smaller atoms, namely, silver and copper atoms, which are able to move with relative ease in the basal planes.

If only nonbasal jumps were to contribute to the perpendicular diffusion of noble elements, one would expect the anisotropy to be $\cong 5.2$ for zinc.[6] From the observed values of anisotropy, one concludes that both types of atomic jumps, basal and nonbasal, are responsible for perpendicular diffusion.

We compare below the experimental values of the differences in the activation energies ($\Delta Q$) for self-diffusion and for diffusion of copper and gallium in zinc with the theoretical predictions[6] based on the simple screened interaction model.

For copper:

$$\begin{aligned}(\Delta Q_{\parallel})_{\mathrm{expt}} &= 7.73\ \mathrm{kcal/mole},\\ (\Delta Q_{\parallel})_{\mathrm{theory}} &= 8.48\ \mathrm{kcal/mole},\\ (Q_{\parallel})_{\mathrm{expt}} &= 29.53\ \mathrm{kcal/mole},\\ (Q_{\perp})_{\mathrm{expt}} &= 29.92\ \mathrm{kcal/mole},\\ (Q_{\parallel})_{\mathrm{theory}} &\cong (Q_{\perp})_{\mathrm{theory}} = 30.29\ \mathrm{kcal/mole}.\end{aligned}$$

The theoretical and experimental values for $(\Delta Q_{\parallel})$, $(Q_{\parallel})$, and $(Q_{\perp})$ differ by about 10%, 2.5%, and 1.3%, respectively.

For gallium:

$$\begin{aligned}(\Delta Q_{\parallel})_{\mathrm{expt}} &= -3.4\ \mathrm{kcal/mole},\\ (\Delta Q_{\parallel})_{\mathrm{theory}} &= -2.61\ \mathrm{kcal/mole},\\ (\Delta Q_{\mathrm{basal}})_{\mathrm{expt}} &= -11.64\ \mathrm{kcal/mole},\\ (\Delta Q_{\mathrm{basal}})_{\mathrm{theory}} &= -8.55\ \mathrm{kcal/mole}.\end{aligned}$$

The theoretical and experimental values for $(\Delta Q_{\parallel})$ and $(\Delta Q_{\mathrm{basal}})$ differ by about 24% and 34%, respectively.

The disagreement between theoretical and experimental values reflects the fact that the theory does not include core and ion size effects.

## ACKNOWLEDGMENTS

We wish to thank K. M. Koliwad, C. J. Santoro, D. R. Campbell, and Dr. Z. P. Chang for their assistance during the measurements. We are indebted to J. M. LoGiudice and F. J. Mastrianni of the Research Division for the use of the counting assembly. One of us (APB) wishes to express his gratitude to the Government of Panjab, India for the grant of leave of absence and to the United States Educational Foundation in India for the Fulbright travel grant.

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# Interatomic Forces in Various Solids

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Inferences are made concerning the nature and range of interatomic forces in several solids, by the use of the observed dispersion relations of the lattice vibrations together with the simple analytical properties of the sum of the squares of all the lattice vibrations corresponding to the same point in reciprocal space. Eleven metals, one alloy, and four semiconductors are treated. The method enables one to separate long-range electromagnetic (i.e., multipole) forces from "overlap" ones. The results suggest in several cases that the former are required to describe the interactions in a realistic way.

## 1. INTRODUCTION

THE thermal motion of atoms in a crystal is determined by the forces existing between them, and the observation of the spectrum of these vibrations should therefore be a tool for inferring the nature of these forces. The process of obtaining this inference is necessarily an inductive rather than a deductive one. Thus, a given force scheme (i.e., an assumed set of "force constants" or "coupling parameters" which tell how the displacement in some direction of any atom in the lattice will affect the motion of any other atom in the lattice) produces one unique set $\omega_i(\mathbf{q})$ of $3n$ lattice vibrations for each wave vector $\mathbf{q}$ ($i=1,\cdots,3n$, $n=$ the number of atoms per unit cell) which one can straightforwardly compute, provided that one agrees on basic theoretical assumptions such as the Born–von Karman theory and the harmonic approximation. The reverse process, which has to be followed in practice, is not a unique one, however; at least as long as the number of experimental observations of $\omega(\mathbf{q})$ is finite and is subject to experimental error, it is always possible to fit the experimental data with any number of possible force schemes. To pick the "correct" force scheme from these, other criteria are necessary—such as goodness of fit, assumption of nature of forces believed for other reasons to exist in certain crystals, shortness of range, simplicity, or general "reasonableness." Mathematically, the "dispersion relation" $\omega_i(\mathbf{q})$ is the $3n$ solutions of an equation of order $3n$ in $\omega^2$, with the force constants

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appearing in a complicated way in the coefficients of that equation; in the solution, therefore, the effects of the various forces are quite mixed up and well concealed rather than separate and obvious to the eye.

