

## Dynamics of Distorted Harmonic Lattices. II. The Normal Modes of Isotopically Disordered Binary Lattices\*†

DANIEL N. PAYTON, III AND WILLIAM M. VISSCHER

*Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico*

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Results of computer calculations of normal modes of certain one-, two-, and three-dimensional harmonic lattices are displayed, discussed, and correlated with the frequency spectra for similar lattices reported in an earlier paper. An interesting feature of the results is that localization of the displacements in the normal modes is associated with certain ranges of concentration and mass ratio.

### INTRODUCTION

IN a previous paper<sup>1</sup> (hereafter referred to as I), we presented certain computer-generated frequency spectra of disordered harmonic lattices. The present paper extends the discussion of the normal modes contained in I to give specific examples of eigenvectors of binary disordered harmonic lattices and to establish correspondences between the natures of the normal modes and their frequency spectra.

Section I contains a brief description of the problem and a discussion of the method of calculation of the normal modes. In Sec. II some of the eigenvectors of linear chains of 200 atoms are illustrated. Square and cubic lattice normal modes are shown in Sec. III, and the relation between their nature and the position of their frequency in the spectrum is discussed. A discussion of the nature of the eigenvectors of these and other lattices is included in Sec. IV.

### I. MODEL AND METHOD OF CALCULATION

The model used in the present investigation represents the atoms of the crystal lattice by point masses connected to their nearest neighbors by central and non-central harmonic springs, such that the motions in each Cartesian direction are independent. The equations of motion have been presented in I and will not be reproduced here. In matrix form they are

$$[\mathbf{M}_n - \omega^2 \mathbf{I}] \mathbf{u} = 0, \quad (1)$$

for an  $n$ -dimensional simple cubic lattice, where  $\mathbf{M}_n$  is the dynamical matrix and  $\mathbf{u}$  is the eigenvector. This equation is the eigenvalue equation for the system. The problem of finding the eigenvectors is equivalent to finding the diagonalizing transformation for the dynamical matrix. For a limited number of atoms in the lattice (depending on the speed and memory of the computer available), this can be done numerically.

The calculations for this paper were done on the IBM 7030 computer, which allowed us to solve for the eigenvectors of lattices containing up to about 300 atoms, using a diagonalization procedure devised by Ortega.<sup>2</sup> This is a combination of the Householder<sup>3</sup> scheme of matrix reduction and the diagonalization procedure proposed by Givens.<sup>4</sup> Ortega reduces the matrix to a tridiagonal form by a series of simple orthogonal similarity transformations which are not plane rotations. A Sturm-sequence technique devised by Givens is then used to find the eigenvalues of the tridiagonal matrix. The eigenvectors of the original matrix are then found by an inverse iteration of the reduction procedure.

### II. THE LINEAR CHAIN

The normal modes of the disordered linear chain have been discussed in the spirit of the present investigation in a paper by Dean and Bacon.<sup>5</sup> By diagonalizing the dynamical matrix, they obtained the normal modes of a chain of 50 atoms and discussed the roles of the modes relative to the frequency spectrum of the disordered chain. They concluded, for example, that the isolated high-frequency peaks in the spectra of disordered chains calculated earlier by Dean<sup>6</sup> correspond to highly localized modes associated with identifiable atomic configurations.

We have also diagonalized the dynamical matrix and obtained the normal modes of linear chains of various lengths. We have calculated eigenvectors for chains varying in length from 50 to 300 atoms, of varying composition (mass ratio, ordering, and concentration of each component). We have reproduced the results of Dean and Bacon and extended them to more

<sup>2</sup> J. M. Ortega, National Aeronautics and Space Administration Technical Report No. TR-64-12 NSG-398, 1964 (unpublished).

<sup>3</sup> A. S. Householder and F. L. Bauer, *Numerische Math.* **1**, 29 (1959).

<sup>4</sup> W. Givens, Oak Ridge National Laboratory Report No. 1574, 1954 (unpublished); *Natl. Bur. Std. (U. S.) Appl. Math. Ser.* **29**, 117 (1953).

<sup>5</sup> P. Dean and M. D. Bacon, *Proc. Phys. Soc. (London)* **81**, 642 (1963).

<sup>6</sup> P. Dean, *Proc. Phys. Soc. (London)* **73**, 413 (1959); **A254**, 507 (1960); **A260**, 263 (1961).

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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.

<sup>1</sup> D. N. Payton and W. M. Visscher, *Phys. Rev.* **154**, 802 (1967).

