Theory of Phonon Dispersion Curves in Silicon Carbide Polytypes*

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A theory is presented to explain fine-structure-dependent details in the phonon spectra obtained by Raman scattering measurements on silicon carbide polytypes, using the method of interactions between planes or atoms. Doublets of small energy splitting represent discontinuities in the dispersion curves within the large zone and are analogous to the band gaps appearing in nearly free-electron band structures. They give a measure of the range of interplanar interactions and of small energy differences between polytypes. These results are used to comment qualitatively on the relative stability of silicon carbide polytypes. The theory also accounts satisfactorily for the infrared (ir) strengths of the weak modes observed in these structures.

I. INTRODUCTION

RECENTLY, Feldman *et al.*[1] have measured phonon dispersion curves along the c axis in silicon carbide, using Raman scattering measurements, by exploiting the existence of polytypes of this substance. Their results showed that, to a good approximation, the phonon frequencies are independent of polytype; that is, they do not depend greatly on the variations in stacking sequence which distinguish these different structures. Nevertheless, there are features in their spectra which do depend on the detailed stacking sequence. The most striking of these are the small doublet splittings which occur at points inside the large zone[1] and may be ascribed to the breaking of translation symmetry in a sense explained below. Another one is the variation of one of the optic modes at zero wave vector (TO_2) with percentage hexagonal stacking.[1] These features must arise from small energy differences between polytypes, the sort of energy differences which have been discussed in the problem of calculating stacking-fault energies[2] and in the rare-earth metals.[3] Their study should provide a means of investigating such small energy differences, and of accounting for and correlating some of the other structure-dependent quantities associated with phonons in these polytypes (e.g., the weak ir strengths[4]). This may also shed some light on the thermodynamic stability and origin of these structures. Although then the main purpose of the Raman scattering experiments was to deduce the structure-independent part of the phonon dispersion curves, we believe that the small structure-dependent parts are also worth investigating and present here a theory which accounts for these features, in particular the doublet splittings within the large zone. We use the method of interactions between planes of atoms which has been used to study stacking-fault energies,[2] the stability and axial ratio of rare-earth metals,[3] and is, in general, useful for analyzing phonon dispersion curves along directions of high symmetry in q space.

Silicon carbide polytype structures are built up by stacking close-packed planes of carbon or silicon atoms along the c axis in certain stacking sequences (ABC$\cdots$, etc.).[5] Figure 1 shows the perpendicular spacing between these planes along the c axis for the polytype $3C$ (zinc-blende or sphalerite structure). The perpendicular spacings for the other polytypes should be the same, apart from small deviations or lattice distortions,[6] but the transverse stacking positions which we have not indicated in Fig. 1 depend on the particular stacking sequence. In terms of the "h k" notation,[7] the pairs of silicon and carbon planes separated $\frac{3}{4}b$ are in either hexagonal h or cubic k stacking positions with respect to neighboring pairs. If the force constant between two planes depended only on their relative separation, and not on their absolute position in the lattice, then we should have the same translation symmetry in our problem as for the $3C$ polytype, and the phonon spectrum should be smooth inside the large zone. In general, however, this translation symmetry is broken and our theory shows that the doublet splittings inside the large zone are determined by the magnitude of the symmetry breaking of the force constants. Indeed, the doublet splittings are analogous to the band gaps which appear in the smooth free-electron parabola on introducing the perturbing lattice potential which breaks translation symmetry in the electron case.

Some of the assumptions and approximations we have made in our analysis should be mentioned here. First, the problem of calculating the small lattice distortions or the deviations from the regular interplanar spacing ($\frac{1}{4}b,\frac{3}{4}b$),[6] which must in part contribute to the breaking of translation symmetry for the force constants, has not been considered in detail. We believe that the splittings $\Delta(\omega^2)$ in the optical bands, which are rather larger than those in the acoustic bands, are largely due to a small variation in the separation of the nearest pairs of planes

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[1] D. W. Feldman, James H. Parker, Jr., W. J. Choyke, and Lyle Patrick, Phys. Rev. **173**, 787 (1968).

[2] A. Blandin, J. Friedel, and G. Saada, J. Phys. Radium **C3**, 128 (1967).

[3] C. H. Hodges, Acta. Met. **15**, 1787 (1967).

[4] Lyle Patrick, Phys. Rev. **167**, 809 (1968).

