μ_H is independent of T. Although the glasses have electrical conductivities which are many orders of magnitude smaller than in Tl-Te, and their activation energies are much larger, μ_H is in the same range for both: 0.1–0.5 cm^2/V sec. This suggests that the electronic behavior in liquid Tl-Te and in the chalcogenide glasses is similar in this respect, and a common explanation may be expected. It would seem that the anomalous situation is closely connected with the atomic disorder which exists in both systems.

At these compositions ($31<X<60$ at.% Tl), analysis of S and σ indicates that an activation energy $E_a=0.25$ eV occurs in the transport behavior. This has been interpreted by Cutler and Mallon[2] in terms of excitation of deep acceptor states. An alternative hypothesis is that it reflects a hopping process. The small-polaron mechanism for hopping has been studied by Holstein and Friedman and others,[8–10] and there has been disagreement between them on whether the Hall mobility is independent of T, as claimed by Schnakenberg,[10] or whether it has an activation energy.[8,9] Holstein and Friedman claim that $\frac{1}{3}$ of the activation energy in σ should appear in μ_H. If they are correct, our results eliminate the possibility of small polaron hopping in Tl-Te, although other hopping mechanisms are conceivable.

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[8] T. Holstein and L. Friedman, Phys. Rev. **165**, 1019 (1968).

[9] Yu. A. Firsov, Fiz. Tverd. Tela **5**, 2149 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1566 (1964)].

[10] J. Schnakenberg, Z. Physik **185**, 123 (1965).

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Vibrations of Disordered Solids

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An important portion of the vibrational spectrum of an infinite disordered solid is attributed to "localized" vibrations. These can be investigated in detail through the study of the vibrations of very small solids: It is argued that any vibrational mode found in a small solid that has the property that atomic amplitudes are very small near the boundary will also be found, with at most slight perturbation, in a large solid. It is observed that such modes appear whenever a group containing light atoms occurs and is bounded by a sufficient number of heavy atoms; the number that is "sufficient" depends somewhat on force model, mass ratio, and dimensionality, but is generally small. The density of these local modes in the spectrum of the large crystal can then be computed from the probability of the occurrence in the large crystal of the configuration of masses that produces it. For the case of the one-dimensional binary alloy, the major features of the earlier direct numerical computation (Dean) can be reproduced and understood by this simple method. Similar features (peaks) are predicted for two- and three-dimensional structures, but their intensity compared to the continuous part of the spectrum is shown to be smaller.

1. INTRODUCTION

It seems now to be commonly agreed that vibrational spectra of disordered solids are, at least in one didimension, irregular, rather than smooth functions. For ordered solids, this fact first obtruded itself when model calculations in two dimensions[1–3] and three dimensions[3,4] became feasible; van Hove[5] explained the ever-present singularities in the vibration spectra by tracing them to critical points (maxima, minima, or saddle points) of the frequency ω in momentum space $\{\mathbf{k}\}$, and showed that a certain minimal number of the latter would necessarily appear in any function that, like $\omega(\mathbf{k})$, is (multiply) periodic. This periodicity of ω in $\mathbf{k}$ is, in turn, a consequence of the periodicity of the mass distribution of an ordered lattice in real space; van Hove had thus traced the observed singularities in the frequency spectra to the fact that the lattice under consideration is ordered.

The preceding argument does not apply to disordered structures; it does not suggest that the vibrational spectra of disordered solids should be anything but smooth. Therefore, the first indication by direct numerical calculation[6] that the spectra of disordered crystals were also highly irregular caused renewed surprise. One-dimensional lattices consisting of disordered binary mixtures[7] were shown to contain many sharp peaks. The explanation now generally accepted[8]

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[1] M. Smollett, Proc. Phys. Soc. (London) **A65**, 109 (1952).

[2] E. W. Montroll, J. Chem. Phys. **15**, 575 (1947).

[3] W. A. Bowers and H. B. Rosenstock, J. Chem. Phys. **18**, 1056 (1950); **21**, 1607 (1953).

[4] G. F. Newell, J. Chem. Phys. **21**, 1977 (1953).

[5] L. van Hove, Phys. Rev. **89**, 1189 (1953).

[6] P. Dean, Proc. Roy. Soc. (London) **A254**, 507 (1960).

[7] By this we mean a one-dimensional chain of atoms of two different masses with the same interaction between all nearest neighbors, regardless of mass. Plausible models for a one-dimensional glass, obtained by letting the force constants vary in a continuous way, do not provide vibrational spectra with the same structure of peaks; see P. Dean, Proc. Phys. Soc. (London) **84**, 727 (1964).

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

is that the peaks are due to "localized vibrations" of certain groups of atoms. A "group" of atoms, such as *L* or *LHL* in a long chain of light atoms *L* and heavy ones *H*, is alleged to produce a localized vibration near its location; and the peak at that frequency in the vibrational spectrum is attributed to the repeated occurrence of that group.

For the time being, let us accept this explanation of "localized" vibrations for the peak structure of the vibrational spectra of one-dimensional disordered lattices. (Later we shall actually present a proof of it.) The calculations that follow are based almost entirely on one further simple thought: If the vibrations of interest are indeed localized—that is to say, if for certain normal vibrations the atomic displacements are considerable only within a small region *R*, but negligibly small outside it—then all the calculations needed for that vibration should be obtainable from studying that small region *R* alone. The many atoms outside that region can be ignored, for they can have no effect if they remain practically at rest; they might as well be replaced by a fixed wall. Thus, if localized vibrations exist in a large crystal, they can be completely analyzed by the study of a much smaller crystal, of the size of *R*, with fixed boundary conditions. In the past, convincing studies of one-dimensional lattice dynamics have involved chains of many thousands of atoms, but region *R* need, as we shall see, often involve only five or ten atoms. We can therefore expect to attain considerable simplification as well as clarification from an approach that starts with configurations involving small groups of atoms.

A more useful statement is obtained if the above argument is inverted: If, for a small crystal of size *R* and with fixed boundary conditions, a mode is found to exist such that the atoms adjacent to the boundary have (practically) zero displacement, then that same mode will also exist in a large enough crystal. (The atoms in *R* that do the moving "do not know" whether beyond their stationary neighbors there is a stationary wall or an array of many more stationary atoms.) All that is necessary is that the crystal be large enough to contain somewhere a region with the same configuration of atomic masses as in *R*. In the usual limit of infinite-size crystals, this is not a restriction at all; to the contrary, it enables us to calculate the probability of the configuration *R* occurring, and from this the frequency of occurrence of the localized mode under discussion follows directly. By considering successively all "small" disordered crystals of the size of *R*, we can find not only all the localized frequencies, but also their density in the frequency distribution. That is, we should be able to calculate not only the position of all the peaks in the frequency distribution, but also their heights, i.e., all the major features of the frequency distribution itself.