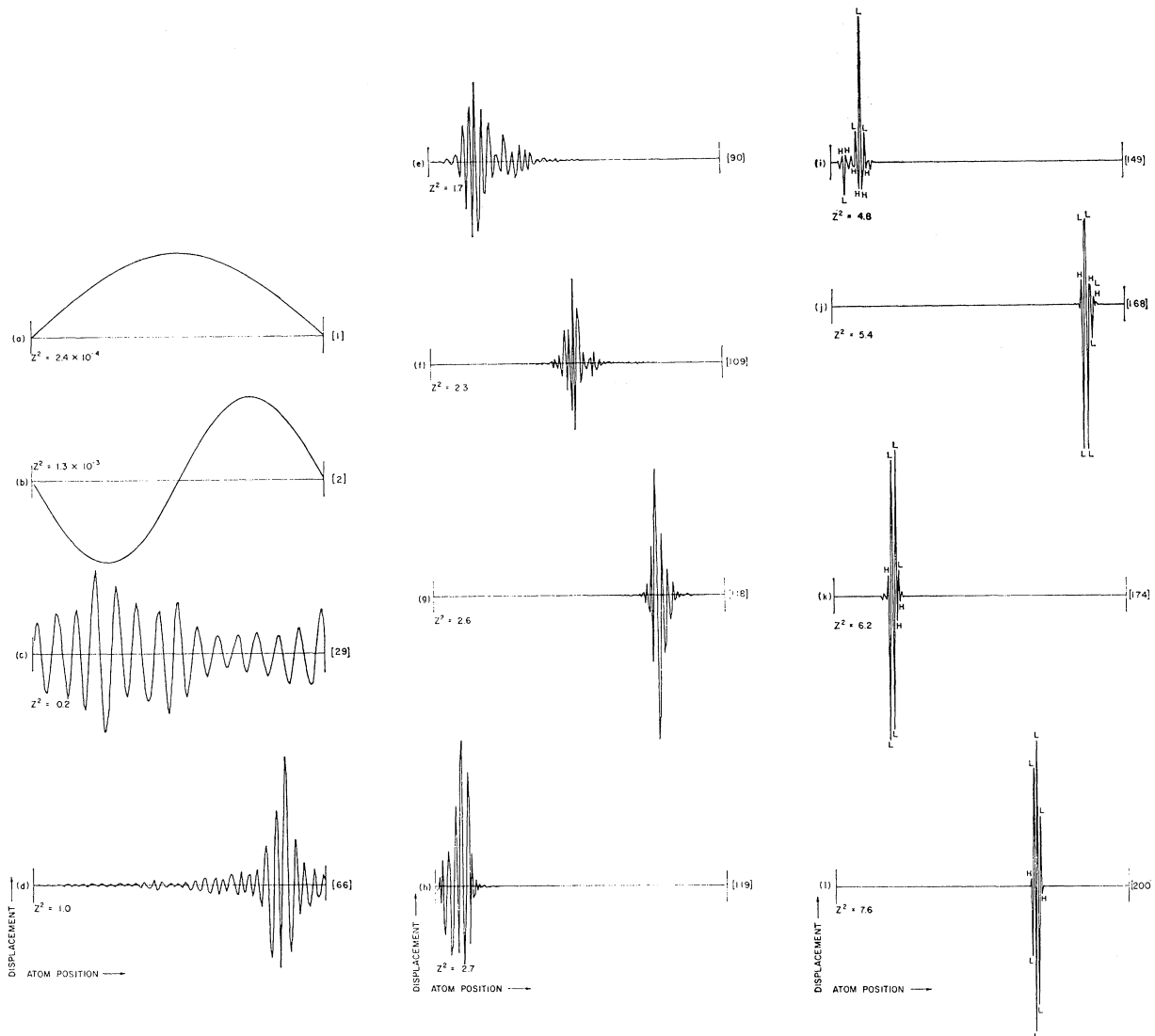


FIG. 1. Normal modes of a random isotopic mixture 200 atoms long, half-heavy atoms and half-light with a mass ratio of three. The mode numbering is from the lowest to the highest frequency. The frequency is given in units of the maximum frequency of the pure light chain ( $z^2 = 8\omega^2/\omega_L^2$ ).

general systems. One conclusion is that the correlation between localization of the normal modes and the peakedness of the frequency spectrum is true for all the disordered chains which we have considered.