[5] A. R. Verma and P. Krishan, in *Polymorphism and Polytypism in Crystals* (John Wiley & Sons, Inc., New York, 1966), Chap. 4.

[6] A. H. Gomes de Mesquita, Acta Cryst. **23**, 610 (1967).

[7] Reference 5, Chap. 5.

about the mean value of $\frac{1}{4}b$. Such variations or deviations from the regular or ideal spacing may also be studied using the method of interplanar interactions. However, the theory is not presented here, as there do not appear to be enough experimental data, either from lattice parameter measurements such as in Ref. 6 or from splittings in the optical branches,[1] to provide a convincing verification at present. This matter is still under investigation. The variation in the $\frac{1}{4}b$ spacing however has very little effect on the acoustic branches, and particularly on the TA branch, as we shall see below. We believe that for these branches, what effect the variation in lattice spacing has may be included in Eqs. (7) or (23), which give the breaking of translation symmetry. We shall therefore be chiefly concerned with the acoustic branches in what follows.

For the transverse branches the results of Feldman *et al.*[1] indicate a large separation in frequency between the optic and acoustic branches and this is presumably due to the fact that the transverse force constant between the planes separated $\frac{1}{4}b$ is much larger than all others. This means that for the TA branch such pairs of planes oscillate to a good approximation as rigid units. The second approximation which was made, therefore, is to neglect the relative motion of the silicon and carbon constituents of such double units. The data on splitting are by far the most complete for the TA branch and we shall once again restrict our attention to this branch in most of what follows. We label our rigid double units from left to right by the subscript j (see Fig. 1) and let U_j be the displacement from equilibrium of the jth such unit. Notice that these are not the pairs of planes in terms of which we previously considered polytype structures to be built up.

In Sec. II the theory is presented using the rigid-atom approximation and it predicts a correlation which should exist between the doublet splittings $\Delta(\omega^2)$ and certain structure factors characteristic of the h k polytype stacking sequence. A plot to verify this using the experimental data shows the theory presented in Sec. II to be in some way deficient. We manage, however, to use our analysis to subtract out the parts of the phonon spectra which are polytype-dependent to leave a dispersion curve which must be that of the $3C$ structure. The results are used to discuss qualitatively the small differences in free energy between different polytypes which may influence their relative stabilities. We discuss possible deficiencies in the theory in Sec. III and conclude that it is necessary to take the effects of polarizable atoms into account as is done in the "shell model."[8] It is apparently more important to take into consideration the relative motion of the atomic cores and shells than that of the silicon and carbon atoms in the double unit. A theory is presented that has been modified to take these effects into account, and it is shown that this now explains adequately the magnitudes of the doublet splittings. In Sec. IV we discuss the magnitudes of the weak ir modes[4] observed by Spitzer *et al.*[9] and Ellis and Moss.[10]

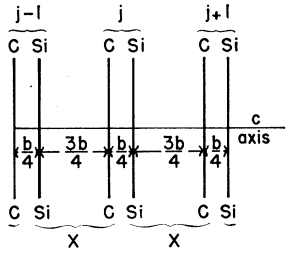

FIG. 1. Spacing of the carbon (C) and silicon (Si) planes along the c axis, showing the double units $j-1$, j, $j+1$, and also the pairs of planes marked x which govern the stacking sequence.

II. RIGID-ATOM MODEL

For phonons with wave vectors lying along the c axis which is either a triad or hexad axis, the dynamic matrix may be factorized in such a way that all TA displacements lie parallel to an arbitrary direction in the basal plane. The problem is thus reduced to that of a linear chain with scalar displacements. Let U_j be the scalar displacement of the jth rigid unit. The normal-mode equation may be written

$$M\omega^2 U_j=\sum_n K_{j,j+n}(U_j-U_{j+n})=\sum_n \Phi_{j,j+n}U_{j+n}, \quad (1)$$

where K are the interplanar force constants, Φ is the dynamic matrix, and M is the mass of one of the double units. If $K_{j,j+n}$ were independent of j, depending only on n, which is true for polytypes $3C$ and $2H$, the phonon curves would be smooth within the large zone. For other polytypes it happens that $K_{j,j+n}$ has a small j dependence, the reason for which we shall see shortly, and we say that translation symmetry is broken. We may then write

$$K_{j,j+n}=K(n)+\Delta K_{j,j+n}, \quad (2)$$

where ΔK contains the j-dependent part of K but is small. As a first approximation, Eq. (1) may be solved neglecting ΔK and as a result phonon frequencics

$$(\omega_q{}^0)^2=\frac{4}{M}\sum_{n>0} K(n)(\sin\tfrac{1}{2}qnb)^2, \quad (3)$$

with normal modes

$$U_j(q)=\mathfrak{N}^{-1/2}e^{iqjb}, \quad (4)$$

are obtained. The quantity $\mathfrak{N}$ is the number of units in the crystal, and q is the phonon wave vector along the c axis. We note that $\omega_q{}^0$ is smooth within the large zone and we interpret it as being the structure-independent part of the phonon spectrum.