We have stated the preceding arguments in terms of one-dimensional (1D) crystals with nearest-neighbor interaction only. This the reader will recognize as a rhetorical convenience rather than an essential restriction. Consider a small 3D crystal, size *R*, with interaction extending to *k*th neighbors, and suppose we find a mode of vibration in which all substantial motion is confined to the interior and all the *k*th neighbors of boundary atoms are (practically) motionless. Then that same mode will occur in the corresponding infinite crystal, and its frequency of occurrence will be the frequency of occurrence of the particular configuration *R*. The argument is valid for any dimension, and worthless only when forces of infinite range exist. The present method should thus enable us to study the motion of two- and three-dimensional crystals as well.

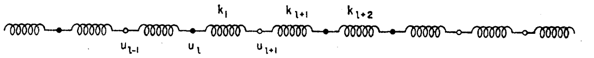

FIG. 1. Model of 1D disordered lattice. ●, light mass; ○, heavy mass.

In Sec. 2, we study the 1D binary disordered lattice. Some of the localized frequencies and normal modes can actually be obtained analytically (Sec. 2 A), and many others numerically, but with little difficulty in view of the small required size of the crystals (Sec. 2 B). The results are then systematized (Sec. 2 C) to give a reasonable picture of the frequency distribution. In Sec. 3, the analogous model of a two-dimensional crystal is treated. Here, the numerical work becomes appreciable even though it involves only "small" crystals, and the "local" modes appear to make only a smaller contribution to the total frequency distribution. In Sec. 4, the three-dimensional structure is discussed briefly. Section 5 presents a summary and suggestions for further work.

2. ONE-DIMENSIONAL SOLIDS

Consider a linear chain of lattice sites l on which particles of mass m_l are located. Let the force constants between atoms $l-1$ and l be k_l, and the instantaneous displacement of m_l be u_l (see Fig. 1). After introducing harmonic time dependence, $d^2/dt^2 \to -\omega^2$, the Newtonian equation of motion for the lth particle becomes

$$k_l(u_{l-1}-u_l)+k_{l+1}(u_{l+1}-u_l)=-m_l\lambda u_l, \qquad (1)$$

where

$$\lambda=\omega^2. \qquad (2)$$

We will generally confine ourselves to the situation where all force constants are the same; hence we will set all $k=1$. Our model is thus a reasonable first approximation to alloys, but not to glasses.[7] This is an important restriction physically; its relaxation would lead to very different mathematical results as well. We also restrict the m_l to two different values. This is a less significant restriction, made for convenience only, and its relaxation will not qualitatively change our results. Equation (1) can now be written as

$$u_{l+1}=(2-m_l\lambda)u_l-u_{l-1}. \qquad (3)$$

For an infinite chain, these equations suffice as they stand. For a finite chain of N atoms there will be N such equations, but they contain $N+2$ variables u_l. The extra two u's, which are u_0 and u_{N+1}, can be determined by the boundary conditions (b.c.) desired. If we want fixed ends, we insert

$$u_0=u_{N+1}=0 \quad \text{(fixed b.c.)}, \tag{4}$$

whereas free boundary conditions are attained by setting

$$u_0=u_1 \quad \text{and} \quad u_{N+1}=u_N \quad \text{(free b.c.)}, \tag{5}$$

thereby making sure that u_0 exerts no force on u_1, thus allowing it to move as if nothing were to its left, and similarly for u_N.

A. Analytical Solutions

For certain mass configurations, the system (3)-(4) or (3)-(5) can be solved exactly. This is mostly true for infinitely long monatomic chains (with only few impurities), and in that sense this subsection represents a digression from our plans, which call for the study of modes in very short chains. The main use of this work is to provide limiting values for the frequencies for some of the groups that we shall treat later. Many defect modes in infinite chains have been previously studied by Bacon, Dean, and Martin.[9]

Consider first a single impurity of mass m (at site zero) in an infinite chain (from $-\infty$ to ∞) of atoms of mass M. Equation (3) then becomes

$$\begin{aligned}(2-\bar{\lambda})u_l&=u_{l-1}+u_{l+1}, \quad \text{for all } l\neq 0\\ (2-\gamma\bar{\lambda})u_0&=u_1+u_{-1}.\end{aligned} \tag{6}$$

Here $\bar{\lambda}=M\lambda$, $\gamma=m/M$. For a solution corresponding to a localized vibration, one tries[10] $u_l=A^{|l|}$, i.e., requiring that the ratio of displacement of neighbors be a constant A. One finds by substituting that

$$\begin{aligned}\lambda&=4[M\gamma(2-\gamma)]^{-1},\\ A&=-\gamma/(2-\gamma).\end{aligned} \tag{7}$$

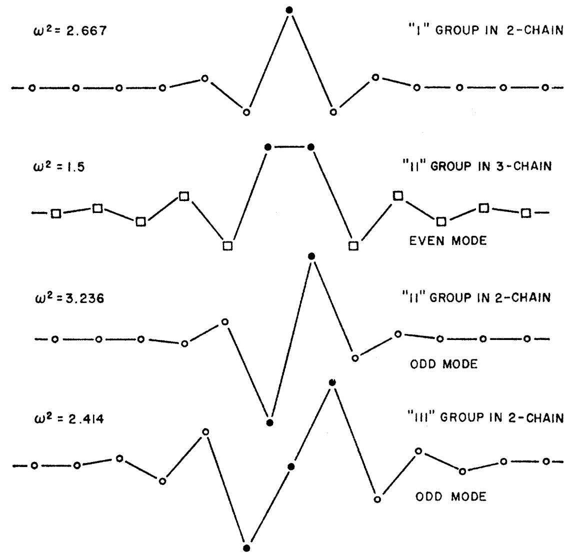

FIG. 2. Localized vibrations of groups of atoms of mass 1 (●) in an infinite chain of masses 2 (○) or 3 (□).

This is physically acceptable as a localized solution only if $A<1$, or, by (7b), $\gamma<1, m<M$. Thus a single impurity in a long monatomic chain is seen to have a localized vibration only if the impurity is a light one, a well-known result; localization increases with mass difference. For an impurity of mass 1 in a chain of masses 2, this mode is illustrated[11] in Fig. 2(a).