Our first example is shown in Fig. 1, which illustrates some of the normal modes of a particular disordered chain of 200 atoms with equal numbers of light and heavy atoms with the mass ratio of 1:3. The mode numbering is from the lowest- to the highest-frequency mode. The reduced squared frequencies are given by  $z^2 = 8\omega^2/\omega_L^2$ , where  $\omega_L$  is the maximum frequency of the pure light-atom lattice. These modes can be located on the frequency spectrum shown in Fig. 3(c) of I. The modes (a)-(c) are eigenvectors corresponding to the low-frequency or long-wavelength portion of the

spectrum which is affected little by the microscopic structure of the chain. The eigenvectors (d)-(h) show some localization even at fairly low frequencies. They might be termed elastic localized modes in that they extend over microscopically large regions and do not depend on the local configuration in a detailed manner. The maximum frequency of the monatomic heavy-atom lattice lies between modes 118 and 119. In one dimension, these two modes are qualitatively similar. In two or three dimensions, as we shall see later, there is a dramatic change in the nature of the modes across this band edge.

The modes shown in Fig. 1 (i)-(l), are some of the strongly localized modes which typify those contributing to the peaks of the frequency spectrum at higher

frequencies. The  $H$ 's and  $L$ 's shown on these modes indicate whether the corresponding atom is a heavy or light atom, respectively. We will consider these highly localized modes individually.

(i) Mode number 149,  $z^2=4.8$ . This mode is localized about the light-atom island configuration

$$-HLHHHHHLHLHLH-$$

which is effectively two islands with overlapping frequency, i.e.,  $-HLH-$  and  $-HLHLHLH-$ . These two islands, when isolated, have normal modes whose frequencies are close together and whose superposition is similar to the eigenvector shown here.

(j) Mode number 168,  $z^2=5.4$ . The predominant mode excited here is the  $(\leftarrow \rightarrow \rightarrow \leftarrow)$  mode of the island of four light atoms. It is perturbed by the pair of light atoms nearby.

(k) Mode number 174,  $z^2=6.2$ . This is a high-frequency mode corresponding to the island

$$-HLLLLHLH-$$

(l) Mode number 200,  $z^2=7.6$ . The highest-frequency mode in this chain is the  $(\leftarrow \rightarrow \leftarrow \rightarrow \leftarrow \rightarrow)$  mode of the  $-HLLLLLH-$  island. In this particular chain the longest-light island contained six atoms; consequently, the highest-frequency mode of this chain is that of the highest frequency of an isolated chain of six atoms as increased by the finiteness of the bounding masses.

We have discussed in I the relation between the structure of the frequency spectra and the occurrence of islands of light atoms, as dictated by the special frequency theorem. As exemplified by Fig. 1, the nature of the normal modes at frequencies above the pure heavy continuum is also largely dictated by the distribution of light islands. The eigenvectors are

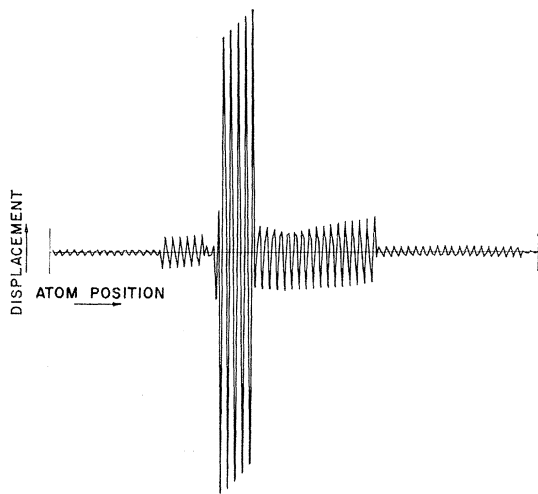


FIG. 2. A typical high-frequency normal mode of a 200-atom chain with 7 heavy impurities 3 times the mass of the host atoms. The blocking of the amplitude takes place at the impurity sites.

simply related to the vibrations of isolated light chains, and their frequencies can be thus correlated. [See Fig. 4(e) of I and of Ref. 7.]

For linear chains composed predominantly of heavy atoms, the localization of the high-frequency modes is even more pronounced than shown in Fig. 1. Quite different is the situation for a chain with dilute heavy impurities. Figure 2 illustrates a typical high-frequency mode of such a chain, with 193 host atoms and 7 atoms with three times the host mass. The impurities are located at the discontinuities in amplitude of the vibration.

### III. THE SQUARE AND CUBIC LATTICES

Because of the simple tridiagonal form of the dynamical matrix, the length of the linear chains for which normal modes were computed was not limited by computer size. The dynamical matrices associated with the square and cubic lattices are more complicated<sup>8</sup> though, and the size of the lattice treated had to be restricted to approximately 200 atoms for practical reasons. Nevertheless, these calculations yield results for the spectra which are quantitatively close to those obtained in I for lattices of much larger sizes. The boundary conditions were the same as used in I, i.e., a set of helical-toroidal periodicities with fixed ends.