[8] W. Cochran, Proc. Roy. Soc. (London) **A253**, 260 (1959); Phil. Mag. **4**, 1082 (1959).

[9] W. G. Spitzer, D. A. Kleinman, and D. Walsh, Phys. Rev. **113**, 127 (1959).

[10] B. Ellis and T. S. Moss, Proc. Roy. Soc. (London) **299**, 393 (1967).

TABLE I. Stacking sequence and values of S_l within one repeat interval r for the polytypes considered in Ref. 1, and the structure factor $S(2q)$ as a function of the reduced wave vector $x=qb/\pi$. We have trivially reordered some of the repeat intervals and choose the origins indicated by arrows to give real structure factors.

Polytype	4*H*	6*H*	15*R*	21*R*
"*h k*" sequence	*h k*	*k h k*	*k h k h k*	*k h k k k h k*
S_l	1 0	0 1 0	0 1 0 1 0	0 1 0 0 0 1 0
	↑	↑	↑	↑
r	2	3	5	7
$S(2q)$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{2}{5}\cos(2\pi x)$	$(2/7)\cos(4\pi x)$

Let us now introduce ΔK as a perturbation and evaluate matrix elements of the corresponding $\Delta\Phi$ between the normal modes given in Eq. (4). These matrix elements are given by

$$\langle q'|\Delta\Phi|q\rangle=\mathfrak{N}^{-1}\sum_{jn}e^{-iq'jb}\Delta\Phi_{j,j+n}e^{iq(j+n)b}$$

and may be shown to be equal to

$$\sum_{n>0}4(\sin\tfrac{1}{2}q'nb)(\sin\tfrac{1}{2}qnb)\Delta K(n,\,q-q'), \qquad (5)$$

where

$$\Delta K(n,\,q-q')=\mathfrak{N}^{-1}\sum_{l}^{\mathfrak{N}}(\Delta K_{l-n/2,l+n/2})e^{i(q-q')lb}. \qquad (6)$$

In Eq. (6), $l=j+n/2$ is summed over integers or half-integers according as n is even or odd.

The j or l dependence of the force constants arises because the interactions between planes must depend on the relative stacking positions of these planes. For example, the value of the force constant $K_{j,j+1}$ between adjacent double units centered at jb and $(j+1)b$ depends on whether the point midway between them at $(j+\frac{1}{2})n$ is a center of hexagonal or cubic stacking. If we were to use the so-called "pairwise force" model chiefly applicable in metals[2,11] the stacking dependence of $K_{j,j+1}$ would arise from the interaction between the Si and C planes separated by $\frac{1}{4}5b$, for this depends upon whether these planes are in "equivalent" (A—A, B—B, etc.) or "inequivalent" (A—B, B—C, etc.) stacking positions.[3]

The largest contribution to $K_{j,j+1}$, however, would arise from the interaction of Si and C planes separated by $\frac{3}{4}b$, and this would be independent of j, since these planes are always in "equivalent" stacking positions. The "pairwise" model shows therefore that we might expect the j-dependent part of $K_{j,j+1}$ to be smaller than j-independent part. As will become clear below, the experimental results show that the j-dependent part of $K_{j,j+1}$ is indeed very much smaller than the j-independent part. On the pairwise assumption, this would imply that the interplanar interactions are decreasing very rapidly with increasing plane separation, and would suggest we might neglect $K_{j,j+2}$ and other force constants altogether in our problem.

[11] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin Inc., New York, 1966).