The local modes for two adjacent impurities in a long chain are found by the same method. It is here convenient to renumber the sites so as to omit site zero, and to put the impurities at sites -1 and $+1$, thus getting for (3)

$$\begin{aligned}(2-\bar{\lambda})u_l&=u_{l-1}+u_{l+1}, \quad |l|\neq 1\\ (2-\gamma\bar{\lambda})u_1&=u_{-1}+u_2,\end{aligned} \tag{8}$$

and seek even solutions, $u_l=A^{|l|-1}$. Substitution into (8) yields

$$\begin{aligned}\lambda&=[M\gamma(1-\gamma)]^{-1},\\ A&=-\gamma/(1-\gamma),\end{aligned} \tag{9}$$

and tells us that a localized even mode does indeed exist for this configuration if $\gamma<\frac{1}{2}$ (otherwise A is greater than 1 and the displacements build up as we move away from the center). Figure 2(b) shows this

TABLE I. Some simple localized modes of impurity groups in an infinite chain of heavy atoms. H=heavy, L=light; γ=ratio of light to heavy mass.

Impurity group in infinite chain	Parity of mode	$m\omega^2$	Ratio of displacements of neighboring atoms	Physical restriction
L	even	$4/(2-\gamma)$	$\gamma/(2-\gamma)$	$\gamma\leq 1$
LL	even	$1/(1-\gamma)$	$\gamma/(1-\gamma)$	$\gamma\leq\frac{1}{2}$
LL	odd	$\dfrac{3-4\gamma+(9-8\gamma)^{1/2}}{2(1-\gamma)}$	$\dfrac{3-2\gamma-(9-8\gamma)^{1/2}}{2(1-\gamma)}$	$\gamma\leq 9/8$
$\left.\begin{matrix}LLL\\ LHL\end{matrix}\right\}$	odd	$1+(1-\gamma)^{-1/2}$	$1-(1-\gamma)^{-1/2}$	$\gamma\leq\frac{3}{4}$

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[9] M. D. Bacon, P. Dean, and J. L. Martin, Proc. Phys. Soc. (London) **80**, 513 (1962).

[10] H. B. Rosenstock and C. C. Klick, Phys. Rev. **119**, 1198 (1960).

[11] Two notes concerning the tables and figures: The displacements u in a 1D crystal should logically be interpreted as displacements in the direction defined by the crystal itself (although the equations of motion for perpendicular displacements would actually be the same). Figures 2–4 should therefore be viewed as plots of the amplitudes u_l versus l rather than as direct pictures of the vibrating solid. The terms "even" and "odd" have the usual meaning, $u_l=u_{-l}$ or $u_l=-u_{-l}$, respectively. However, this does not coincide with "symmetric" and "antisymmetric" as commonly used in the description of the vibrations of linear molecules in the study of infrared spectra [see G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand, Inc., New York, 1945), pp. 66, 83].

TABLE II. Quasilocalized modes in very short chains with fixed boundary conditions.

Chain	Parity	$m\omega^2$	Ratio of displacements of neighboring atoms
HLH	even	$1+\gamma+(1+\gamma^2)^{1/2}$	$-\gamma/[1-\gamma+(1+\gamma^2)^{1/2}]$
HLLH	even	$(\frac{1}{2})\{1+2\gamma+[1+(2\gamma)^2]^{1/2}\}$	$-2\gamma/\{1-2\gamma+[1+(2\gamma)^2]^{1/2}\}$
HLLH	odd	$\frac{1}{2}[3+2\gamma+(9-8\gamma+4\gamma^2)^{1/2}]$	$-2\gamma/[3-2\gamma+(9-8\gamma+4\gamma^2)^{1/2}]$

mode for $\gamma=\frac{1}{3}$. An odd solution for the same configuration is obtained by trying $u_l=A^{l-1}$ for $l>0$ and $u_{-l}=-u_l$ in (8). This gives

$$\lambda=(3-4\gamma+s)/[2M\gamma(1-\gamma)],$$
$$A=(3-2\gamma-s)/[2(1-\gamma)], \quad \text{with} \quad s=(9-8\gamma)^{1/2}, \tag{10}$$

and represents a physically acceptable solution ($|A|<1$) for $\gamma<9/8$. See Fig. 2(c).

For three adjacent light atoms in the heavy chain, an odd mode, $u_0=0$, $u_l=u_{-l}=A^{|l|-1}$, is found by a simple method to be

$$\lambda=[1+(1-\gamma)^{-1/2}]/M\gamma,$$
$$A=1-(1-\gamma)^{-1/2}, \tag{11}$$

valid for all $\gamma<\frac{3}{4}$. The fact that the center atom in this mode is at rest makes its mass irrelevant; it follows that this mode will exist for the *LHL* impurity group in the infinite *H* chain as well as for the *LLL* impurity group. An even mode which also exists requires the solution of a fifth-order algebraic equation for detailed investigations.

All these modes are summarized in Table I and exhibited in Fig. 2. Related calculations have been published by Dean.[12]

The other limit in which modes can be calculated exactly is that of a very short chain. The "chain" consisting of three atoms *HLH* with fixed boundary conditions gives, by direct solution of the determinantal equation resulting from Eqs. (3) and (4), three modes, one of which has a somewhat "localized" appearance,

$$\bar{\lambda}=1+\gamma^{-1}+(1+\gamma^{-2})^{1/2}$$

with displacement ratio $u_1/u_2=[1-\gamma^{-1}-(1+\gamma^{-2})^{1/2}]$. For 2-1-2 masses, that ratio becomes $-1/3.263$. For *HLLH* we find a well-localized odd mode,

$$\bar{\lambda}=1+(\tfrac{3}{2}\gamma)+s', \quad A=1-(\tfrac{3}{2}\gamma)-s',$$

where $s'=[1-\{4/(2\gamma)\}+\{9/(2\gamma)^2\}]^{1/2}$. For $\gamma=\frac{1}{2}$, the displacement ratio becomes $u_1/u_2=4.45$. The even mode for this configuration has a displacement ratio of only 1.41 for the mass ratio $\frac{1}{2}$ and can therefore hardly be called "localized" in this case; for $\gamma=\frac{1}{3}$ the displacement ratio is -2.30. These numbers are also summarized[11] in Table II.

