If the mass ratio is such that local modes are formed, this high-frequency spectrum has a peaky, jagged structure. If the impurities are heavier than the host mass, resonance modes are formed at the lower frequencies.

The frequency spectra of small finite crystals were calculated using the method outlined earlier. As can be seen by close examination of the method of counting negative eigenvalues, the calculational time will be dependent upon several factors. It depends directly on the number of mesh points and the length of the lattice. The time also depends directly upon the square of the number of atoms in a cross section of the lattice. This is analogous to the width in the square lattice. It is for this reason that long, thin crystals were chosen. The effects of the boundaries which were fixed along the length of the lattice and helical-toroidal in the other two directions were investigated and found to be similar in kind and magnitude to those found in the square lattice. The calculational time required for a lattice of 6×6×25 atoms was about 30 sec per mesh point.

In Fig. 9 are shown some spectra obtained for disordered simple cubic lattices with varying amounts of light impurities (*FA*). Superimposed on Fig. 9(a) is the analytic spectrum of the monatomic host lattice. The mass ratio is 2:1. Even though the calculational mesh is quite coarse and the lattice is rather small (6×6×28 atoms) the general features are what one would have expected on the basis of previous cases calculated.

The critical percolation concentration for the simple cubic lattice is approximately 0.28,[13] and consequently the role of host and impurity play a less important part in concentrations of light atoms from about $FA=0.28$ to $FA=0.72$. At this point the roles are interchanged; the heavy atoms are isolated in islands and low-frequency resonance modes are prominent.[14] This trend can be seen in Figs. 9(a)–9(d).

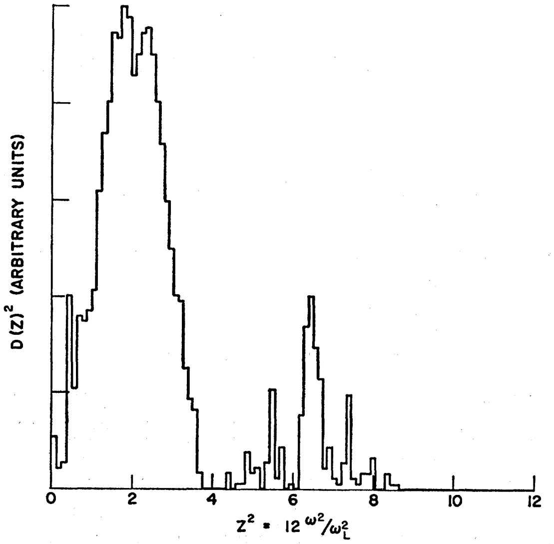


FIG. 10. The frequency spectrum of a 6×6×40 atom randomly disordered simple-cubic lattice calculated on a finer mesh than Fig. 9, for a mass ratio of 3 and a light-atom concentration of 10%.

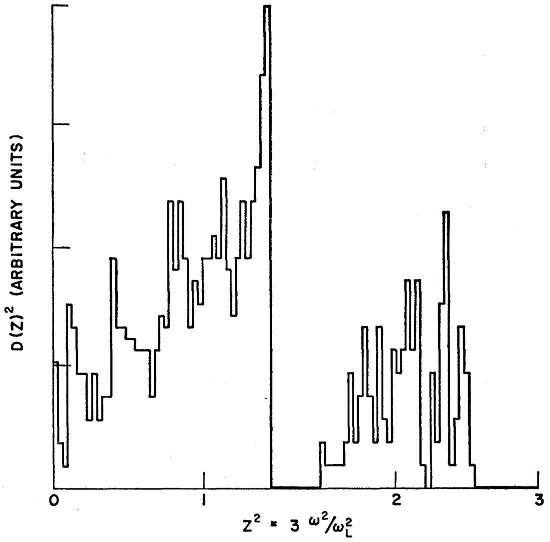


FIG. 11. The frequency spectrum for a triangular lattice 10×50 atoms with a mass ratio of 3 and light-atom concentration of 25%.

Figure 10 shows the spectrum of a 6×6×40 atom simple cubic lattice, calculated on a finer frequency mesh in order to show more detail in the high-frequency structure. As we will show in a subsequent paper, many of the peaks can be identified with certain modes of isolated islands of light impurities. Although our calculations for the cubic case have been on a coarser mesh than for the square and linear lattices, they are consistent with the hypothesis that special frequencies exist for the simple cubic lattice. Specifically, for example, the integrated spectra for the cases of mass ratio 3, 5, and 1000 coincide at the normal-mode frequencies of isolated single and double light atoms in a very heavy lattice.