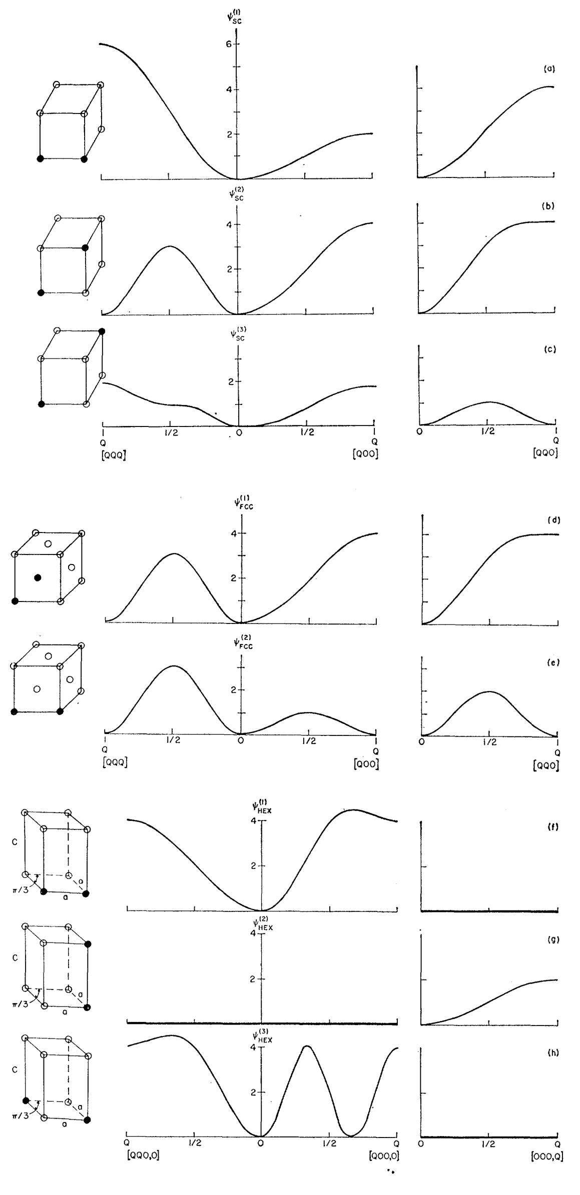

FIG. 1. $Q$ dependence, in three directions, of contributions of various interacting atoms to the sum. Interaction between the atoms shown in black on the left side of each figure produces the curve shown on the right. (a), (b), and (c): simple cubic lattice. (d) and (e): face-centered cubic lattice. (f), (g), and (h): close-packed hexagonal lattice.

It is for this reason that it has been suggested[1,2] that in many cases the analysis might be simplified by studying, instead of dispersion relations themselves, the "sum function" $\sum_{i=1}^{3n}\omega_i^2(\mathbf{q})$ which, although it does not contain all the information that the dispersion relation does, it does contain some of the information in a particularly direct and simple way. That sum function can in fact be written in the form

$$\sum_{i=1}^{3n}\omega_i^2(\mathbf{q})=\text{constant}+\sum_k \beta_k\psi^{(k)}(\mathbf{q}). \qquad (1)$$

The sum on the left is the sum of the squares of all the phonon frequencies at $\mathbf{q}$, and the index $k$ over which the sum on the right is taken is over the various forces existing in the crystal.[3] The major points which provide the simplicity which we have referred to are two in number: first, the contributions from the various forces are not involved in the complicated solution of a high order algebraic equation, but appear in a simple additive form in the sum appearing on the right-hand side of (1); and, second, many of the forces which are present in the crystal provide only a constant contribution and contribute to the sum over $k$ not at all, thereby permitting a particularly straightforward analysis of some of those forces which are less obviously seen in the dispersion relation itself than the rest. It is also important in practice that the $\psi^{(k)}$ are usually very simple and easily computed functions, viz., the contribution to the trace of the dynamical matrix. Since mathematically the left hand side of (1) is the trace of the dynamical matrix, the forces which contribute only a constant term to the right-hand side (1) have been called trace-constant forces, and those that do contribute to the $\mathbf{q}$-dependent sum on the right hand side have been called trace-variable forces. The two classes of forces that are trace-constant are[2] (1) all forces between unlike atoms in the crystal and (2) all forces which are electromagnetic in nature. The trace-variable forces, whose effect should be seen from the sum function in a particularly simple additive way are therefore the nonelectromagnetic forces between like atoms. In Fig. 1, the $\psi$'s corresponding to the most common trace-variable interactions are shown for the simple cubic, the face-centered cubic, and the close-packed hexagonal lattices, along certain crystallographic symmetry directions. Even though only the effects of very near neighbors are shown in these diagrams, it seems likely that these may be the only trace-variable forces that will appear in many crystals—as can be illustrated by the example of alkali halides of the NaCl structure. Crystallographically, these are face-centered cubic crystals with two atoms per cell. Figures 1(d) and 1(e) therefore apply, and the next-strongest trace-variable force would be between third like neighbors, i.e., across the body-diagonal of the unit cell shown in the left part

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[1] *Proceedings of the International Conference on Lattice Dynamics, Copenhagen*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965).

[2] H. B. Rosenstock, in Ref. 1, p. 205. See also H. B. Rosenstock, Phys. Rev. **129**, 1959 (1963).

[3] A sum rule similar to (1) but with validity for more restricted forces has been obtained by R. Brout, Phys. Rev. **113**, 43 (1959), and in a somewhat different connection also by G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, p. 247; M. Blackman, Proc. Roy. Soc. (London) **A181**, 58 (1942).

of the figure. Since one like atom is directly in between these interacting atoms (as well as unlike atoms nearby but not shown in the figure), overlap forces between them would be expected to be very small, if not absent.

The purpose of the present paper is to look at experimental results of dispersion relations that have been obtained by others in the past few years to see what understanding, in addition to that provided by the authors of these experimental papers themselves, can be attained for these substances by an analysis along the lines suggested by Eq. (1). Although the information will necessarily be restricted, one can hope that it may in some cases be of more direct physical significance than the straightforward least-squares fitting of assumed force models, with many arbitrary parameters, to the observed dispersion relations.