Numerous calculations were made for the square lattice to determine the general nature of the eigenvectors for various compositions. Figure 3 shows the spectrum for a particular  $14 \times 14$  lattice for which we

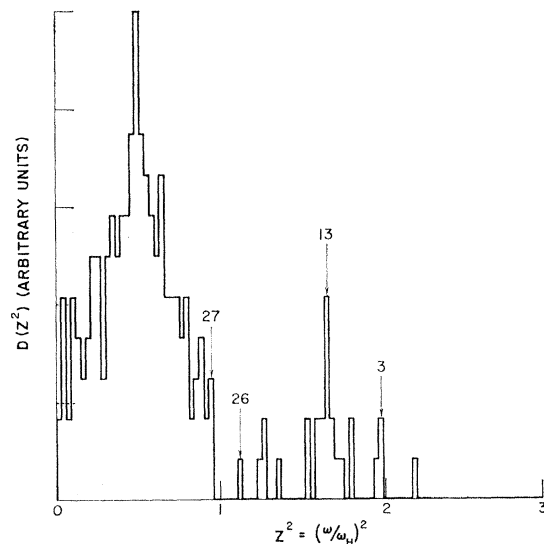


FIG. 3. Frequency spectrum for the  $14 \times 14$ -atom square lattice whose normal modes are shown in Fig. 4. The numbering refers to the mode numbering of Fig. 4.

<sup>7</sup> H. Matsuda, Progr. Theoret. Phys. (Kyoto) **31**, 161 (1964); **34**, 314 (1965).

<sup>8</sup> D. N. Payton, III, Ph.D. thesis, University of Missouri at Rolla, 1966 (unpublished); Los Alamos Scientific Laboratory Report No. LA-3510 (unpublished).

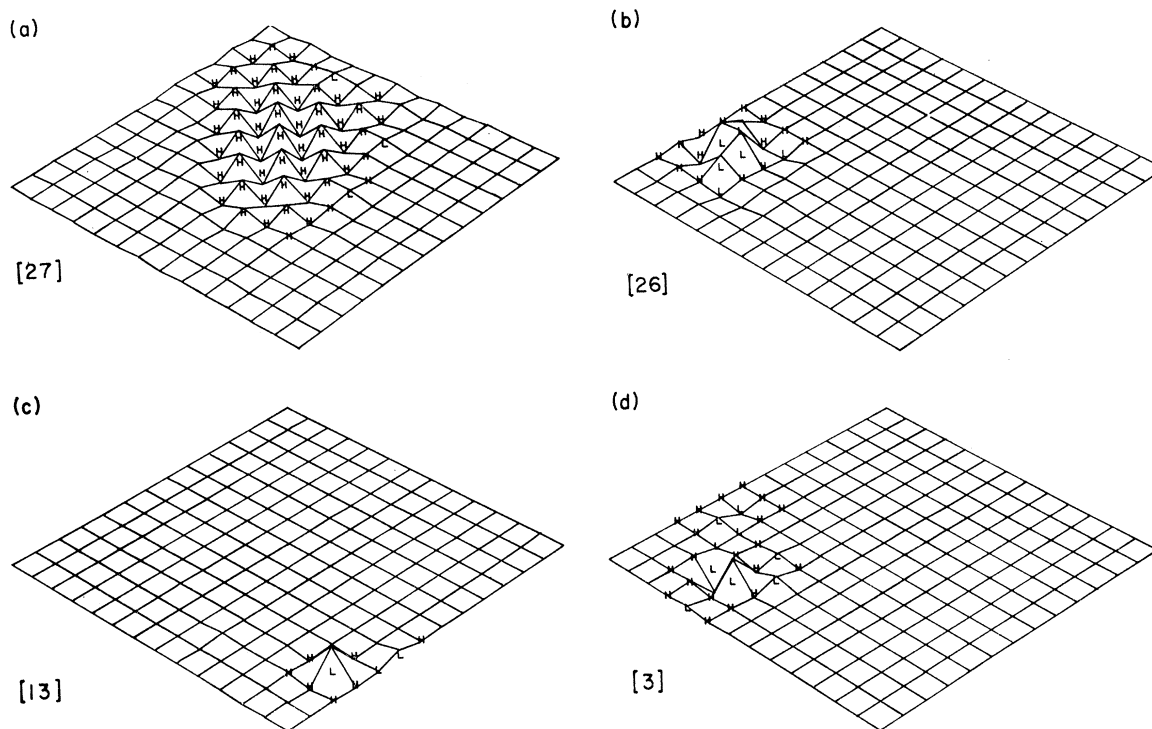


FIG. 4. Normal modes of a square lattice of  $14 \times 14$  atoms with 15% of the atoms having masses one-third the mass of the host mass. The isotopic impurities are distributed randomly. The central and noncentral force constants are equal. The displacements are plotted in the out-of-plane direction instead of one of the degenerate Cartesian in-plane directions.