In covalent semiconductors the pairwise model is no longer expected to be strictly valid[12] and so-called "many atom" forces may be important. However, such forces should be largest for neighboring atoms or planes and the conclusions drawn from the pairwise model above are still almost certainly valid in such solids. A further conclusion which may be drawn is that the force constant $K_{j,j+1}$ is virtually unaffected by the stacking positions of any atoms other than those belonging to the double planes j and $j+1$. We may therefore assume that $K_{j,j+1}$ depends only on whether the point $(j+\frac{1}{2})b$ is a center of hexagonal or cubic stacking. As a result we may write Eq. (2) as

$$K_{l-\frac{1}{2},l+\frac{1}{2}}=K_{\rm cub}+[K_{\rm hex}-K_{\rm cub}]S_l, \qquad (7)$$

understanding that in what follows we are only concerned with $n=1$. In this equation, $S_l=1$ if the point $lb=(j+\frac{1}{2})b$ is a position of hexagonal staking, but $S_l=0$ if cubic. The second term in Eq. (7) represents ΔK. Equation (6) now becomes

$$\Delta K(1,\,q-q')=(K_{\rm hex}-K_{\rm cub})\{\mathfrak{N}^{-1}\textstyle\sum_l S_l e^{i(q-q')lb}\}, \qquad (8)$$

where the quantity in curly brackets is essentially a structure factor $S(q-q')$. For periodic polytype structures S_l will repeat in a certain interval r, i.e., $S_l=S_{l+r}$, and this restricts the structure factor to being nonzero only for

$$q-q'=(m/r)(2\pi/b), \qquad (9)$$

where m is an integer. The quantity r is related to the number N appearing in the Ramsdell symbol.[1,5] For rhombohedral polytypes $r=\frac{1}{3}N$, but for hexagonal polytypes with a 6_3 screw axis $r=\frac{1}{2}N$. In Table I we plot S_l in its repeat cell for the various polytypes considered by Feldman *et al.*,[1] and given corresponding expressions for the structure factors $S(q-q')$. It should be noted that for $q=q'$ the structure factor $S(0)$ is simply given by the percentage number of hexagonal stacking positions in the solid, a quantity which has been used to correlate some of the structure-dependent properties of polytypes.[1,3]

The perturbing matrix elements $\langle q'|\Delta\Phi|q\rangle$ are responsible for the introduction of small gaps in the phonon spectrum when $q'=-q$, in analogy with the electron case. From Eq. (9) these splittings occur when $q=m\pi/rb$, or at positions $x=m/r$, inside the large zone where x is the reduced wave vector $q/q_{\rm max}$ used by Feldman *et al.*[1] In hexagonal polytypes with a 6_3 axis all these values of q plot back into the center of the small zone and are therefore accessible by Raman scattering. In rhombohedral polytypes only those values for which m is even plot back to $q=0$ and are accessible. These are just the values of q for which Raman scattering has been observed in the TA branch.[1] Solution of the secular equation for such wave vectors gives

$$(\omega_q)^2=(\omega_q{}^0)^2+M^{-1}(\langle q|\Delta\Phi|q\rangle\pm|\langle -q|\Delta\Phi|q\rangle|). \qquad (10)$$

[12] V. Heine and R. O. Jones, J. Phys. C2, 719 (1969).

Using Eqs. (5) and (8), Eq. (10) becomes

$$(\omega_q)^2=(\omega_q{}^0)^2+(4/M)(K_{\rm hex}-K_{\rm cub})(\sin\tfrac{1}{2}qb)^2 \times[S(0)\pm|S(2q)|], \quad (11)$$

and in the same approximation Eq. (3) becomes

$$(\omega_q{}^0)^2=(4/M)K_{\rm cub}(\sin\tfrac{1}{2}qb)^2. \quad (12)$$

Equation (11) indicates that the doublet splitting $\Delta(\omega^2)$ at q should be proportional to $|S(2q)|(\sin\frac{1}{2}qb)^2$. In Fig. 2 we have plotted $\Delta(\omega^2)/|S(2q)|$ for the TA branch against $(\sin\frac{1}{2}qb)^2$. The general behavior expected is obtained approximately, but a deviation from the straight line predicted by Eq. (11) seems to be indicated. The reason for this discrepancy will be discussed in Sec. II. We may also use Eq. (11) to calculate $(\omega_q{}^0)^2$ from the frequencies of the doublet members at q. For each value of q there are two possible values of $(\omega_q{}^0)^2$ according to whether $K_{\rm hex}$ is greater or less than $K_{\rm cub}$ .The possible values of $(\omega_q{}^0)^2/(\sin\frac{1}{2}qb)^2$ are plotted in Fig. 3 and we see that a straight line passes nicely through the upper series of values, showing that $K_{\rm hex}<K_{\rm cub}$. Since all S_l are zero for the $3C$ polytype, $\omega_q{}^0$ must represent the phonon dispersion curve for this structure. Using Eqs. (11) and (12) our results indicate a value of $K_{\rm cub}/M$ of approximately 20 000 cm^{-2}, but a value of $(K_{\rm cub}-K_{\rm hex})/M$ of 1500 cm^{-2}. As discussed above, if we neglect the small lattice distortions, and use a pairwise interaction model, $K_{\rm cub}-K_{\rm hex}$ is determined by the stacking dependence of the force constants between Si and planes separated $\frac{5}{4}b$, but $K_{\rm cub}$ mainly by the constant between those separated $\frac{3}{4}b$. One can show that the magnitudes of the $\frac{5}{4}b$ constants are roughly the same as their stacking dependence and may deduce that they are roughly one-tenth the magnitude of the $\frac{3}{4}b$ force constant. This suggests that these constants decrease very rapidly with increasing plane separation.