Some words need to be said about two terms we have just used—"like" and "electromagnetic." The meaning of the term "like" is unambiguous in crystals that have more than one atom per unit cell; for example, in a sodium chloride crystal, all sodium atoms are "alike," and all sodium atoms are "unlike" all the chlorine atoms; similarly, in diamond, carbon atoms located in equivalent crystallographic sites are like, and they are different from those carbon atoms which are located in the other crystallographic site in the diamond lattice. Matters are slightly more involved, however, in Bravais lattices, in which crystallographers recognize only one single atom in their minimum unit cell. In that case we must for our purposes construct a larger unit cell which contains more than one atom in sites which, in terms of that new unit cell, are crystallographically not equivalent. Physically, this is a simple enough process, and indeed the larger unit cell that we deal with here has usually a simpler shape than the crystallographically minimal unit cell; for example, in the case of body-centered-cubic metals such as sodium, we deal with a unit cell which is a cube, containing one atom at each corner (all these atoms, and those located at the corners of all the other unit cells, are "like") and one atom at the center of that cube (and of course all atoms located at the center of any other such cube are considered "like"). By contrast, the crystallographic unit cell of minimal size has only one half the volume of that cube and a fairly complicated shape (which is well known and, in its most symmetric form, is exhibited in Fig. 5 of Ref. 1). The fact that we are now dealing with a unit cell with two atoms in it means that a calculation will give us six phonons for each point in our reciprocal space, which we refer to as **Q** space, whereas the experimenter will provide us with only three phonons for each point in **q** space; we must therefore determine which points in **q** space correspond to the same point in **Q** space before applying our analysis to Eq. (1) in the now suitable form

$$\sum_{i}^{3N} \omega_i^2(\mathbf{Q}) = \text{constant} + \sum_{k} \beta_k \psi^{(k)}(\mathbf{Q}). \qquad (2)$$

($N$ is now the number of atoms in the new larger unit cell, usually a simple multiple of $n$.) This matching procedure, however, is a formally simple one, described earlier.[2] It is found that, for example, in the body-centered-cubic lattice the points $(a,b,c)$ and $(a, b, 1-c)$ in **q** space correspond the same point in **Q** space, while in the face-centered-cubic lattice, the points $(a,b,c)$, $(a, b, 1-c)$, $(a, 1-b, c)$, and $(a, 1-b, 1-c)$, in **q** space correspond to the same point in **Q** space.

In discussing "electromagnetic" versus "nonelectromagnetic" forces, the distinction is between forces which in the dynamical matrix can be described simply as coulomb, dipole, quadrupole, etc. forces and which have long range, versus those which are usually called "overlap" or "short range" or "repulsive "forces. It is true, of course, that these forces are, in a basic sense, also electromagnetic in nature, as are, indeed, all forces dealt with in the realm of atomic physics—that is to say, in the realm in which nuclear and gravitational forces are negligible. The crucial distinction between electromagnetic forces in our sense and those which, here as elsewhere, are considered nonelectromagnetic is whether they can, or cannot, be described in terms of an electromagnetic potential classically, rather than quantum-mechanically, as the so-called "overlap" forces must be. It should also be said that the sum rule (2), or (1), remains valid in the face of charge distortion if this can be validly described in terms of a shell model.[4] If that model is applied to the present sum rule, the electromagnetic forces, core-core, core-shell, and shell-shell, would contribute nothing to the sum, whereas "springlike" forces between core-core and shell-shell would contribute; spring-like forces between core and shell would not because cores and shells would count for "unlike" particles. If a shell model is therefore a valid description of the forces in a crystal, then the number of forces remaining to provide a contribution to the sum (2) should be particularly small and the form of the sum particularly simple.

The rest of this paper deals with analysis of dispersion data on individual substances, with all substances that have the same structure treated in the same section and results shown in the figure bearing the same number as the section. The symbol $\Sigma$ is used throughout for what is essentially the sum on the left-hand side of (2), appropriately normalized and with the zero fixed at $Q=0$; that is,

$$\Sigma \equiv \left[\sum_i \omega_i^2(Q) - \sum_i \omega_i^2(0)\right] / \sum_i \omega_i^2(0). \qquad (3)$$

Section 2 deals with the body-centered-cubic metals, Sec. 3 with $\beta$-brass which is also a body-centered cubic structure and Sec. 4 with white tin, which is basically body-centered tetragonal, but more complicated in detail. Section 5 concerns face-centered-cubic metals.

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[4] B. G. Dick and H. W. Overhauser, Phys. Rev. **112**, 90 (1958); W. Cochran, Proc. Roy. Soc. (London) **A253**, 260 (1959).

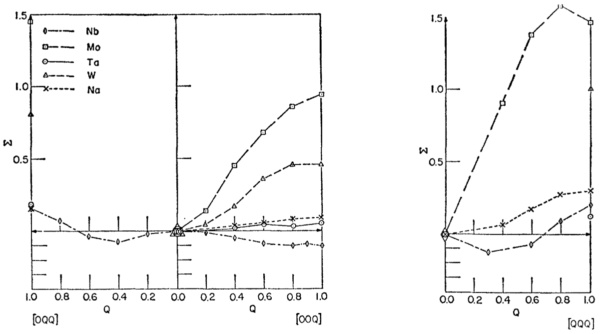

FIG. 2. Σ for some body-centered cubic metals.

For our purposes, the unit cell is a simple cube in all these sections (except Sec. 4, where it is a rectangular parallelopiped with one side shorter than the other two). Section 6 deals with the diamond, or zincblende, structure, face-centered-cubic for our purposes (we are not aware of any new work on any NaCl-type alkali halides, which would also be face-centered cubic here[1]). Finally, in Sec. 7 hexagonal structures are discussed. Section 8 summarizes the results.

## 2. BODY-CENTERED CUBIC METALS

Dispersion relations from neutron scattering are available for five body-centered-cubic metals: Na[5], W[6], Mo,[7] Ta[8] and Nb.[9] For our purposes, the body-centered-cubic lattice is treated as a simple cubic lattice with two atoms per unit cell and the theoretical effect of the interaction between first, second and third like-neighbors (which are second, third and fifth neighbors irrespective of likeness) is shown by Figs. 1(a), (b), and (c). These should be compared with Fig. 2, in which the quantity Σ computed from the actual dispersion data for the five metals are shown. Only in one direction, $[00Q]$, do we have fairly complete data for all these substances; in that direction, unfortunately all three forces considered in Fig. 1 give a very simple curve, of the same shape. Only for some metals do we have fairly complete data in other, more interesting, directions; but the value of Σ for the points (011) and (111) is available for all. This last fact suggests using the three points (001), (011), (111) for a unified analysis of all substances. The values of Σ at these points are given in Table I.