have calculated the normal modes. Upon comparison with Fig. 6(a) of I, one sees that, even though the lattice is quite small, the general features of the spectrum of a much larger lattice are still present. The unit of the abscissa on Fig. 3 is the square of the maximum frequency of the pure heavy lattice, and the numbering of the modes starts at the highest-frequency mode. The numbers on Fig. 3 identify the modes shown in Fig. 4. Both figures illustrate properties of a square lattice with 15% light atoms with masses one-third those of the host lattice. These impurity atoms are dispersed randomly throughout the lattice. The central and noncentral force constants are equal for the spectrum shown, and consequently the host continuum portion has a single logarithmic singularity. Figure 4 displays four of the eigenvectors of this lattice.

For the square lattice as well as for the linear chain we can interpret the isolated peaks of the frequency spectrum at higher frequencies as the normal mode frequencies of modes localized about islands of light impurities. Consider the four shown in Fig. 4. The normal modes are shown in an isometric projection with the displacements in the vertical direction. This is done for ease of viewing, since the displacements are actually along one of the in-plane crystal axes. These pictures are halves of stereo pairs plotted by the computer.

(a) Mode number 27,  $z^2=0.96$ . This mode is the uppermost mode in the host-lattice continuum. It

exhibits the form characteristic of all modes with lower frequencies in that the displacements are not highly localized and the heavy atoms possess large displacements. The letters *L* and *H* have been placed at the equilibrium positions of a few of the pertinent atoms

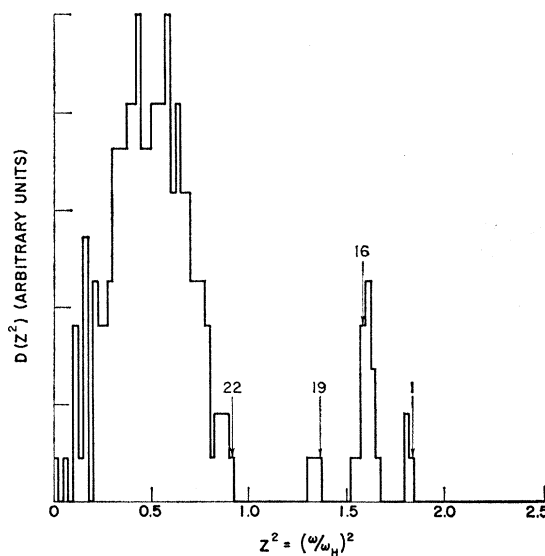


FIG. 5. Frequency spectrum for the  $6 \times 6 \times 6$  simple cubic lattice whose normal modes are shown in Fig. 6. The numbering refers to the mode numbering of Fig. 6.