At certain points in q space the states $|q\rangle$ and $|-q\rangle$ are no longer distinct, and Eq. (10) is no longer applicable. This happens at $q=0$ and at $q=\pi/b$, the edge of the large zone. Here the shift in frequency $(\omega_q)^2-(\omega_q{}^0)^2$ is given simply by the diagonal element $\langle q|\Delta\Phi|q\rangle$. This is proportional to $S(0)$, which is the fractional number of hexagonal stacking positions in the solid. Such behavior is shown by the TO_2 mode at $q=0$ in the optic branch as reported by Feldman *et al.*,[1] and indicates that a theory rather similar to that for the acoustic branches is probably valid for the optic branches. Nevertheless it is difficult to see why the frequency of the TO_1 modes (although not varying with θ, the direction of propagation) should not be polytype-dependent in the same way.

At this point we may make some remarks concerning the thermodynamic stability of silicon carbide polytypes. There is a connection between $K_{\rm cub}-K_{\rm hex}$, the difference in force constants for the TA branch, and the difference in interplanar interactions $\phi=\Phi_i-\Phi_e$,[13] which has been used to study the stability and occurence

[13] The notation here is that of Ref. 3.

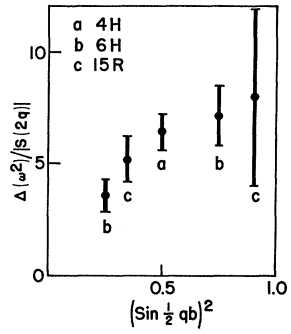

FIG. 2. Experimental splittings $\Delta(\omega^2)$ divided by the structure factor $|S(2q)|$ plotted in units of 10^3 cm^{-2} against $(\sin\frac{1}{2}qb)^2$. The splittings for larger values of q seem to be lower than expected.

of rare-earth polytypes.[3] If we assume that the interaction between two planes varies smoothly as we make a relative transverse displacement (e.g., A−A, → A−B), ϕ is very simply related to the difference in force constants by

$$\phi\simeq(3a^2/8\pi^2)(K_{\rm cub}-K_{\rm hex}), \quad (13)$$

where a is the interatomic spacing in one of the close-packed planes. We need, however, to exclude in Eq. (13) any contribution to $K_{\rm cub}-K_{\rm hex}$ from the small lattice displacements from the ideal structure, and so far we have not separated out this effect. Our result that $K_{\rm cub}>K_{\rm hex}$ probably indicates that at absolute zero the $3C$ polytype is the most thermodynamically stable of the polytypes studied by Feldman *et al.*[1] We may also discuss qualitatively the contribution to the free energy from the phonons. On the c axis away from the small zone or superlattice zone boundaries Eq. (11) becomes

$$(\omega_q)^2\simeq(\omega_q{}^0)^2-(4/M)(K_{\rm cub}-K_{\rm hex})(\sin\tfrac{1}{2}qb)^2S(0). \quad (14)$$

Thus, for most of the modes on the c axis, the phonon frequencies are lowest for the hexagonal polytypes. If this remains true on the whole for the modes lying off the c axis, then the vibrational contribution would tend to stabilize the hexagonal polytypes at high temperatures. We must emphasize here, however, that our analysis indicates the interplanar interaction ϕ in Ref. 3, as well as the interplanar force constants, to be decreasing very rapidly with increasing plane separation. The interaction ϕ is therefore probably of very short range. Thus, no thermodynamic theory such as is presented in Ref. 3 can by itself explain the occurrence of particular long-period polytypes which may have values