TABLE I. Values of Σ at certain points for body-centered cubic metals.

| | Na | Nb | Mo | Ta | W |
|---|---|---|---|---|---|
| Σ(100) | 0.10 | −0.100 | 0.94 | 0.063 | 0.46 |
| Σ(110) | 0.15 | 0.154 | 1.38 | 0.179 | 0.81 |
| Σ(111) | 0.29 | 0.199 | 1.49 | 0.130 | 1.01 |

Truncating the right hand side of Eq. (2) after three terms and writing it out for $Q=(100)$, (110), (111), we obtain, from Fig. 1,

$$\begin{bmatrix}\Sigma(100)\\ \Sigma(110)\\ \Sigma(111)\end{bmatrix}=\begin{bmatrix}2&4&4\\ 4&4&0\\ 6&0&2\end{bmatrix}\begin{bmatrix}\beta_1\\ \beta_2\\ \beta_3\end{bmatrix}$$

which can be solved for the β's, to give Table II. These numbers can be taken seriously as an indication of the relative strength of forces between first, second and third like-neighbors only when they fall off rapidly (i.e. for Na, W, Mo); in these cases one can infer also that further neighbors probably interact only slightly. For the other metals the figures merely indicate that truncation after the third like-interaction was unjustified and that longer range forces are physically active. We proceed with a description of the data for each metal.

TABLE II. Values of the coefficients $\beta_k$, as defined by Eq. (2).

| | Na | Nb | Mo | Ta | W |
|---|---|---|---|---|---|
| $28\beta_1$ | 1.26 | 1.30 | 6.84 | 0.75 | 4.74 |
| $28\beta_2$ | −0.21 | −0.23 | 2.82 | 0.50 | 0.93 |
| $28\beta_3$ | 0.28 | −1.13 | −0.34 | −0.44 | −0.08 |

### Na

It is clear from Table II that forces between first like-neighbors (i.e., second neighbors) are present and that second and third like-neighbors interact much more weakly. Indeed, experimental errors (∼0.03) alone might produce the ratio of 1:2:3 for Σ(100):Σ(110):Σ(111) as would be produced by first like-neighbor forces alone. However, as pointed out by the authors[5] a somewhat better fit can be obtained by including second and third like-neighbor forces of small magnitude.

### W

Of the forces between like-neighbors that show up in the analysis of Σ, $\psi^{(1)}$ is by far the strongest one, but a contrast to the situation in Na, the simple ratio 1:2:3 for the three special points considered in Table I, that would indicate the effects of first like neighbors alone, can definitely not be obtained within experimental error here. On the other hand, a force between third like-neighbors is not needed for a fit; but a comparatively small but definitely present force between second like-neighbors is needed. This tends to confirm the results of the analysis of the experimenters[6] who, in attempting to fit the dispersion relations themselves by taking successive neighbors into account, find a very strong second-neighbor force, a force between third neighbors

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[5] A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, and R. Bowers, Phys. Rev. **128**, 1112 (1962).

[6] S. H. Chen and B. N. Brockhouse, Solid State Commun. 2, 73 (1964).

[7] A. D. B. Woods and S. H. Chen, Solid State Commun. 2, 233 (1964).

[8] A. D. B. Woods, Phys. Rev. **136**, A781 (1964).

[9] Y. Nakagawa and A. D. B. Woods, Phys. Rev. Letters **11**, 271 (1963).

about $\frac{1}{5}$ in strength of that, but note that no further improvement can be obtained by going out to neighbors as far as six and independent parameters as many as fifteen. Our results here, viz., the apparent vanishing of forces between third like-neighbors, and by implication of nonelectromagnetic forces between further like-neighbors, suggests that explanation of the pecularities of the dispersion relation of tungsten be sought in electromagnetic forces.

### Mo

Both $\Sigma$ and the errors in obtaining it are quite large here; in both the $(00Q)$ and $(QQQ)$ direction, the shape of the $\Sigma$ curve is, within experimental error a simple $1-\cos Q$ one. Third-like-neighbor interaction may be absent, by inspection of Table II, but strong forces between second as well as first like-neighbors are seen to be necessary; this does not agree with the authors' attempted fit,[7] which gives force constants for second like-neighbors only about $\frac{1}{10}$ in magnitude for those for first like-neighbors. However, one must note that the authors attempted to make a least-squares fit to many of the points of the original dispersion relation whereas our analysis is based on only three points of the derived function $\Sigma$. Because only the longitudinal branch was measured in great detail by the experimentists near the point (111) where a "Kohn anomaly" is believed to exist, the quantity $\Sigma$ could not be computed there.

### Nb

Here, as in Ta (below) the numbers in Table II merely indicate the presence of nonelectromagnetic forces well beyond third like-neighbors. The original authors[9] have attempted to fit their dispersion data by interactions out to eighth neighbors without getting a perfect fit, and therefore doubt the physical significance of such "force constants." The points shown in Fig. 2 for Nb are subject to both experimental and transcriptional errors but are significant, on both side of the zero line; at least some negative values for force constants are thereby indicated. It seems likely that many more experimental details, including dispersion relations at more closely spaced points, will be needed before an analysis capable of unscrambling the many forces which are physically present will be possible.