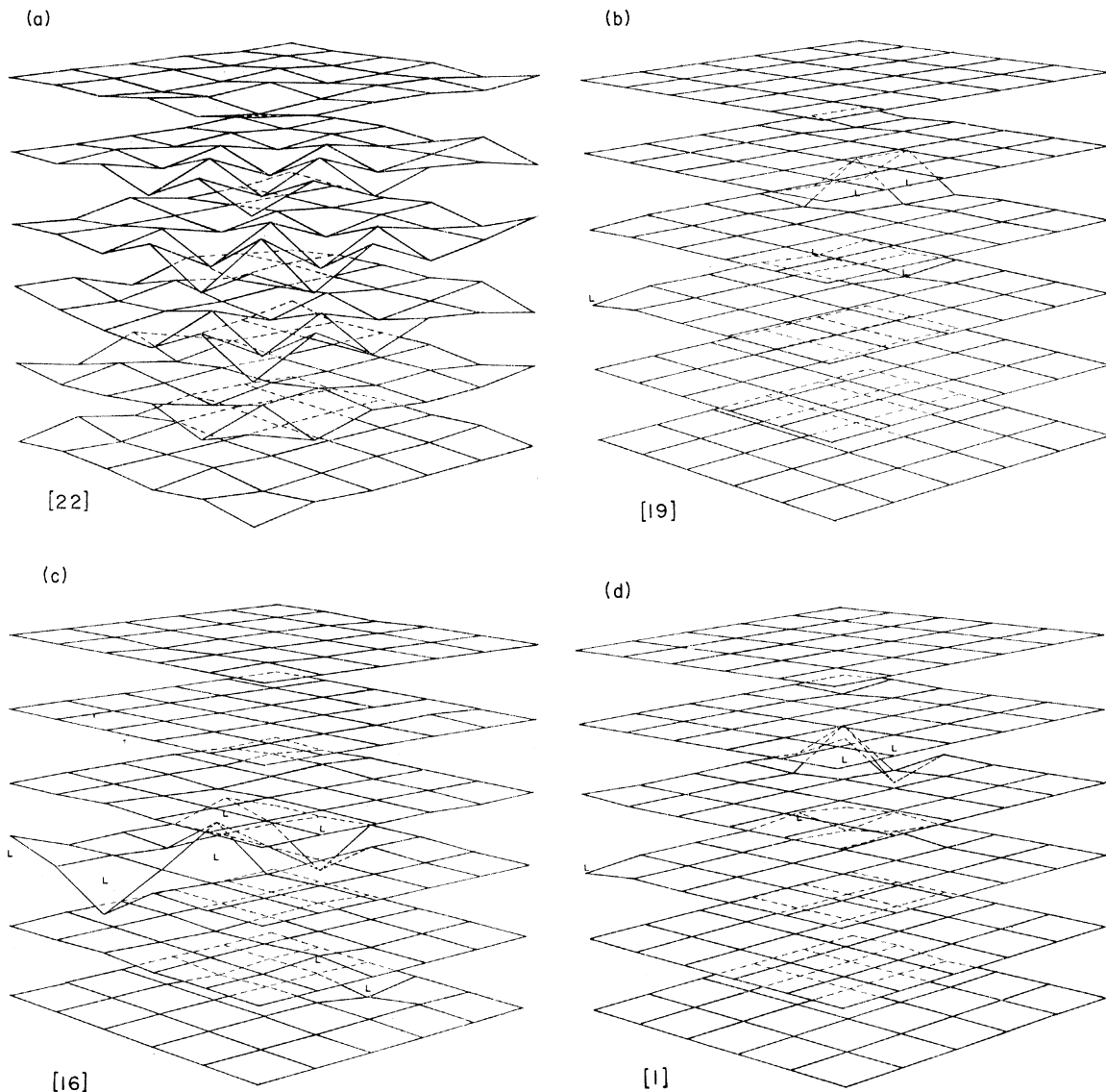


FIG. 6. Normal modes of a simple cubic lattice of  $6 \times 6 \times 6$  atoms with 15% of the atoms having masses one-third the mass of the host mass. The impurities are isotopic and randomly distributed. The central and noncentral constant forces are equal.

and correspond to that site being occupied by a light or heavy atom, respectively.

(b) Mode number 26,  $z^2=1.1$ . This is the first mode above the continuum. All the modes above the continuum are quite strongly localized. This one has all of the atoms very near their equilibrium positions except those on or closely neighboring the island of four light impurities

$$\begin{pmatrix} L & L \\ L & L \end{pmatrix}$$

which is in its lowest symmetric mode

$$\begin{pmatrix} \rightarrow & \rightarrow \\ \rightarrow & \rightarrow \end{pmatrix}.$$

Other modes for this island will be the

$$\begin{pmatrix} \rightarrow & \rightarrow \\ \leftarrow & \leftarrow \end{pmatrix}$$

mode at  $z^2=1.36$ , the

$$\begin{pmatrix} \leftarrow & \rightarrow \\ \rightarrow & \leftarrow \end{pmatrix}$$

mode at  $z^2=1.8$ , and the mode

$$\begin{pmatrix} \leftarrow & \rightarrow \\ \leftarrow & \rightarrow \end{pmatrix}$$

at  $z^2=2.2$  which is the uppermost mode on Fig. 3.

(c) Mode number 13,  $z^2=1.7$ . This mode contributes to the large high-frequency peak in Fig. 3. It is the localized mode of a single isolated light atom. The size of the peak reflects the fact that there are several isolated impurities in the lattice and also that many islands of odd numbers of light atoms have modes which are almost degenerate with those of the isolated light atom.

