Sum Rule for Lattice Vibrations; Application to Forces in Diamond Structures

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It is shown that in a crystal of any number n atoms per unit cell many interatomic forces—to wit, all forces which are electrostatic in nature (Coulomb, dipole, $\cdots$, multipole), and all forces which act only between unlike atoms—contribute only constant terms to the trace of the dynamical matrix. Therefore, the sum $\Sigma_i \omega_i^2(q)$ over the $3n$ squared frequencies when the wave vector is q is, in fact, independent of q in crystals in which all forces fall into one of these classes; conversely, if experiment shows that sum to actually be a function of q, then forces which fall into neither class—to wit, forces, not electrostatic in nature, between like atoms—must be present. Analysis of data for germanium and diamond suggests that such forces are present in the latter, but, within experimental uncertainty, absent in the former.

THE sum rule for lattice vibrations

$$\sum_i \omega_i^2(\mathbf{q}) = \text{const}, \tag{1}$$

where $\omega_i(\mathbf{q})$ is the frequency in the ith branch when the wave vector is q, has been derived by Brout.[1] The rule was said to be valid for diatomic ionic crystals whose constituent ions interact only by two forces—Coulomb forces between all ions and repulsive interaction between nearest neighbors alone—and to be useful as a check on numerical computation. The purpose of this note is to point out that (1) can (with simple modifications in some cases and no modifications at all in other cases) also be applied to more general force models and to non-ionic crystals, and may also be useful for extracting information about forces acting in a crystal from experimental measurements of the frequencies. As an example, data for the diamond structure are analyzed.

The significant fact about the sum rule (1) is that its right-hand side is independent of q. The way in which the sum rule is obtained can be qualitatively summarized as follows. The sum of the eigenvalues of any matrix is equal to the trace of that matrix, and the sum of the squared frequencies of a vibrating lattice is, therefore, equal to the trace of the dynamical matrix. The 36 elements of the dynamical matrix of a (3-dimensional) diatomic lattice with two atoms per unit cell can be labeled $D_{\alpha\beta}{}^{ij}$, where $\alpha, \beta = 1, 2, 3$ denote the three Cartesian directions and $i, j = 1, 2$ the two atoms in a cell. The q-dependent part of any interaction between two unlike atoms appears[2] in elements $D_{\alpha\beta}{}^{12}$ or $D_{\alpha\beta}{}^{21}$, and the diagonal elements $D_{\alpha\alpha}{}^{11}$ and $D_{\alpha\alpha}{}^{22}$ (and, hence, the trace) therefore contain no q-dependent terms referring to interaction between unlike atoms and thus, in particular, no q-dependent terms referring to

interaction between nearest neighbors (which are necessarily unlike atoms). As to Coulomb forces, q-dependent terms due to them do appear in the diagonal terms, but their sum vanishes when the trace is formed. To see this, consider the contributions to $D_{\alpha\alpha}{}^{ii}$ from one particular atom of kind i. It is the restoring force in the α direction that this atom, when displaced in the α direction, experiences on account of the i atom at rest at the origin. The contribution is, therefore, proportional to the second derivative with respect to x_α of the potential between the special i atom we are considering and the one at the origin; and the sum of this over the three α's, which appears in the trace, will vanish because electrostatic potentials obey Laplace's equation.[3] It follows from those two separate arguments that neither nearest-neighbor forces nor Coulomb forces contribute q-dependent terms to the trace; i.e., that the left-hand side of (1) is, in fact, a constant.