### Ta

From the near-constancy of $\Sigma$ in the $(Q00)$ direction alone we may conclude that the nonelectromagnetic forces between like neighbors in this metal are rather weak compared to similar forces in other metals. Only the points (001) (011) and (111) are of significance, the others being exceeded, or comparable to, experimental error [and for that reason some points in the $(QQQ)$ direction are not shown]. The authors[8] have found it difficult to fit dispersion data to a realistic force model; they used seventh-neighbor general models, and a tenth-neighbor "axially symmetric" model. Detailed conclusions as to forces cannot be read from either the figure or the table; however, the smallness of $\Sigma$ suggests that attempts to fit dispersion relations should be based on electromagnetic forces (which go to infinity in a specified way) rather than by arbitrarily adding more and more neighbors.

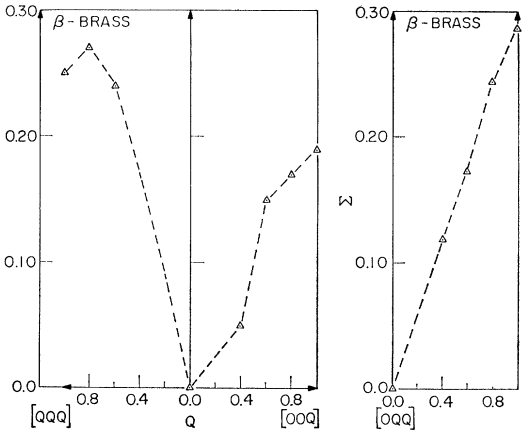

FIG. 3. $\Sigma$ for beta-brass.

## 3. β BRASS

Measurements on beta brass are available at room temperature.[10] The structure is that of CsCl, which is a simple cubic lattice with two atoms per unit cell. We can therefore consider this alloy together with the body-centered cubic metals of Sec. 2. The computation of $\Sigma$ is actually slightly simpler here, as complete dispersion data give six phonons for every point in $Q$ space rather than three, and the matching of two sets of three points is not necessary in the present case. Unfortunately, even though the experimental study of the dispersion relation has been quite extensive,[10] it is only at a few points that all six phonons are actually given, and our $\Sigma$, shown in Fig. 3, is quite incomplete. Also, the cumulative error in $\Sigma$, due to error of experiment and transcription, is considerable. Thus, even though the peak that shows up in the $(QQQ)$ direction would be indicative of a noticeable force between second like-neighbors, (which is likely to exist), we cannot be sure that it is real for that reason. An indication of second like-neighbor interaction is not surprising, as a least-squares analysis of the data[10] themselves has already suggested strong interactions between neighbors out to fourth and possibly weak ones out to seventh. For the points (001), (011), (111) we have (subject to errors of nearly 0.05) values of $\Sigma$ of 0.19, 0.29, and 0.26. Analysis in the manner of Table II of Sec. 2 then gives 1.24, 0.79, and $-0.08$ respectively for $28\beta_1$, $28\beta_2$, and $28\beta_3$. This may be a confirmation of the authors contention[10] that forces

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[10] G. Gilat and G. Dolling, Phys. Rev. **138**, A1053 (1965).

of and beyond third like-neighbors (fifth neighbors) are small. More detailed analysis must await complete dispersion data for more points in reciprocal space.

## 4. WHITE TIN

White tin, or β-Sn, can be most easily described in terms of a tetragonal unit cell with four atoms in each, located at the points (000), $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},0,\frac{1}{4})$, $(0,\frac{1}{2},\frac{3}{4})$; for our purposes however we must use the primitive "body-centered tetragonal cell" of half that volume, shaped as the body centered cubic cell (Fig. 5 of Ref. 2) but with the *c* axis shorter than the other two, and with two atoms in it.[11,12] That is, it consists of two interpenetrating sets of body centered tetragonal lattices. "Like" atoms for our purposes are those that, in the first cited scheme, are in positions (000) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; since the *c* axis is much shorter than the *a* axis, the first like-neighbor of (000) is located at positions $(00\pm1)$ and those located at $(\pm\frac{1}{2}\pm\frac{1}{2}\pm\frac{1}{2})$ are second like-neighbors. (If the *c* axis were equal in length to the *a* axis, the situation would be reversed.) The contributions to the trace from first and second like-neighbors are,

$$\psi^{(1)}=1-\cos 2Q_3\,,$$
$$\psi^{(2)}=1-\cos Q_1\cos Q_2\cos Q_3\,,$$

(with $Q_i=\varphi_i|\varphi_{i\max}$). In the (00*Q*) direction (direction of the *c* axis), these two functions take on the form

$$\psi^{(1)}=1-\cos 2Q_3\,,$$
$$\psi^{(2)}=1-\cos Q_3\,;$$

these functions are illustrated respectively in Fig. 1 as $\psi_{\mathrm{FCC}}^{(2)}$ and $\psi_{\mathrm{SC}}^{(1)}$ in the (*Q*00) direction, respectively. The function Σ, computed from the neutron-scattering data[13] and shown in Fig. 4 clearly shows the effects of both forces. Since $\psi^{(1)}$ goes to 0 at (001), the value of Σ at that point, 0.24, is a measure of the coeffient of $\psi^{(2)}$, and since this implies that $\psi^{(2)}=0.12$ at (0,0,0.5), the value of Σ there decreased by 0.12, or $0.60-0.12=0.48$ is a measure of the coefficient of $\psi^{(1)}$. [Here we have written 0.6 for Σ(0.5) even though Fig. 4 shows 0.5 there because an anomaly clearly exists at that point.] That anomaly, deriving from the LO branch, has been interpreted as a Kohn anomaly[13] with some hesitancy due to the somewhat uncertain boundary of the Fermi surface. In the case of the function Σ, it is not even certain that it should appear at all; this is because the experimental error in the transverse optic (TO) branch, together with the large value of ω(TO) in this material, produces a possible error in the squared quantity $\Sigma\omega^2$ that may be larger than the dip itself. Although interactions between both first and second like-neighbors may be considered to have been demonstrated even by the failry crude data shown in Fig. 4, more detailed and less uncertain data will be required before more distant forces will be capable of being investigated.