(d) Mode number 3,  $z^2=1.99$ . This is the higher-frequency mode of the isolated pair of light impurities. This mode is the antisymmetric mode ( $\leftarrow\rightarrow$ ) and is accompanied by the symmetric mode ( $\rightarrow\rightarrow$ ) at  $\omega^2=1.26$ .

Following the same procedures, the simple cubic lattice can be analyzed. Again, the complicated form of the dynamical matrix limits us to lattices of approximately 200 atoms. The use of a central-noncentral force model again allows the motions to be separated along the Cartesian axes. The spectrum of a typical crystal of  $6\times 6\times 6$  atoms is shown in Fig. 5. This lattice again has a 3:1 mass ratio and a light impurity concentration of 15%, and comparison with Fig. 10 of I shows that the spectrum of the small lattice approximates that of the larger one described in that paper. The unit of the squared frequency is the maximum frequency of the infinite host lattice. The numbering of modes again is in descending order of frequency and corresponds to the modes shown in Fig. 6. Again, the isometric projections of the normal modes are halves of stereo pairs produced directly on microfilm by the computer, after diagonalization of the dynamical matrix. The displacements of the atoms in each normal mode are shown. The lines represent noncentral springs; to minimize clutter, the central springs, which would be in the vertical direction, are omitted. The equilibrium positions of the light and heavy atoms which are pertinent to the discussion are labeled in the three higher-frequency modes by *L* or *H*, respectively. We will now examine these modes individually.

(a) Mode number 22,  $z^2=0.9$ . This mode is the uppermost mode in the host continuum. It is characteristic of the nonlocalized nature of the continuum modes.

(b) Mode number 19,  $z^2=1.36$ . This is the familiar symmetric mode due to an isolated pair of light atoms. Because of the low concentration of light atoms in this crystal, the localized modes are due to only two configurations of light impurity atoms, the pair  $-LL-$  and the single atom. However, since these individual islands are not completely isolated, their normal-mode frequencies, corresponding to ( $\rightarrow\rightarrow$ ), ( $\rightarrow\leftarrow$ ), and ( $\leftarrow$ ), are broadened.

(c) Mode number 16,  $z^2=1.6$ . This mode is localized about an arrangement of single-light impurities interspersed with the host masses in a chainlike island in

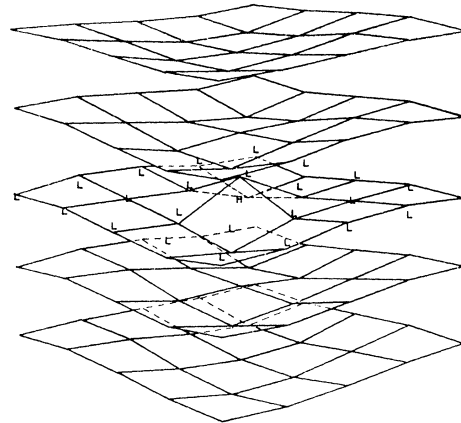


FIG. 7. A typical normal mode in the neighborhood of the low-frequency resonance in a  $5\times 5\times 5$  simple cubic lattice. The lattice contains a single heavy atom with mass three times that of the host lattice.

which alternating atoms are light impurities:

$$\begin{pmatrix} L & & & & L \\ & H & & & H \\ L & & L & & L \\ & & & H & \\ & & & & L \end{pmatrix}.$$

This is the

$$\begin{pmatrix} \rightarrow & & & & \rightarrow \\ \cdot & & & & \cdot \\ \leftarrow & \cdot & \rightarrow & \cdot & \leftarrow \end{pmatrix}$$

mode, which has a frequency quite close to the isolated impurity frequency.

(d) Mode number 1,  $z^2=1.84$ . This is the antisymmetric mode of the pair of impurities ( $\rightarrow\leftarrow$ ) shown in mode number 19.

The low-frequency resonance which appears in the spectrum of lattices with low concentrations of heavy impurities [see Figs. 6(d) and 9(d) of I] is not, at least on superficial observation, accompanied by any specially recognizable features of the eigenvectors, except in the limit of no interaction between impurities. A lattice with just one heavy impurity, though, has many normal modes in the neighborhood of the low-frequency resonance, which are localized near the impurity. An example is shown in Fig. 7 for a  $5\times 5\times 5$  lattice with a heavy impurity in the center position, with mass three times the host mass.