When the derivation of the sum rule (1) is presented as in the preceding paragraph, three extensions of its validity suggest themselves. First, and perhaps trivially, it is the q-dependence contributed by the Coulomb forces of *each atom* (and not only of the sum of them taken over all the atoms in the entire lattice) to the trace that vanishes; hence, the rule is valid for all sorts of lattices, regardless of their structure, and is not confined to the NaCl type or other simple substances, nor even to diatomic lattices (i will run from 1 to $3n$ in an n-atomic crystal). Second, and more importantly, the reasoning involving Coulomb forces goes through just as well for any other electrostatic force, being based only on obedience to Laplace's equation; therefore, the validity of the sum rule extends beyond purely Coulomb forces to multipole forces of all kinds, and its interest therefore extends also to valence or other non-ionic crystals in which Coulomb forces are absent but higher multipole forces are important.[4] Third, the argument regarding the absence of contributions from nearest

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[1] R. Brout, Phys. Rev. 113, 43 (1959). The value of the constant is given in this paper, but is not of interest to us here.
[2] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), p. 68. By "like" ("unlike") atoms we mean atoms located at equivalent (non-equivalent) sites of the unit cell.

[3] G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII p. 247; M. Blackman, Proc. Roy. Soc. (London) A181, 58 (1942).
[4] See, e.g., M. Lax, Phys. Rev. Letters 1, 133 (1958); W. Cochran, Proc. Roy. Soc. (London) A253, 260 (1959); F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. VII, X.
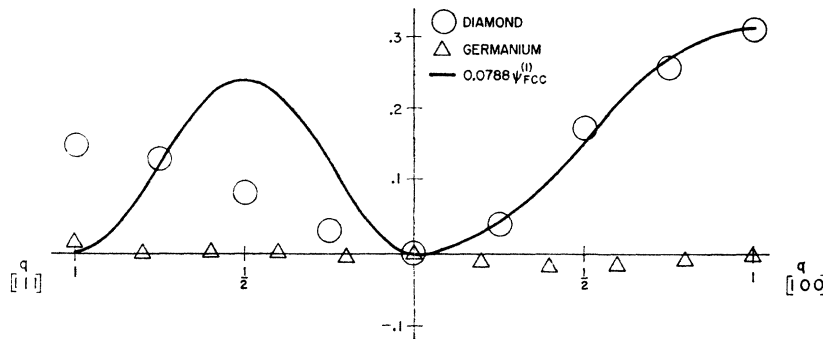
FIG. 1. The q-dependent part of $\sum_i \omega_i{}^2(\mathbf{q})$. Curve—second-neighbor interaction in the diamond lattice-theoretical. Circles—diamond (Hardy and Smith, reference 9). Triangles—germanium (Brockhouse and Iyengar, reference 8).

neighbors "repulsive" (more accurately we should call them "short-range" or, for our purposes, "nonelectrostatic") forces applies not only to interaction between first neighbors, but to all interactions between all unlike atoms in the lattice regardless of their distance, for only interaction between like atoms contributes q-dependent terms to the trace.

Summarizing the preceding paragraph, we may say that (1) will apply to all crystals all of whose atomic interactions fall into at least one of these two classes: (1) electrostatic, (i.e., Coulomb, dipole, $\cdots$, multipole); and (2) interaction between unlike atoms. For brevity, let us call forces which fall into either of these classes "trace-constant" forces, and those which fall into neither of these classes "trace-variable" forces. (A trace-variable force is, then, a force that is not electrostatic in nature[5] and acts between like atoms). If, then, an experimental measurement reveals that $\sum_i \omega_i{}^2(\mathbf{q})$ depends on q, then this dependence may be attributed to the presence of trace-variable forces. Thus, the sum rule provides a direct and simple method for checking on the presence of trace-variable forces—one computes $\sum_i \omega_i{}^2(\mathbf{q})$ from experimental data and sees if (1) is obeyed; this is a method which is not only simpler and demanding of less data, but also more sensitive than analysis of the entire dispersion relation would be, for in a scheme in which the effects of trace-constant forces do not vanish rigorously, they are likely to be strong enough to mask the effects of the (presumably weaker) trace-variable ones.