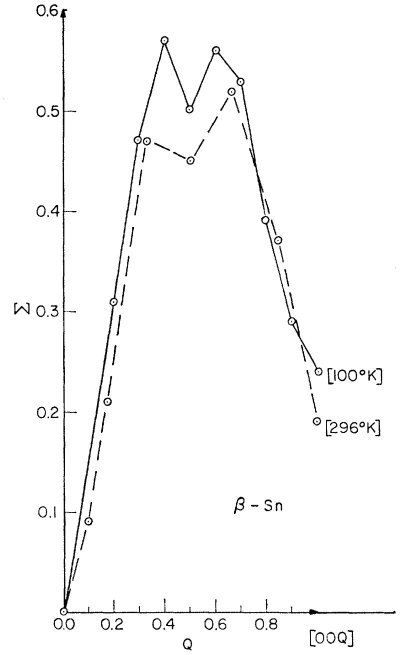

FIG. 4. Σ for white tin.

## 5. FACE-CENTERED CUBIC METALS

For our purposes, we are again dealing with a simple cubic lattice. As pointed out earlier, this now contains four atoms per unit cell, and therefore in order to compute Σ for any point (*abc*) one requires all the phonons at this as well as three other points. It is only for few substances that such complete data are available at a number of points sufficient to draw detailed conclusions (Fig. 5). The work on lead[14] has already been analyzed[2] and shown to imply strong forces through at least third like-neighbors. The results for nickel,[15] also shown in Fig. 1, provide a considerable contrast; Σ is very small throughout and may indeed be 0 everywhere (within the experimental error). Thus, nonelectromagnetic forces may be absent even between first like neighbors (which is to say, second neighbors—see Fig. 5). In analyzing their results by the method of least squares, the authors[15] have fitted their data well by a scheme involving fourth neighbors, or fifth neighbors in an axially symmetric model, with more than nine independent force constants. While our Fig. 1 does not exclude the possibility that many independent force

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[11] R. W. G. Wyckoff, *Crystal Structure*, (Interscience Publishers, Inc., New York, 1963), 2nd ed., Vol. 1, p. 29.

[12] For a pictorial representation, see F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 5.

[13] J. M. Rowe, B. N. Brockhouse, and E. C. Svensson, Phys. Rev. Letters **14**, 554 (1965).

[14] B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. **128**, 1099 (1962).

[15] R. J. Birgeneau, J. Cordes, G. Dolling, and A. D. B. Woods, Phys. Rev. **136**, A1359 (1964).

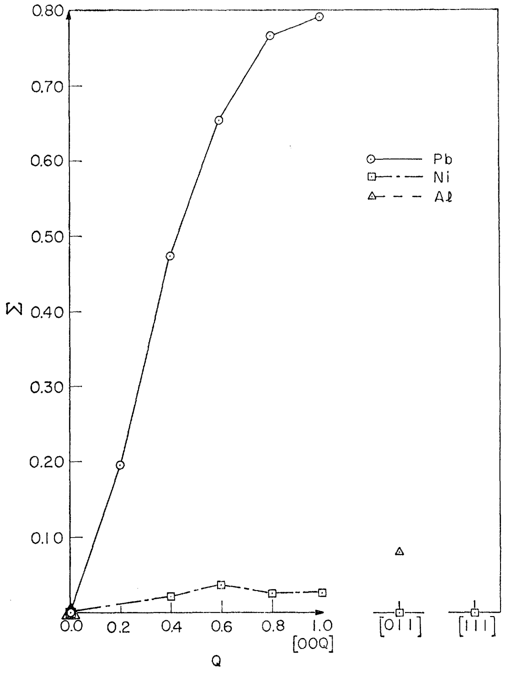

FIG. 5. Σ for some face-centered cubic metals.

constants may have physical significance, it does suggest that a much smaller number of independent forces, but electromagnetic in nature, may provide a better physical understanding.

Data for aluminum[16] are available in detail, but only in two directions; we were therefore able to compute Σ for only one point in addition to the origin.

## 6. DIAMOND STRUCTURE

In the past three years, neutron scattering data on GaAs has been presented and analyzed[17] and the existing data on Ge,[18] Si,[19,20] and Diamond[21,22] have been refined. Our results for Σ are shown in Fig. 6.

It has been previously noted[2] that Σ is 0 throughout for Si and Ge, but significantly different from 0 for diamond. It was concluded that in diamond, but not in silicon and germanium, strong nonelectromagnetic second neighbor forces were present, and the conclusion that diamond is therefore not homologous to the other two elements seems now generally accepted.[22] The new results Yarnell *et al.* obtained by neutron scattering in essence confirm the dispersion curves that Hardy and Smith obtained earlier from less direct examination of optical data; only the polarization has been shown to have been incorrectly assigned near the zone boundary in the [100] direction; this results in a reduction of the value of Σ (since in that direction the transverse, not the longitudinal, frequency is degenerate). The results remain consistent, within experimental error, with a second-neighbor force, as is shown by comparison with Fig. 1. The new data on Si[20] on the other hand, confirms and, on account of their greater accuracy and coverage of all three main symmetry directions, reinforces the belief that no such nonelectromagnetic second-neighbor force exist here. Inclusion of such a force for the purpose of improving earlier models for Si, as has been suggested,[23] would therefore not be physically realistic, and present results suggest that improvement of the already quite involved models[20] must be sought in further long-range electromagnetic forces. The theory of the vibrations of semiconductors of this structure has been studied in great detail, with forces through 6th neighbors, by Herman[24] for the point-ion model, and by Cochran for the shell model.[25] Herman concluded that no good fit can be obtained without going beyond fourth neighbors. The absence of any indication of such forces in the form of Σ suggests the need for consideration of long-range electromagnetic force for a realistic description.