B. Short Chains

We have reasoned that if a certain mode (defined by its vibrational frequencies and atomic amplitudes) is found in a short chain and has the property of being "localized" in the sense that the atoms near all its boundaries are practically undisplaced, then that same mode will also be found in any chain long enough to contain that particular short configuration somewhere. This now leads us to search numerically for modes in short chains. We use a method of solving Eqs. (3) and (4) that gives both eigenvalues and eigenvectors without the usual solution of a determinantal equation,[13] as follows. Use the boundary condition $u_0=0$, set $u_1=1$ (arbitrary scaling), pick some λ, use Eq. (3) successively to compute $u_2, u_3, \cdots, u_N, u_{N+1}$. The question now is whether u_{N+1} turns out to be zero as according to Eq. (4) it should be, or not. If it is, then the λ that we have chosen is an eigenvalue and the computed u's are eigenvectors; if it is not, then we discard the u's and try another λ. (For an arbitrarily chosen λ, u_{N+1} will, of course, rarely turn out to be exactly zero; but in the actual computation, one can utilize the fact that u_{N+1} is a continuous function of λ; therefore an eigenvalue is known to lie between any two trial λ's for which the corresponding u_{N+1}'s have different signs.)

We begin with the five-atom chain. Let us fix the masses m_l as 1 and 2 and compute the five eigenvalues, each with five eigenvector components, for each of the $2^5=32$ possible chains. If we arbitrarily define a mode as "local" if the largest atomic displacements exceed both u_1 and u_5 by a factor of 4, then we find four modes out of the total of 160 that meet our criterion; they are exhibited in Table III. The selection of any mode as "local" in a chain whose total length is only five atoms may seem like stretching the concept beyond its reasonable limit. Yet there are things to be learned from Table III. First, local modes arise from islands of light atoms embedded in a heavy neighborhood; in this case, the groups are {1}, {11}, and {111} embedded among mass-2 atoms. The great similarity between line 3 and line 4 confirms this particularly well. Second, the simi-

TABLE III. The four normal modes that are "localized" that were found among the 160 modes of the binary chains of five atoms.

Mode number	Mass configuration	Squared frequency	Atomic displacements
1	22122	2.6617	(1, −3.32, 10.04, −3.32, 1)
2	21121	3.216	(1, −4.49, 4.60, −1.24, 1)
3	21122	3.230	(1, −4.46, 4.48, −1.05, 0.23)
4	21112	3.517	(1, −5.03, 6.63, −5.03, 1)

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[12] P. Dean, Proc. Phys. Soc. (London) 90, 479 (1967).

[13] H. B. Rosenstock and R. E. McGill, J. Math. Phys. 3, 200 (1962).

TABLE IV. Frequencies of some localized modes of groups containing light atoms, in chains of heavy atoms of various lengths. Light mass 1, heavy mass 2.

Local group	Parity	Chain	Squared frequency	Remarks
1	even	22122	2.6617	(=8/3)
		$2^3\ 12^3$	2.6661	
		$2^\infty\ 12^\infty$	2.6667	
11	odd	221122	3.2355	
		$2^3\ 112^3$	3.236	
		$2^\infty\ 112^\infty$	3.23607	$(=1+\sqrt{5})$
11	even		(not localized)	
111	even	$2^2\ 1^3\ 2^2$	3.52119	
		$2^3\ 1^3\ 2^3$	3.521372	
		$2^6\ 1^3\ 2^6$	3.521379	
111	odd	$2^2\ 1^3\ 2^2$	2.406	
		$2^3\ 1^3\ 2^3$	2.4128	
		2 132	2.4142	$(=1+\sqrt{2})$
121	even	$2^2\ 121\ 2^2$	2.8378	
		$2^3\ 121\ 3^3$	2.8391	
		$2^4\ 121\ 2^3$	2.8392	
121	odd	$2^3\ 121\ 2^3$	2.4128	same as odd mode of 111
1111	even	$2^2\ 1^4\ 2^2$	2.8378	
		$2^3\ 1^4\ 2^3$	2.8391	
		$2^4\ 1^4\ 2^4$	2.8392	
1111	odd	$2^2\ 1^4\ 2^2$	3.67506	
		$2^3\ 1^4\ 2^3$	3.67513	
		$2^6\ 1^4\ 2^6$	3.67514	
1221	even	$2^4\ 1221\ 2^4$	2.592	combination of two {1} groups
1221	odd	$2^4\ 1221\ 2^4$	2.726	
1211		$2^4\ 1211\ 2^4$	3.258	perturbation of {11} mode
1211		$2^4\ 1211\ 2^4$	2.623	perturbation of {1} mode

larity between the local modes of the five-chain and those found in Sec. 2 A above for both the limit of even shorter chains and the limit of infinitely long chains is striking. For the 1-island in the chain of three atoms we found a frequency of 2.618, and in the infinite chain, 2.666···. Here in the five-chain, 2.662 is intermediate, as expected, but already very close—within three parts in 1000—to the infinite chain. This last fact confirms the utility of studying small, even very small, chains to obtain information about local modes in long ones. Perhaps we should add explicitly that this statement is true for local modes only; the majority of the modes in the five-atom chain, which are not local in character, bear no resemblance to modes found in longer chains. The reader can make similar comparisons for the 11- and the 111-islands.

This suggests that the local modes produced by each island be next investigated in chains of heavy atoms of various lengths. The results for masses of 2 and 1 are shown in Table IV and, for masses of 3 and 1, more concisely, in Table V. Only the eigenvalues and the parity of the modes are listed. The form of the modes (that is, the atomic displacements) are shown pictorially in Fig. 3 for selected cases. In both crystals, $\lambda=4$ (the maximum frequency of the infinite monatomic chain of atoms of mass 1) is an upper limit on the possible frequencies.

The main qualitative observation from these two figures and tables is confirmation of the localized nature of the modes about groups that consist in part of light atoms and are surrounded by heavy ones. Heavy atoms are symbolized by open circles, light ones by dots. In Fig. 3, the environment is three heavy atoms on the left and three on the right; the local groups shown are L (one even mode), LLL (one even and one odd mode), and LHL (one even and one odd mode, the latter identical to the odd mode of LLL). Figure 4 repeatedly shows the same mode of one particular group—the LL group—in three different environments; it illustrates clearly that neither the frequency nor the atomic displacements are substantially affected by the environment, provided only that the local group is bounded on each side by at least two heavy atoms. (On the other hand, when the embedding environment is changed so as to contain fewer than two heavy atoms on one side, the vibrational mode generally changes beyond recognition.)

TABLE V. Frequencies of localized modes of groups containing light atoms, in chains of heavy atoms of verious lengths. Light mass 1, heavy mass 3.