V. NONSEPARABLE MODELS

Calculation of the frequency spectrum for models more realistic than those we have been using is more difficult. Since the equations for motions in the *x*, *y*, and *z* directions are not separable in general, the complete system of *nN* variables and equations must be dealt with. In this section we will show the results of calculations of the frequency spectra of the triangular and the body-centered cubic lattices.

The equations of motion and the model used for the calculation of the triangular lattice have been displayed in Sec. I. An example of the spectra calculated for this lattice is shown in Fig. 11. Certain features which were established in the simple cubic lattices of one, two, and three dimensions are reproduced in the triangular lattice spectrum. At lower frequencies the continuum of the host lattice appears with isolated peaks at higher

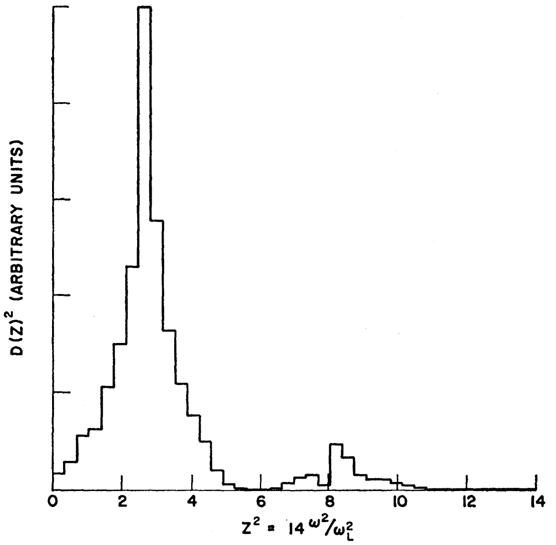


FIG. 12. Body-centered cubic-lattice spectrum for a concentration of 10% light impurities with $\frac{1}{3}$ the host mass. The next-nearest-neighbor force constants are 10% of the nearest-neighbor constants, and the central and noncentral constants are equal.

frequencies. These higher peaks correspond to modes localized about light-atom clusters. The lattice used for the spectrum shown in Fig. 11 was 10×50 atoms with a mass ratio of 3:1 and impurity concentration of 0.25. This particular calculation employed equal central and noncentral force constants.

The spectra for body-centered cubic lattices are still more difficult and time consuming to calculate. The equations of motion and the model employed have been presented elsewhere.[15] We have included the nearest- and next-nearest-neighbor interactions with central and noncentral force constants. The calculation of the frequency spectrum is quite slow, and consequently the lattices calculated are quite small. The lattice used for the calculation shown is made up of 5×5×12 atoms with a mass ratio of 3:1 and an impurity concentration of 0.1. The lower frequency portion of the spectrum closely resembles the published spectra for the body-centered cubic lattices such as vanadium. At higher frequencies there appear to be local modes present just as in the lattices previously studied. These modes are not resolved into single peaks or bands because of the rather coarse calculational mesh employed. It is hoped that larger lattices of this type can be calculated in more detail to allow comparison with experiments done on the inelastic scattering of neutrons by disordered crystals.

VI. DISCUSSION

We have presented some results of our numerical experimentation with binary, isotopically disordered harmonic lattices. They corroborate and extend previous one- and two-dimensional investigations to larger and more varied one- and two-dimensional systems and to three dimensions.

Some general statements can be made about the nature of the spectra and their dependence on the parameters which we have varied. For an impurity concentration less than the percolation concentration and for impurity mass much less than the host mass, the spectra are close to the exactly calculable infinite-mass-ratio spectra. As the impurity mass is increased the spectra remain peaky, but the peaks get progressively broader until a mass of approximately half the host mass is reached. At that point the peaks largely disappear, along with the valleys between them, where the forbidden frequencies were. As the mass is further increased, so that the impurity mass becomes much larger than the host mass, a fairly smooth peak rises out of the host continuum. If the impurity concentration is between c_p and $1-c_p$, where c_p is the critical percolation concentration, the spectra are relatively smooth. It is only for light-impurity concentrations $c<c_p$ that the jagged structure of the spectrum with forbidden frequencies occurs. In a forthcoming paper we will correlate this behavior with the nature of the displacements in the normal modes. It happens that for $c<c_p$ all the normal modes above the host continuum are localized about islands of light atoms. For $c>c_p$, on the other hand, most of the modes at those frequencies have considerable extent.

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[15] D. N. Payton, III, Los Alamos Scientific Laboratory Report No. LA-3510, 1966 (unpublished).