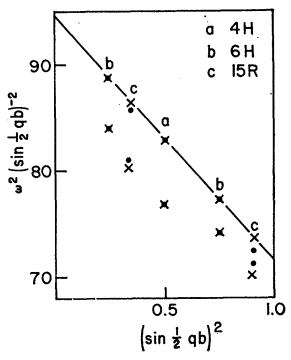

FIG. 3. Phonon frequencies ω^2 divided by $(\sin\frac{1}{2}qb)^2$ plotted in units of 10^3 cm^{-2} against $(\sin\frac{1}{2}qb)^2$. Circles indicate experimentally observed doublet members and crosses, possible values of $(\omega_q{}^0)^2/(\sin\frac{1}{2}qb)^2$. The line represents our choice of $(\omega_q{}^0)^2/(\sin\frac{1}{2}qb)^2$ as a function of q.

of N up to 100 or so. To explain the origin of such structures we must turn to some theory based on other considerations such as the Frank dislocation theory.[5,14]

III. SHELL MODEL

In this section it is our aim to examine the reason for the deviation from a straight line in the plot in Fig. 2, and to generalize our model to take account of this discrepancy. Perhaps the most serious approximation made up until now is the assumption that our double-plane units oscillate rigidly. On a more refined theory there are two separate effects which could be introduced here, the first being the relative motion of the silicon and carbon atoms, and the second the polarization of the atoms themselves such as occurs in the shell-model theory.[8] By looking at the structure-independent part of the phonon curves in Fig. 3 we may easily verify that the second of these effects is much more important than the first. The negative slope of the line in Fig. 3 represents a flattening of the TA branch towards the zone boundary and is a manifestation of nonrigid atom or shell-model effects. In contrast to this the relative motion of the carbon and silicon atoms would cause a positive slope in Fig. 3. We choose to generalize our model still assuming that the Si and C atomic cores within one double unit oscillate rigidly with displacement U_j. However, we now have to consider in addition the motion of the atomic shells,[8] which will be displaced relative to the atomic cores. We have for simplicity chosen to consider only the average displacement V_j of the shells relative to the cores in one double unit j, thus ignoring differences in the atomic properties of the silicon and carbon atoms.

The magnitudes of the quantities V_j indicate the degree of deviation from rigid-ion behavior. It may be observed from Fig. 3 that the flattening of the bands near the zone boundary in the TA branch is not very large. Thus, the degree of deviation from rigid-ion behavior is not great and the V_j are expected to be small. This will be confirmed below. Accordingly we shall make an expansion of the harmonic lattice potential energy Φ in ascending powers of the V_j as follows:

$$\Phi=\tfrac{1}{2}\sum_{j,n}\{K_{j,j+n}|U_j-U_{j+n}|^2+J_{j,j+n}\times[(V_j-V_{j+n})^*(U_j-U_{j+n})+\text{c.c.}]+k\delta_{n,0}|V_j|^2\}. \quad (15)$$

The first term, which contains $K_{j,j+n}$, is the usual expression appearing in the rigid-ion approximation. The only contribution to Eq. (15) from $n=0$ arises from the interaction of the shells with the cores within one double unit; they are assumed to be coupled with a spring constant k, which is large but independent of the stacking sequence. The force constant K and J are expected to be rather smaller than k, and as stated above V_j is expected to be small ($<U_j$). Accordingly, we have neglected powers of $(V_j)^2$ in the terms which arise from the interactions between different double units. To obtain the equation for normal modes we differentiate Φ with respect to the independent variables U_j^c, U_j^s which represent the displacement of the cores and shells from equilibrium and are given by

$$U_j^c=U_j, \quad U_j^s=U_j+V_j. \quad (16)$$

This will give the forces acting on the cores and shells. The shells, however, are assumed to have zero mass and therefore

$$\left.\frac{\partial\Phi}{\partial U_j^s}\right|_{U_j^c}=\left.\frac{\partial\Phi}{\partial V_j}\right|_{U_j}=0. \quad (17)$$

In view of Eq. (17) the equation of motion for the cores becomes

$$M\omega^2U_j=\left.\frac{\partial\Phi}{\partial U_j^c}\right|_{U_j^s}=\left.\frac{\partial\Phi}{\partial U_j}\right|_{V_j}. \quad (18)$$