For GaAs, on the other hand, overlap, (i.e., non-electromagnetic) second-neighbor forces are seen to be essential, as was indeed realized[17] in the model developed by the experimenters, who have added overlap forces

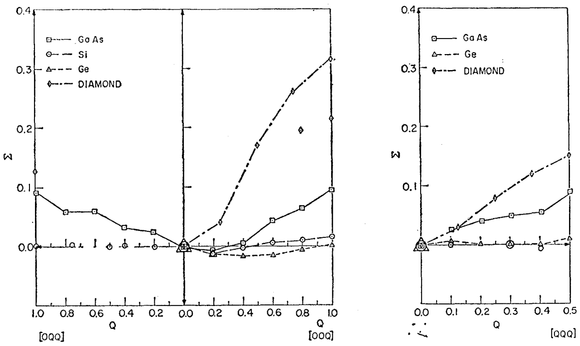

FIG. 6. Σ for some semiconductors of the diamond structure. For diamond, the connected points are derived from the optical data of Hardy and Smith (Ref. 21), since the recent neutron data of Wenzel, Warren, and Yarnell (Ref. 22) give the frequency of *all* the branches which are needed for computing Σ, at only four points. Two of these are shown at (0,0,0.8) and (001), two others in the (*QQQ*) direction fall very close to the curve shown.

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[16] J. L. Yarnell, J. L. Warren, and S. H. Koenig, in Ref. 1, p. 57.

[17] G. Dolling and J. L. T. Waugh, Ref. 1, p. 19. See also J. L. T. Waugh and G. Dolling, Phys. Rev. **132**, 2410 (1963).

[18] B. N. Brockhouse and P. K. Y. Iyengar, Phys. Rev. **111**, 747 (1958).

[19] B. N. Brockhouse, Phys. Rev. Letters **3**, 256 (1959).

[20] G. Dolling, in *Proceedings of the Chalk River Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), p. 40.

[21] J. R. Hardy and S. D. Smith, Phil. Mag. **6**, 1163 (1961).

[22] J. L. Warren, R. G. Wenzel, and T. L. Yarnell, *Proceedings of the Symposium on Inelastic Scattering of Neutrons, Bombay, 1964* (International Atomic Energy Agency, Vienna, 1965), Vol. 1, p. 361; see also J. L. Yarnell, J. L. Warren, and R. G. Wenzel, Phys. Rev. Letters **13**, 13 (1964).

[23] Reference 20, conclusion.

[24] F. Herman, J. Phys. Chem. Solids **8**, 405 (1959).

[25] W. Cochran, Proc. Roy. Soc. (London) **A253**, 260 (1959).

between second as well as first neighbors to their "dipole approximation" (modified shell-model) calculation. The fit of the GaAs results in Fig. 6 to the effect that second-neighbor forces are shown to produce in Fig. 1 are not perfect, to be sure, but deviations may be due to experimental uncertainties. The model used[17] is quite elaborate and contains many parameters, yet does not fully satisfy the proposers in representing the data. It would therefore be very valuable if experimental error in obtaining dispersion relations could be reduced to the point where one could decide unambiguously whether our $\Sigma$ does, or does not, fit the curve of Fig. 1 for second-neighbor forces; this would enable one to decide whether in further refining the "dipole-approximation" model, one should introduce third-nearest-neighbor overlap interaction, or long-range electromagnetic (for example, "quadrupole") forces.

## 7. CLOSE-PACKED HEXAGONAL METALS

The close-packed hexagonal lattice may be visualized as follows: Place a number of spheres of equal radius as closely together as possible on a table top. The well-know arrangement of linked equilateral triangles (or face-centered hexagons) results. Call this plane *A*. On top of this, as closely as possible, place an identical plane of spheres. There will be two optimal positions for this new plane, each slightly displaced from that of the plane below it. Call this second plane *B*. A third identical plane can again be put on top in 2 ways-either in position *A* or in a third position which we can call *C*. A lattice consisting of planes *ABAB*··· is called close packed hexagonal, one consisting of planes *ABCABC*··· is called close-packed cubic or face-centered cubic (that the close-packed cubic lattice is indeed the face-centered cubic lattice, which many people are accustomed to viewing from a different angle, is a fact, though perhaps not an obvious one). Thus even though the face-centered cubic lattice has only one atom per unit cell, the close-packed hexagonal one has two (viz., atoms *A* and atoms *B*); each *A* atom has twelve nearest neighbors, six of which are *A* and six *B*—a situation different from earlier considered cases in which nearest neighbors of any given atom were always different from it. We have here, therefore, one case where the sum rule can give information about nearest neighbor interactions also. However, on account of the lattice anisotropy it is not at all obvious that the interaction between nearest neighbor *AA* pairs is the same as that between nearest neighbor *AB* pairs. In addition we should note that in real crystals, the ratio $c/a$ between distances between second like-neighbors and nearest neighbors may differ from the value $(2\sqrt{6})/3 \cong 1.633$ (if one wants to retain the "close-packed" language, one can think of close-packed spheroids rather than spheres); for zinc and beryllium, for example, these ratios are 1.856 and 1.567.[26]

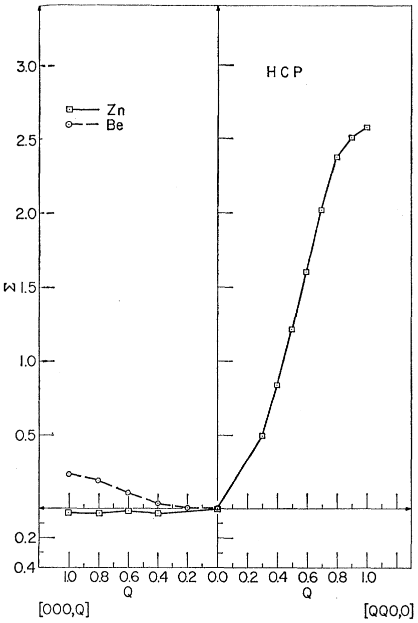

FIG. 7. $\Sigma$ for some close-packed hexagonal metals.