Local group	Parity	Chain	Squared frequency
1	even	3^2 1 3^2	2.3995
		3^4 1 3^4	2.4000
		3^∞ 1 3^∞	2.4
11	odd	3^2 11 3^2	3.13742
		3^4 11 3^4	3.13746
11	even	3^2 11 3^2	1.4869
		3^3 11 3^3	1.497
		3^∞ 11 3^∞	1.5
111	even	3^3 1^3 3^3	3.4757
	odd	3^3 1^3 3^3	2.2243
131	odd	3^3 131 3^3	2.2243
	even	3^3 131 3^3	2.5399
1^4	odd	3^4 1^4 3^4	3.6505
	even	3^4 1^4 3^4	2.7399

Some further qualitative comments on the tables and figures follow: The degeneracy of the odd modes of *LLL* and *LHL* is significant (the central atom is at rest; hence its mass does not matter), but that between the even modes of *LHL* and *LLLL* is accidental (a consequence of the choice of $\frac{1}{2}$ for the mass ratio L/H: Two neighboring atoms which are displaced the same amount—as the central ones will be in any even mode—exert no force on each other, and hence behave exactly as if they were rigidly connected, or as if they consisted of one atom of twice the mass). The modes of the {121} group can be interpreted as modes of each of the two mass-1 atoms perturbed by the nearness of the other; one looks like an odd, and the other like an even, linear combination of the two—the former somewhat lower (2.41), the latter somewhat higher (2.83), in frequency than the unperturbed mode (2.67). Finally, we note that the modes of groups consisting of light atoms exclusively have frequencies only slightly dependent on their environment (e.g., the highest mode of a mass-1 atom has a frequency of 3.67 in an environment of 2's, of 3.65 in an environment of 3's). This, too, can be thought of as a consequence of the localization itself. If all atoms except for the local group are barely moving, their mass cannot be of great import. This then suggests the case of a binary crystal with infinite mass ratio, which can be treated exactly,[14] not only as the limit, but also as an actual approximation for the calculation of local modes for these particular groups. The frequencies of the modes of N adjacent light atoms (mass-1) embedded in an infinite chain of heavy ones are in this approximation just those of the linear chain of N atoms with fixed boundary conditions. Our numerical experiments show that for mass ratios between $\frac{1}{4}$ and $\frac{1}{2}$, only the first few, if any, of these N modes are actually local in nature. It is then instructive to construct Table VI, which shows the modes of groups of 1, 2, $\cdots$, atoms of mass 1 embedded in an infinite chain of mass $M>1$ as a function of M. As expected, the infinite chain is a fairly good approximation for those modes that are most localized and highest in frequency.

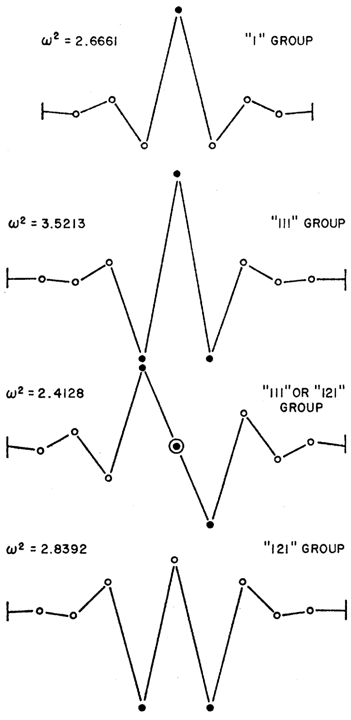

FIG. 3. Local modes of groups of light atoms surrounded by three heavy atoms on each side. ●, mass 1; ○, mass 2.

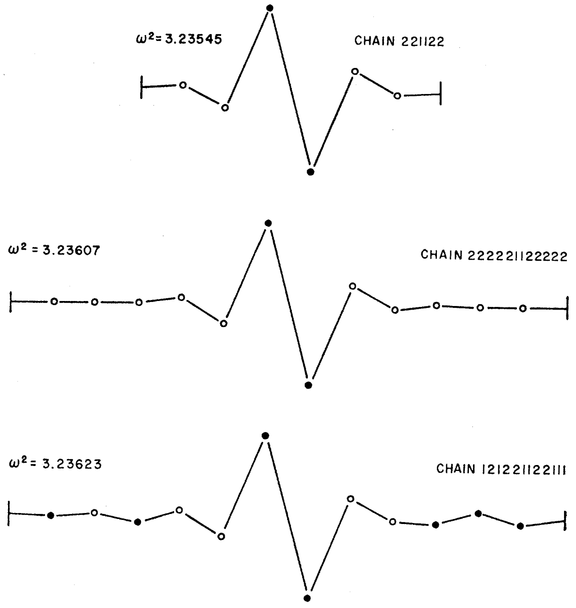

FIG. 4. The odd local mode of two adjacent light atoms in various environments. Mass 1, ●; mass 2, ○.

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[14] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963), p. 192.

TABLE VI. Modes of groups of light particles embedded in infinitely long chains of heavy particles. Light mass, 1; heavy mass, M (as shown). Abbreviations in last column: LL, lower limit (monatomic lattice); IIA, analytical calculation in Sec. A; N, numerical calculation; UL, upper limit [Eq. (9)].

Chain	Parity	M	Squared frequency	Source
M^∞ 1 M^∞	odd	1	(4)	LL
		2	2.667	IIA
		3	2.4	IIA
		4	2.28	IIA
		∞	2	UL
M^∞ 11 M^∞	odd	1	(4)	LL
		2	3.333	IIA
		3	3.236	IIA
		4	3.137	IIA
		∞	3	UL
	even	1	(4)	LL
		2	(2)	IIA
		3	1.5	IIA
		4	1.333	IIA
		∞	1	UL
M^∞ 1^3 M^∞	even	1	(4)	LL
		2	3.545	N
		3	3.475	N
		4	3.457	N
		∞	3.414	UL
	odd	1	(4)	LL
		2	2.414	IIA
		3	2.225	IIA
		4	2.155	IIA
		∞	2	UL

C. Density of Frequencies

We have established the approximate rule that a group containing l light and h heavy atoms will produce local modes if and only if it is bounded by two or more heavy atoms at each end. If the concentration of heavy atoms is C, then the frequency of occurrence of such a configuration will be $C^{h+4}(1-C)^l$, and this will also be the frequency of occurrence of each of the local normal modes of that group. This enables us to estimate the frequency spectrum of a binary disordered lattice as a function of both mass ratio and concentration. The results are shown in Fig. 5 for the example of mass ratio 1:2 and for three different concentrations. Only the higher ranges of frequency (in the case of 1:2 mass ratio, $2<\omega^2<4$), in which the local peaks dominate the spectrum, are shown; for the lower frequencies, for which $g(\omega^2)$ is comparatively smooth, an approximation based on continuous behavior,[15–17] such as a moment approximation, could be joined to our "δ-function" approximation. The original curve of Dean,[6] corresponding to our Fig. 5(b), is reproduced in Fig. 6. We have written in the identifications for the more prominent peaks; the reader will have no trouble identifying the others by reference to our Table IV. Quantitative agreement is thus excellent as far as position of the peaks is concerned. It appears also to be good for the number of modes under each peak if account is taken of the finite peak width in the bottom portion of Fig. 6.