Let us put this on a more quantitative basis and work out some examples. To have a sum rule that applies to crystals with trace-variable forces we must replace (1) by

$$\sum_i \omega_i{}^2(\mathbf{q}) = \text{const} + \sum_n \beta_n \psi^{(n)}(\mathbf{q}), \qquad (2)$$

where $\psi^{(n)}$ is the contribution to the trace of the nth (labeled arbitrarily) trace-variable force and the β_n are constants independent of q and related to the strength

of the force. Let us, e.g., consider central forces between second neighbors. [This might well be suspected to be the dominant trace-variable force in some crystals, for short range interaction between first and third neighbors will fall into class (2) for most crystal structures while "short-range" interaction between fourth and more distant neighbors is likely to be extremely weak, and "long range" interactions are likely to fall into class (1).] Quantitatively, the effect of such second-neighbor forces on the trace must be separately calculated for each lattice, but this is easy to do for several important ones. In the CsCl lattice, the second neighbors form a simple cubic lattice, so that the contribution to the right-hand side of (1) is[6] $\psi_{\text{bcc}}{}^{(1)} = 3 - (C_1 + C_2 + C_3)$, where $C_k = \cos\pi q_k$ and in both the NaCl lattice and the diamond lattice, the second neighbors form a face-centered cubic lattice, so that the contributions to the right-hand side of (1) is[7] $\psi_{\text{fcc}}{}^{(1)} = 3 - (C_1 C_2 + C_2 C_3 + C_3 C_1)$. The contribution $\psi^{(2)}(q)$ from central forces between fourth neighbors can also be read off these formulas[6,7] $\psi_{\text{bcc}}{}^{(2)} = \psi_{\text{fcc}}{}^{(1)}$ and $\psi_{\text{fcc}}{}^{(2)} = 3 - (C_1{}^2 + C_2{}^2 + C_3{}^2)$.

We have attempted to carry out this analysis for germanium and diamond, using the phonon spectra derived, respectively, by Brockhouse and Iyengar[8] from neutron scattering and by Hardy and Smith[9] from infrared absorption measurements. Our results are shown in Fig. 1. In each case we used data of $\omega_i(\mathbf{q})$ in the [100] and [111] directions (the only directions in which they are given), computed $\sum_i{}^6 \omega_i{}^2(\mathbf{q})$ for several q values, subtracted the constant $\sum_i{}^6 \omega_i{}^2(0)$, divided by the same constant and plotted the result. In terms of Eq. (2), what is plotted is $\sum_n \beta_n \psi^{(n)}(\mathbf{q})/\sum_i \omega_i{}^2(0)$. (Division by $\sum_i \omega_i{}^2(0)$ was a form of normalization to make the data for the two substances roughly comparable with each other and with the experimental uncertainty in each case.) The results for germanium are seen to be strikingly different from those for diamond: $\sum_n \beta_n \psi^{(n)}$ seems to be essentially zero for

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[5] Although the meaning of "electrostatic" interaction may be intuitively clear to the reader, it is not easy to give a rigorous definition, since, in the final analysis, all atomic forces are presumably dependent on electric charges of the constituents. We may perhaps define as nonelectrostatic, those interactions that cannot be correctly described by the *classical* behavior of some multipole distribution.

[6] See, e.g., H. B. Rosenstock, Phys. Rev. **97**, 290 (1955), Eq. (3).
[7] Footnote 6, Eq. (5).
[8] B. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958), Fig. 5.
[9] J. R. Hardy and S. D. Smith, Phil. Mag. **6**, 1163 (1961), Fig. 2.

Ge, but to be a definite and apparently monotonically increasing function of q in both directions for diamond.