#### IV. DISCUSSION

The square and cubic lattices which have been illustrated have had fairly low (15%) concentrations of light substitutional impurities. The general character of the normal modes of these lattices—localization for frequencies above the host continuum—is preserved as the concentration is increased, until the critical percolation concentration is reached. At this point (which is defined as the concentration at which, in an infinite lattice, the probability of occurrence of a connected

impurity island of infinite extent becomes unity) many of the high-frequency eigenvectors suddenly lose their localized character, just as the spectrum loses its peakedness. The critical percolation concentrations are known to be 0.5 and 0.28 for the square and simple cubic lattices,<sup>9</sup> respectively; these values are consistent with the concentrations at which the nature of the results of our numerical experimentation on these lattices changes.

The mass ratios given by the special frequency theorem (discussed in I) mark boundaries between domains of jaggedness and relative smoothness in the spectra (see Figs. 4 and 7 of I). These same mass ratios also signal a change (but a less sharp one) from the

<sup>9</sup> M. E. Fisher, *J. Math. Phys.* **2**, 620 (1961).

highly localized high-frequency normal modes associated with light dilute impurities to extended modes. This ratio is higher than the mass ratio at which the localized mode at a single isolated impurity appears, which is unity for the linear and square lattices and is roughly 3:2 for the simple cubic lattice.

The authors, with Rich, have recently completed a numerical study<sup>10</sup> of heat conductivity in disordered harmonic and anharmonic one- and two-dimensional lattices. The results of the present paper are very helpful in understanding the physics underlying the heat-conduction processes studied there. The connection will be discussed in detail in a forthcoming paper.

<sup>10</sup> D. N. Payton, M. Rich, and W. M. Visscher, *Bull. Am. Phys. Soc.* **11**, 728 (1966); and (to be published).

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## Errata

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**Some Comments on the Photomagnetolectric Effect in Silicon**, R. E. BARKER, JR. [*Phys. Rev.* **149**, 663 (1966)]. The phrase just before and including Eq. (10) should read: "we have a charge density  $\sigma \approx \epsilon \epsilon_0 F_y / e$  and a voltage  $V_{\max} \approx \sigma L / \epsilon \epsilon_0 \approx B_z v_x L$ ". The sentence following Eq. (13) should read: "Its logarithm should be a linear function of  $1/T$  with a  $\ln T$  term added and . . . ."

**Conditions for Rotational Invariance of a Harmonic Lattice**, DENOS C. GAZIS AND RICHARD F. WALLIS [*Phys. Rev.* **151**, 578 (1966)]. Equations (15) and (16) imply Cauchy's relation for a simple Bravais lattice and are therefore unsatisfactory. The error stems from the assumption of Eq. (13) which is violated at the boundary. Equation (12) follows from a first-order rotational invariance condition obtainable from Eqs. (5) and (9) and differing from Eq. (11) in the replacement of  $X(l\kappa, l'\kappa')$  by  $X(l'\kappa', l_0\kappa_0)$ . The assertion that the Lengeler-Ludwig model is not rotationally invariant is unjustified on the basis of Eq. (16). We wish to thank Dr. M. Lax and Dr. W. Ludwig for bringing our attention to these points.

**Exact Solution of the Integral Equations for the Anomalous Skin Effect and Cyclotron Resonance in Metals**, L. E. HARTMANN AND J. M. LUTTINGER

[*Phys. Rev.* **151**, 430 (1966)]. Owing to a very unfortunate typographical error the most important equations of this paper contain misprints. In (2.28), (2.29), and (2.34),  $\sin(2\pi z_i/3)$  should be replaced by  $\sin^2(\pi z_i/3)$ .

**Theory of Oscillatory Photoconductivity in Semiconductors: Boltzmann-Equation Approach**, H. J. STOCKER AND H. KAPLAN [*Phys. Rev.* **150**, 619 (1966)]. The letter  $q$  in Eqs. (52) and (75) should be replaced by the number 9.

In the definition of  $\alpha$  below Eq. (73),  $\tau_0$  should be replaced by  $\tau_1$ .

In the Figure captions for Figs. 3, 4, and 5, the expression: "Same as Fig. 1, . . . ." should read: "Same as Fig. 2, . . . ."

A subtitle "H. Optical Phonon Scattering" should be placed on the top of the left-hand column on p. 623. The letters "H" and "I" preceding the following two subtitles should be replaced by "I" and "J," respectively.

The  $\delta$  function in Eq. (32) should read  $\delta(\sigma - z)$ , not  $\delta(\sigma - 2)$ .

The first term of Eq. (12) should be

$$\frac{1}{\tau_{a0}} \left( \frac{\hbar\omega_0}{E(k)} \right)^{1/2} \frac{d}{dE} \left\{ E^2(k) \left[ \frac{f_0(k)}{kT} + \frac{d}{dE} f_0(k) \right] \right\}.$$