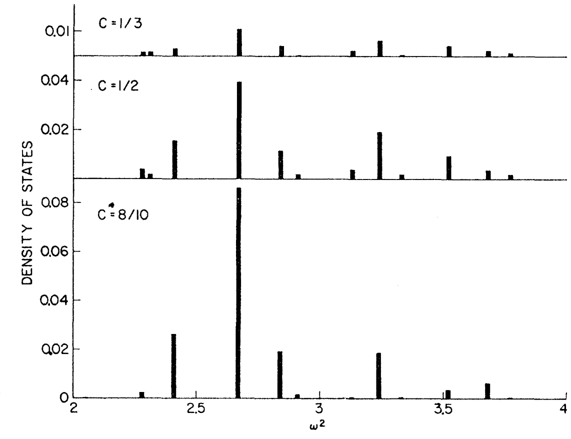

FIG. 5. Density of the most important modes of the 1D binary alloy with masses 1 and 2, shown for three concentrations C of heavy masses.

The validity of these rules depends to some extent on the detailed nature of the model. All properties involving localization would, for example, be weakened by smaller mass differences between component constituents, and by the presence of long-range forces. They would be strengthened if the mass differences were large, but they would not be greatly affected by the presence of more than two atomic components.[18]

3. TWO-DIMENSIONAL SOLIDS

Even though the major part of this paper has been devoted to one-dimensional illustrations, the theoretical results are just as applicable to higher-dimensional crystals, and some higher-dimensional crystal models can be discussed in detail without very great mathematical complications. We choose here the model of a two-dimensional simple cubic lattice with interactions that act between nearest neighbors only but have a noncentral, as well as a central, component. This model is well known from the theory of ordered crystals[19]; its virtue is simplicity rather than physical realism.[20–22] It leads to a secular determinant of order 1, rather than D, for a D-dimensional ordered crystal, and to a secular determinant of order N, rather than ND, in the D-dimensional disordered crystal containing N atoms. The noncentral-force component can be small, but is necessary to provide an essentially D-dimensional behavior;

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[15] H. B. Rosenstock, Phys. Rev. **97**, 290 (1955).

[16] E. W. Montroll, J. Chem. Phys. **10**, 219 (1942).

[17] C. Domb, A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Phys. Rev. **115**, 18 (1959); **115**, 24 (1959); see also Ref. 14, p. 202 ff.

[18] For related discussion of one-dimensional problems, see also J. Hori and M. Fukushima, Proc. Phys. Soc. Japan **19**, 296 (1964); K. Okada and H. Motsuda, Progr. Theoret. Phys. (Kyoto) **39**, 1153 (1968).

[19] H. B. Rosenstock and G. F. Newell, J. Chem. Phys. **21**, 1067 (1953).

[20] R. F. Wallis, Phys. Rev. **116**, 302 (1959).

[21] P. N. Keating, Phys. Rev. **169**, 758 (1968).

[22] Work relevant to multidimensional disordered crystals and possible band gaps in their spectra has recently been done by J. Hori, J. Phys. **1**, 312 (1968).

Table VII. Local vibrational mode of a small crystal containing one light mass. ○, mass 2; ●, mass 1.

Masses	○ ○ ○ ○ ● ○ ○ ○ ○	○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ 2 2 2 2 2	○ ● ○
Frequencies	2.799	2.839	2.842
Displacements	3 −41 3 −41 171 −41 3 −41 3	0 −1 11 −1 0 −1 3 −42 3 −1 11 −42 166 −42 11 −1 3 −42 3 −1 0 −1 11 −1 0	0 0 0 −3 0 0 0 0 0 −1 12 −1 0 0 0 −1 3 −42 3 −1 0 −3 12 −42 165 −42 12 −3 0 −1 3 −42 3 −1 0 0 0 −1 12 −1 0 0 0 0 0 −3 0 0 0

in its absence, the equations of motion degenerate into one-dimensional ones. For other two- and three-dimensional calculations, see Payton and Visscher.[23]

The equations of motion for the x component u_{lk} of the displacement of the atom at site (l,k) is

$$(2+2\sigma-M_{lk}\lambda)u_{lk}=(u_{l-1,k}+u_{l+1,k})+\sigma(u_{l,k+1}+u_{l,k-1}), \quad (12)$$

with $\sigma=\beta/\alpha$, $\lambda=\omega^2/\alpha$, where α is the central, and β the noncentral, force constant. We were not able to obtain analytical solutions of this system with disordered masses, and therefore solved it numerically for various small crystals with fixed boundary conditions and $\sigma=\frac{1}{10}$. The special method of Sec. 2 applies to one-dimensional crystals only, and we had to use the "usual" matrix-diagonalization methods. We hoped again to find modes so localized that the displacements of atoms near the boundaries would be small. Such modes would be expected to persist in larger crystals. This was indeed found: Results are shown in Tables VII–IX.

In Table VII we see the highest-frequency mode of a single impurity of mass 1 at the center of 3×3, 5×5, and 7×7 lattices of atoms of mass 2. Localization is apparent in each, even with the almost trivially small 3×3 crystal; frequencies are nearly the same in all three cases, and also very close to the value 2.666 that would be approached if the noncentral-force constant were to approach zero (Table IV). [To be precise, we should say the the displacements shown in Table VII are not the u_{lk} resulting from solving (12), but the symmetrized sum $u_{lk}+v_{lk}$, where v_{lk} denotes the displacement in the y direction of the atom at site (l,k), obeys an equation quite analogous to Eq. (12), and has the same eigenfrequencies.]

Table VII thus confirms that in higher dimensions, as well as in one dimension, localized modes exist whose frequencies can be computed from small-crystal models. This will be possible whenever an impurity group is isolated. The question now is what constitutes sufficient isolation. In one dimension we established the approximate rule that two heavy atoms on each end of a group containing light ones was sufficient. What is the corresponding rule now? Table VIII is designed to answer this.