In interpreting this result, we must remember that the original data are subject to considerable experimental uncertainty—about 12% for Ge and 9% for diamond are the maximum probable deviations estimated by the experimenters[8–10] themselves. The slight scatter about zero of the points for Ge in Fig. 1 is, therefore, physically not significant—we may conclude that trace-variable forces are absent in Ge within the limits of present-day experimental precision. By contrast, the deviation from zero of the points for

diamond exceeds the experimental uncertainty by a considerable margin, and indicates that trace-variable forces are active in that crystal; their contribution to the trace seems roughly describable by a function $1-\cos\pi q$ in the [111] direction and by $2(1-\cos\pi q)$ in the [100] direction. The curve which has been drawn into Fig. 1 is the function const. $\times \psi_{\text{foo}}^{(1)}$, which the points should follow if the only trace-variable force in the crystal were a central interaction between second neighbors; the fact to notice is that along [111] they do not do this, showing that central second-neighbor interaction cannot explain our results. The reader may verify, by plotting $\psi_{\text{foo}}^{(2)}$, that fourth-neighbor central interaction would not work either. It seems likely, therefore, that a trace-variable force in diamond is a long-range, nonelectrostatic one, or a short-range one with a noncentral component.

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[10] In addition, we should quote Hardy and Smith's (reference 9) description of their own results as "somewhat tentative"—a necessary consequence of the rather involved analysis required to translate infrared absorption into phonon energies. Analysis of neutron scattering is comparatively straightforward.

Temperature Dependence of Nuclear Magnetic Resonance of Fe^{57} in Magnetite

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A report is made of an attempt to fit the temperature dependence of the observed nuclear magnetic resonance (NMR) frequencies for the two sublattices in magnetite to the measured temperature dependence of the magnetization. It is shown that when the microwave g_{eff} values as reported in the literature are used in this calculation, no fit between the NMR experiment and the moment measurement is obtained. If a $g_{\text{eff}} = 2$ is assumed, however, the data may be brought into good agreement.

THE temperature dependence of the nuclear magnetic resonance (NMR) frequency for Fe^{3+} ions has been shown to be a good measure of the sublattice magnetization in many ferrimagnetic oxides (e.g., YIG[1–4] GdIG,[2–4] and $Li_{0.5}Fe_{2.5}O_4$ [5]). In this paper a report is made of the temperature variation of the sublattice magnetization in Fe_3O_4 where both Fe^{3+} and Fe^{2+} ions are present. Magnetite in the cubic phase, above 118°K, is an inverse spinel with all tetrahedral sites occupied by Fe^{3+} ions, and with Fe^{2+} and Fe^{3+} ions occurring in equal numbers in octahedral sites. Verwey[6] has proposed that there is a rapid interchange of electrons among the iron ions in octahedral symmetry to explain the high conductivity of cubic magnetite. The NMR data are analyzed in terms of this model and in terms of the published values for the electronic g

factor as measured by microwave means. It is shown that the Verwey model holds for this analysis but that the microwave g factor does not indicate an unquenched orbital moment.

Some features of the nuclear resonance of Fe^{57} in magnetite have been published elsewhere and need only be briefly described.[7] The signals come from the bulk of the material rather than domain walls as in the case of the magnetic metals. The resonance from the Fe^{3+} ions in tetrahedral symmetry is a sharp single line. That from octahedral ions is a very broad distribution of resonances, the distribution being due prinicpally to a dipolar magnetic field acting on these ions due to the rest of the magnetic lattice. The shape of the resonance distribution from octahedral sites unambiguously shows that it is from octahedrally located ions and that these ions are in the bulk of the material. Figure 1 shows the observed frequencies of the tetrahedral resonance, the distribution of the octahedral resonance and the magnetic moment (as measured by a force balance) versus temperature. The NMR data were taken

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[2] LeDang Khoi and M. Buyle-Bodin, Compt. Rend. **253**, 2514 (1961).

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[5] H. Yasuoka, A. Hirai, M. Matssura, and T. Hashi, J. Phys. Soc. Japan **17**, (1962).

[6] E. J. W. Verwey and P. W. Haaijman, Physica **8**, (1941).

[7] E. L. Boyd and J. C. Slonczewski, J. Appl. Phys. **33**, 3 (1962).