Equations (17) and (18) can be written in terms of a generalized dynamic matrix $\mathbf{\Phi}$ acting on a general vector (U_j,V_j). Matrix elements of $\mathbf{\Phi}$ taken between any two states $(U_j'^*,V_j'^*)$ and (U_j,V_j) may be shown to be equal to

$$\langle|\mathbf{\Phi}|\rangle=\tfrac{1}{2}\sum_{j,n}[(U_j'-U_{j+n}')^*K_{j,j+n}(U_j-U_{j+n})+(V_j'-V_{j+n}')^*J_{j,j+n}(U_j-U_{j+n})+(U_j'-U_{j+n}')^*J_{j,j+n}(V_j-V_{j+n})+k\delta_{n,0}(V_j')^*V_j]. \quad (19)$$

Let us now write corresponding to Eq. (2)

$$K_{j,j+n}=K(n)+\Delta K_{j,j+n}, \quad J_{j,j+n}=J(n)+\Delta J_{j,j+n}, \quad (20)$$

with

$$K(n)=K(-n), \quad J(n)=J(-n). \quad (21)$$

If only the translationally invariant parts $K(n)$, $J(n)$ were included in the problem, the normal modes (suitably normalized) would be given by

$$U_j=\mathfrak{N}^{-1/2}e^{iqjb}, \quad V_j=[V(q)/\sqrt{\mathfrak{N}}]e^{iqjb}. \quad (22)$$

When we come to the problem of symmetry breaking we are going to be involved in taking matrix elements of $\mathbf{\Delta\Phi}$ between the states or normal modes given by Eq. (22). We shall therefore determine the translationally symmetric modes and frequencies by evaluating the matrix element $\langle q|\mathbf{\Phi}|q\rangle$ and minimizing with respect to $V(q)$, rather than working from Eqs. (17) and (18). Using Eq. (19), (21), and (22) the diagonal matrix element becomes

$$\langle q|\mathbf{\Phi}|q\rangle=\sum_{n>0}(2\sin\tfrac{1}{2}qnb)^2\times\{K(n)+J(n)[V(q)^*+V(q)]\}+\tfrac{1}{2}k|V(q)|^2. \quad (23)$$

[14] F. C. Frank, Phil. Mag. 42, 1014 (1951).

Minimization of Eq. (23) with respect to $V(q)$ is equivalent to Eq. (17). As in Sec. II for the rigid-ion model, terms with $n>1$ in Eq. (23) will be neglected. As a result, we obtain

$$V(q)=-[2J(1)/k](2\sin\tfrac{1}{2}qb)^2. \quad (24)$$

We see that $V(q)$ is real, i.e., the shells in the double plane j move in phase with the cores. The significance of the force constants J now becomes clear. They represent interactions from neighboring atoms which act to polarize the atom and displace the shells relative to the cores. The shell-core interaction k on the same unit j acts to limit this displacement. Substitution of Eq. (24) back into Eq. (23) gives the translationally invariant phonon frequencies

$$M(\omega_q{}^0)^2/(2\sin\tfrac{1}{2}qb)^2=K(1)-8[J(1)]^2k^{-1}(\sin\tfrac{1}{2}qb)^2. \quad (25)$$

The form of Eq. (25) is just that indicated in Fig. 3. If we assume that $J(1)$ is roughly equal to $K(1)$ then we may conclude from Fig. 3 that the maximum value of $V(q)$, which occurs at the zone boundary, is roughly $\frac{1}{4}$.

We now turn to the problem of symmetry breaking. We shall make the same assumptions concerning the j dependence of the force constants as before, but shall also assume that the degree of breaking in K and J is proportional to $K(1)$ and $J(1)$, respectively; i.e., we shall write

$$\begin{aligned}\Delta K_{l-\frac{1}{2},l+\frac{1}{2}}&=\Delta K_{l+\frac{1}{2},l-\frac{1}{2}}=S_l\epsilon K(1),\\ \Delta J_{l-\frac{1}{2},l+\frac{1}{2}}&=\Delta J_{l+\frac{1}{2},l-\frac{1}{2}}=S_l\epsilon J(1),\end{aligned} \quad (26)$$

where ϵ is some small constant. In an analysis similar to the development of Eqs. (5)–(8), the matrix elements of $\mathbf{\Delta\Phi}$ are calculated using Eqs. (26), (22), and (19) as

$$\langle q'|\mathbf{\Delta\Phi}|q\rangle=4\epsilon(\sin\tfrac{1}{2}q'b)(\sin\tfrac{1}{2}qb)S(q-q')\times\{K(1)+J(1)[V(q')^*+V(q)]\}. \quad (27)$$