Table VIII, similar in organization to Table VII, therefore shows the perturbing effect of other nearby light atoms on the local mode of the light atom at the center. All crystals are 5×5 here [hence, diagonalization of a 25×25 matrix, with coefficients defined by Eq. (12), was involved each time]. The xy symmetry no longer exists; hence we show the computed u_{lk} directly, rather than $u_{lk}+v_{lk}$. The highest frequency and, where it is of interest, the second-highest frequency are shown in each case. Table VIIIe, where the two light atoms are nearest neighbors in the direction of motion, is an exceptional case, to be discussed later in connection with Table IX. There are two requirements if we are to conclude that the mode will persist in

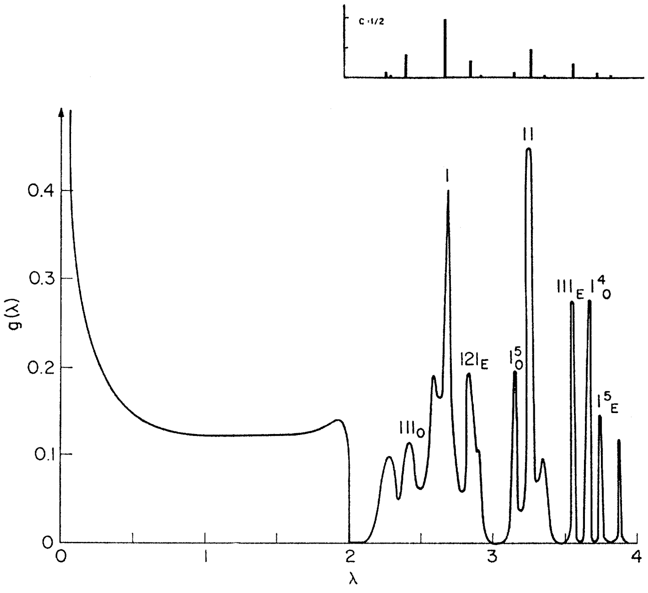

Fig. 6. Frequency spectrum of 1D binary alloy of masses 1 and 2, equal concentration. Curve taken from Dean (Ref. 6). Inset reproduced from our Fig. 5. Identification of peaks from this work—Fig. 5 and Tables I–IV.

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[23] D. N. Payton and W. M. Visscher, Phys. Rev. 156, 1032 (1967).

TABLE VIII. Effect of nearby light atoms on the local vibration of a light atom in a 5×5 crystal. ●, mass 1; ○, mass 2.

Masses	● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○	○ ○ ○ ○ ○ ● ○ ○ ○ ○ ○ ○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○	○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○	○ ○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○	○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ● ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○
Frequencies	2.839	2.841	2.839	2.841	3.427
Displacements	1 0 0 0 0 −1 3 −5 3 1 11 −37 83 −37 11 −1 3 −5 3 −1 0 0 0 0 0	0 0 0 0 0 −8 6 −6 3 −1 11 −37 83 −37 11 −1 3 −5 3 −1 0 0 0 0 0	5 −12 5 −2 1 −1 4 5 3 −1 11 −37 82 −37 11 −1 3 −5 3 −1 0 0 0 0 0	6 −19 44 −19 6 −2 4 −7 4 −2 9 −31 71 −31 9 −1 2 −4 2 −1 0 0 0 0 0	0 0 0 0 0 1 −3 3 −1 0 −20 67 −67 21 −5 1 −3 3 −1 3 0 1 −1 0 0
	a	b	c	d	e

Masses	○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ● ○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○		○ ○ ○ ○ ○ ○ ● ○ ○ ○ ○ ○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○		○ ○ ○ ○ ○ ○ ○ ● ○ ○ ○ ○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○	
Frequencies	2.939	2.378	2.877	2.778	2.919	2.750
Displacements	0 0 0 0 0 −2 3 −4 2 −8 43 −44 72 −30 8 −2 3 −4 2 −1 0 0 0 0 0	0 0 0 0 0 5 −1 −3 3 −2 −80 19 45 −30 12 5 −1 −3 3 −2 0 0 0 0 0	1 −3 2 −1 0 −22 54 −26 9 −3 9 −30 63 −28 8 −1 2 −4 2 −1 0 0 0 0 0	−2 4 −2 1 0 27 −65 28 −8 2 6 −22 54 −25 7 −1 2 −3 2 −1 0 0 0 0 0	1 −2 3 −2 1 −7 26 −59 26 −7 7 −26 59 −26 7 −1 2 −3 2 −1 0 0 0 0 0	−1 2 −3 2 −1 8 −28 58 −27 8 8 −28 58 −27 8 −1 2 −4 2 −1 0 0 0 0 0
	f	g	h	i	j	k

TABLE IX. Local modes in a 6×5 crystal containing two adjacent impurities. ●, mass 1; ○, mass 2.

Masses	○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ● ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○		○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ● ○ ○ ○ ○ ● ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○	
Frequencies	3.431	2.051	2.920	2.750
	0 0 0 0 0 0	12 −21 26 −26 21 −12	0 0 0 0 0	0 0 0 0 0
	0 1 −3 3 −1 0	−12 21 −26 26 −21 12	1 −2 3 −2 1	−1 2 −4 2 −1
Displacements	5 −21 67 −67 21 −5	0 0 0 0 0 0	−7 26 −59 26 −7	8 −27 58 −27 8
	0 1 −3 3 −1 0	12 −21 26 −26 21 −12	7 −26 59 −26 7	8 −27 58 −27 8
	0 0 0 0 0 0	−12 21 −26 26 −21 12	−1 2 −3 2 −1	−1 2 −4 2 −1
			0 0 0 0 0	0 0 0 0 0

large crystals: The frequencies must not be changed greatly from the "fully isolated" case of Table VII (i.e., from 2.84), and localization must be apparent from the smallness of displacements of atoms that are near the boundary. For the situations of Tables VIIIa–VIIId, both criteria are fully satisfied; indeed, the frequency change is only about 0.01 in each of these four cases. In Table VIIIf, where the light atoms are third neighbors in the direction of motion, the localization criterion fails for both modes shown. For Tables VIIIj and VIIIk (nearest neighbors in a direction perpendicular to that of the motion), localization is adequate, but the frequency somewhat more affected (deviations of 0.09 from the isolated case). For Tables VIIIh and VIIIi (second-nearest neighbors, diagonal direction), one of the modes appears satisfactory.