It is customary in describing hexagonal crystals to note directions by four rather than three indices $(\xi\eta\zeta,\rho)$. The last one denotes the special, or "$c$" direction, the others the three equivalent axes parallel to a line of nearest neighbors in the *A* plane described above. Our results for contributions to the trace are as follows: for interaction between nearest like neighbors

$$\psi_{\text{HEX}}^{(1)} = 1 - \cos 2Q + 2[1 - \cos Q_1 \cos Q_2]$$

for interaction between second like-neighbors

$$\psi_{\text{HEX}}^{(2)} = 1 - \cos Q_3$$

and for third like-neighbors

$$\psi_{\text{HEX}}^{(3)} = 1 - \cos 2Q_2 + 2[1 - \cos 3Q_1 \cos Q_2].$$

Here the $Q$'s are Cartesian coordinates chosen so that $Q_3$ coincides with the special or $c$ axis, $[Q_1 = Q_2 = 0$ thus denotes the (000,1) direction$]$, $Q_1$ coincides with a line of nearest neighbors perpendicular to the $c$ axes $[Q_3 = Q_2 = 0$ thus coincides with the (100,0) direction$]$, and $k_2$ is perpendicular to both $[Q_1 = Q_3 = 0$ is thus a $(1\bar{1}0,0)$ direction$]$. Fig. 1[(f), (g), (h)] shows these interacting atoms and the forms that the functions $\psi_{\text{HEX}}$ take in these special directions.

As for the available data (Fig. 7), interactions between second neighbors may be inferred for Be,[27] with possible further interactions affecting the $k_3$ direction hidden in the uncertainty of the data, and no data available for the "in-plane" directions. Somewhat more

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[26] Reference 11, p. 11.

[27] R. E. Schmunk, R. M. Brugger, P. D. Randolph, and K. A. Strong, Phys. Rev. **128**, 562 (1962).

information can be read from the zinc data[28]: the constancy along the direction (000,1) suggests strongly that interactions between other than first neighbors are absent in directions out of the basal planes; by contrast, the in-plane interactions, as manifested by the magnitude of the curve in the (110,0) direction, must be quite strong. This agrees with the comment of Borgonovi *et al.* on the strong anisotropy and easy cleavage perpendicular to the basal planes. In the $\Sigma$ curve, the nearest-neighbor interaction $\psi^{(1)}$ is clearly dominant, although the effects of third like-neighbors $\psi^{(3)}$ is noticeable in the increase of $\Sigma$ above the simple 1-cos$Q$ curve at the higher $Q$ values. This effect appears to be larger than the experimental error and indicates that interactions through "fourth neighbors," as tried by Borgonovi,[28] following Collins,[29] would not suffice for a complete description (the third like-neighbors that give rise to our function $\psi^{(3)}$ would be "fifth neighbors" in the scheme of Collins). Measurements in the (100,0) direction should be particularly interesting, in that the rather unusual-looking curve of Fig. 1(f) should provide the dominating feature, providing an opportunity for more detailed analysis of the relative strengths of the in-plane forces.

## 8. SUMMARY

A scheme which enables one to see the effects of some interatomic forces from experimental dispersion relations in a simple additive way has been used to study data available for sixteen solids, mostly metallic elements. Considerable differences are found among elements even of the same crystallographic structure. Analysis is restricted by the need to have the energies of *all* the phonons at more than one point in reciprocal space, as well as by experimental error. In a number of cases apparent absence of "overlap" forces between close neighbors support the presence of long-range electromagnetic ones.

## ACKNOWLEDGMENT

It is a pleasure to thank Dr. John L. Yarnell for useful correspondence.

## APPENDIX

Table III indicates the errors probably inherent in each case in the quantity $\Sigma$ shown in Figs. 2–7. The number shown under $\Delta\Sigma$ for any substance is the largest value of $2\sum_i \omega_i \Delta\omega_i$ for any point; the largest value $\Sigma_{\max}$ of $\Sigma$ itself for that substance is also shown. When $\Delta\Sigma$ is of the same magnitude as $\Sigma_{\max}$, no substantial affirmative statements can, of course, be made in our analysis, but the inference that $\Sigma$ is zero throughout within experimental error can nonetheless be a significant conclusion, particularly if $\Delta\Sigma$ is small. $\Delta\omega$ contains contributions from various sources: where the experimenters give $\omega$ in a table that includes estimated errors for each point, these estimated errors were the ones we used for $\Delta\omega$; when such a table was not available, we had to rely on verbal statements in the paper (e.g. ". . . estimated errors of 1 or 2% . . .") and had to also include possible errors of our own in reading points off a published figure.

TABLE III. Errors in $\Sigma$ for various materials.

| | $\Delta\Sigma$ | $\Sigma_{\max}$ |
|---|---|---|
| Na | 0.03 | 0.3 |
| Nb | 0.04 | 1.1 |
| Ta | 0.05 | 0.13 |
| W | 0.06 | 1.0 |
| Mo | 0.13 | 1.5 |
| $\beta$-brass | 0.05 | 0.3 |
| $\beta$-Sn | 0.2 | 0.6 |
| Pb | 0.06 | 0.8 |
| Ni | 0.05 | 0.04 |
| Al | 0.06 | 0.005 |
| C | 0.06 | 0.16 |
| Si | 0.06 | 0.015 |
| Ge | 0.1 | 0.04 |
| GaAs | 0.02 | 0.1 |
| Be | 0.1 | 0.23 |
| Zn | 0.1 | 2.5 |

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[28] G. Borgonovi, G. Caglioti, and J. J. Antal, Phys. Rev. **132**, 683 (1963).

[29] M. F. Collins, Proc. Phys. Soc. (London) **80**, 362 (1962).