Finally, using Eqs. (24) and (10) the doublet frequencies are given by

$$(\omega_q)^2=(\omega_q{}^0)^2+\epsilon(\sin\tfrac{1}{2}qb)^2g(q)[S(0)\pm|S(2q)|], \quad (28)$$

where the factor $g(q)$ is given by

$$\tfrac{1}{4}Mg(q)=K(1)-16[J(1)]^2k^{-1}(\sin\tfrac{1}{2}qb)^2. \quad (29)$$

Using Eq. (25) we may easily deduce empirical values of $g(q)$ from Fig. 3. In Fig. 4 we have plotted the doublet splittings in the TA branch $\Delta(\omega^2)/S(2q)$ against $g(q)\times(\sin\frac{1}{2}qb)^2$. Much better agreement with the theory is obtained than in Sec. II.

IV. INFRARED-STRENGTHS

Our theory, based on the breaking of translation symmetry, may also be used to estimate the strengths of the weak ir modes found by Spitzer *et al.*[9] and Ellis and Moss,[10] which have been identified by Lyle Patrick.[4] To do this our theory must be generalized to take account of the relative silicon carbon motion within one double unit j, since we shall be concerned with both the optic and acoustic modes here. Though we have no quantitative theory for the optic modes as yet, a formal generalization may be made in the same way as we took account of the relative core shell motion in Sec. III. If translation symmetry held the normal modes would be given by

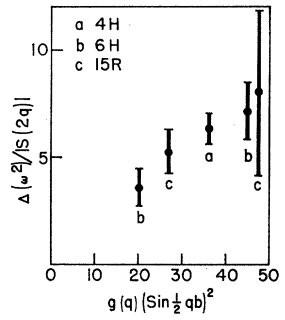

FIG. 4. Experimental splittings $\Delta(\omega^2)$ divided by $|S(2q)|$ plotted against $g(g)(\sin\frac{1}{2}qb)^2$. Both axes are in units of 10^3 cm^{-2}.

$$U_j{}^{\mathrm{C}}=U_{q\lambda}{}^{\mathrm{C}}e^{iqjb},\quad U_j{}^{\mathrm{Si}}=U_{q\lambda}{}^{\mathrm{Si}}e^{iqjb}, \quad (30)$$

where $U_j{}^{\mathrm{C}}$, $U_j{}^{\mathrm{Si}}$ are the displacements from equilibrium of the carbon and silicon consituents of the jth double plane. The index λ in Eq. (30) refers to the optic or acoustic branch. Of these modes only those belonging to the optic branches at $q=0$ will have nonzero dipole moments and thes are the strong modes which we denote by $|s\rangle$. When translation symmetry is broken these strong modes can mix in small amounts into others having nonzero values of $q=2\pi m/rb$, which we denote by $|q\rangle$. The result is a weak mode which has a dipole moment D_w given by

$$D_w/D_s=[(\omega_q{}^0)^2-(\omega_s{}^0)^2]^{-1}\langle s|\mathbf{\Delta\Phi}|q\rangle, \quad (31)$$

where D_s is the dipole moment of the strong mode and $\langle s|\mathbf{\Delta\Phi}|q\rangle$ is a matrix element of $\mathbf{\Delta\Phi}$ in a similar sense to Eq. (19). The ir strengths should be in the ratio of the squares of the dipole moments. Although $\langle s|\mathbf{\Delta\Phi}|q\rangle$ cannot yet be calculated in detail these matrix elements might be expected to be of the order of magnitude of the doublet splittings. From the data of Spitzer and Kleinman[9] we have estimated the strength of the LO mode at $x=\frac{2}{3}$ in $6H$ to be 1/400th of the strong mode.[15] Using the data of Ellis and Moss[10] we have estimated a strength ratio of about 1/4000 for the LA modes in $6H$ and $15R$. From these values and Eq. (21) $\langle s|\mathbf{\Delta\Phi}|q\rangle$ is calculated to be 10 000 cm^{-2} and 7500 cm^{-1} for the weak LO and LA modes, respectively. This agrees satisfactorily with the order of magnitude of doublet splittings observed.

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[15] Our estimate of 1/400 seems to be in disagreement with the value of about 1/40 given in Ref. 9.