Table IX is designed to illustrate the modes due to an adjacent pair of light atoms in a symmetrical environment of heavy atoms. We see, as we have already noted in Table VIIIe, VIIIj, and VIIIk, that the pair mode appears only if the light atoms are neighbors in the direction of the motion; otherwise two modes (one "even," one "odd") very similar to that of a single light atom appear. The difference in environment between this case and that of Table VIII affects the value of the frequency only very slightly.

The rough conclusion to draw from Table VIII is that an impurity, or impurity group, is sufficiently isolated for the persistence of its normal frequency, independent of the nature of its more distant environment, if it is bounded by at least two heavy atoms in the direction of motion and by one heavy atom in the direction perpendicular to this. Quantitatively, this leads us to the expression $C^6(1-C)$ for the probability of occurrence of, or the density in the frequency spectrum of, the mode due to the single light atom [replacing $C^4(1-C)$ in the 1D case], $C^8(1-C)^2$ for the two adjacent light atoms [replacing $C^4(1-C)^2$], and generally, $C^{2l+4}(1-C)^l$ for l light atoms along one main crystallographic direction [replacing $C^4(1-C)^l$]. More complex isolated groups, such as three light atoms in an L configuration, for which each local normal mode would not involve displacements in one of the crystallographic directions alone, will lead to more complicated expressions.

The method of finding important modes in large crystals by considering small ones has thus involved more numerical labor (diagonalization of a 25×25 matrix) than in the 1D case, but the relative saving over actually solving the case of the large crystal of N atoms on edge (an $N^2\times N^2$ matrix) is even larger. We have found that the density in the frequency spectrum of the local mode due to a single light atom is somewhat reduced from the 1D case, and that of the other isolated groups is more greatly reduced. There will thus be more quasilocal modes of smaller intensity, except for the mode due to the single light atom, and the many peaks in the structure of the spectrum as a whole may, if a detailed calculation for a large crystal is done, be hard to detect unless the interval for the histogram is taken extremely small. We must again remember that our conclusions are at least somewhat sensitive to the details of the forces and masses in the crystal model.

4. 3D SOLIDS

We have performed no detailed calculations for 3D crystal models, but extrapolation now seems quite justified. Local modes, which could be calculated for a single atom or for a neighboring group containing light atoms in a small crystal (of perhaps 27 or 125 atoms) containing otherwise only heavy atoms, can be expected to appear as well in the spectrum of a large disordered crystal. Following the reasoning of the last section, we would expect their intensity to be further reduced, to $C^8(1-C)$ for the mode of the single light atom, and to $C^{4l+4}(1-C)^l$ for the modes of l light atoms in a row. The density of more elaborate groups is harder to estimate, and again we must add our caveat about possible sensitivity to forces in the model.[22]

5. RESUME

We have shown that the existence of peaks in the frequency spectra of 1D infinite isotopically disordered crystals can not only be explained in terms of local vibrations of groups containing light atoms, but can also be predicted in some detail by easy calculations on very small crystals. The arguments are not qualitatively sensitive to dimensionality. Hence, similar peaks are also predicted for 2D and 3D disordered crystal models. However, the intensity of the peaks should be smaller in higher dimensions.

Extension of this work should be useful in several directions. Clearly, numerical work should be performed in three dimensions, and in any dimension with more realistic models. Most importantly, the dependence on mass ratio of our criteria for localization and persistence should be established. (Our own simple force model—forces independent of the atoms involved— applies best to so-called isotopically disordered lattices, but not so well to lattices with mass ratios of 2:1 or higher.) Also, solids with more than two constituents could be studied.

We should finally note that when each atom has an electric charge (ionic crystals), the dipole moment of each of the modes can be readily found from the atomic displacements we have already calculated. The dipole moment of local modes that are odd is, of course, zero, but that of other local modes is likely to be considerable, and to provide a prominent feature in the absorption spectra of crystals, as most "lattice" modes themselves lack a dipole moment. The present work can be applied rather directly to mixed crystals AX_CY_{1-C}, in which the concentration C can be varied. The absorption spectra of these crystals thus provide a simple tool for observation and the semiquantitative comparison of present results with experiment.[24]

ACKNOWLEDGMENT

Thanks for many useful discussions are due to Dr. Marvin Hass.

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[24] M. Hass, H. B. Rosenstock, and R. E. McGill, Solid State Commun. (to be published).

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Ion-Size Effects in Color Centers

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A modification of the point-ion model is proposed which provides an approximate correction for ion-size effects. The difference between the optimum pseudopotential for the smoothest pseudo-wave-function and the point-ion potential is treated as an ion-size correction to the Hamiltonian, appropriate to a smooth variational trial function. By neglecting the variation of the trial function over the ion cores in the evaluation of matrix elements, one obtains a simple, approximate form for the pseudopotential: $V_p = V_{\mathrm{PI}} + \Sigma_\gamma [A_\gamma + (\bar{V} - U_\gamma)B_\gamma]\delta(\mathbf{r} - \mathbf{r}_\gamma)$, where V_{PI} is the point-ion potential, U_γ is the potential at ion γ due to the other ions, and $\bar{V}$ is the average potential. The coefficients A_γ and B_γ are properties of the ions alone, and have been computed for a large set of ions. The approximate pseudopotential is applied to the calculation of ionization potentials of alkali atoms, where it works well, and of F-band energies in alkali halides and alkaline-earth fluorides, where it is found that all of the coefficients A_γ must be reduced by a factor of 0.53 in order to obtain agreement with experiment. With the adjusted pseudopotential coefficients, the theory accounts well not only for the Ivey law in alkali halides, but also for deviations from the Ivey law. In addition, the seemingly anomalous F-band energy in BaF_2 is accounted for. The empirically adjusted constants may be useful in other color-center problems as well.

I. INTRODUCTION

A RIGOROUS formulation of the electron-excess color-center problem requires that all of the electrons be treated equivalently. However, a vast simplification results from the recognition that the occupied ion-core states are much more tightly bound than the states associated with the color center, and the consequent assumption that the ion-core electrons simply contribute to the potential seen by the excess electrons. Models based on this assumption include the point-ion model of Gourary and Adrian (GA),[1] with which we shall be primarily concerned, as well as continuum and semicontinuum models.[2] In the point-ion model, the ions are replaced by point charges, and the resulting potential is used with a smooth variational trial function which is subsequently orthogonalized to

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[1] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

[2] B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. X, pp. 127–247.