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# Green's-function calculation of the lattice response near the vacancy in silicon

M. Lannoo and G. Allan
*Laboratoire de Physique des Solides,* I.S.E.N. 3, rue F. Baës,*
*59046-Lille Cedex, France*

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The lattice response near a vacancy in covalent systems is determined using a Green's-function technique. The phonon Hamiltonian is taken from a valence-force-field description. The calculation is done by two different techniques, a fully numerical one and an analytic approximate one. This last method is shown to lead to a clear understanding as well as to a good precision. A first application is made to the vibration entropy of the vacancy in an undistorted environment, found to be of order $3k$. Then the effective force constants describing the response to forces applied on the neighbors of the vacancy are determined. They are found to lie midway between those of two previous cluster calculations which were differing by a factor of 2 to 3. Finally the influence of local changes in force constants is studied, and it is shown that they can lead to a dramatic increase in the lattice response and in the formation entropy.

## I. INTRODUCTION

Since the pioneering work by Coulson and Kearsley,[1] there has been almost continuous interest concerning the properties of vacancies in group-IV semiconductors. This is especially true for silicon, where very precise EPR information obtained by Watkins[2,3] has demonstrated the existence and given the symmetry of Jahn-Teller distortions. These are charge-state dependent, being tetragonal for $V^+$ (the positive charge state) and mixed tetragonal plus trigonal for $V^-$ (the negative charge state). Most of the older theory has thus concentrated on the prediction of these Jahn-Teller distortions, starting from the defect-molecule model of Coulson and Kearsley and trying to obtain, with limited success, the amplitudes and energies of the distortions.[4,5] In this context one major problem was the relative magnitude of many-electron effects (the multiplet splitting of the one-electron levels) and Jahn-Teller energies.[6–8] which has received recent elements of solution.[9]

The theoretical understanding of the vacancy has been greatly improved within the last years through self-consistent one-electron calculations[10–13] using a pseudopotential plus local-density formalism. These calculations have provided more accurate values for the energies and have led to a prediction of the Jahn-Teller forces on the nearest neighbors of the vacancy site. The results have allowed Baraff, Kane, and Schlüter[14–16] to propose that the three charge states $V^{2+}$, $V^+$, and $V^0$ of the vacancy form a negative-$U$ center, a conjecture which has then been confirmed experimentally by Watkins and Troxell.[17] The theoretical model was based on two essential parameters: (i) the forces on the nearest neighbors of the vacancy, obtained from the self-consistent calculation and (ii) the response of the neighboring lattice to these forces, which can be described in terms of effective response frequencies for the nearest neighbors. Two sets of values were derived for these parameters, a theoretical and an experimental set. Both sets were found to be in fairly good agreement with one another, but the effective frequencies were found to be in disagreement with those obtained by Larkins and Stoneham long ago,[18] a discrepancy which is difficult to explain.

A final and apparently unrelated problem corresponds to the very large ($\sim 10-15k$) measured value for the high-temperature self-diffusion entropy in silicon. Apart from various hypotheses ranging from extended defect[19–21] to divacancies[22,23] and to the split vacancy,[24] the only theoretical proposal due to Van Vechten and Thurmond[25,26] was that there is a large ionization entropy associated with the vacancy in silicon. Another more recent possible explanation was given by Lannoo and Bourgoin,[27] who showed, on the basis of an Einstein model, that the vibrational contribution to the vacancy entropy can undergo a large increase for relatively small values of the changes in force constants in the neighborhood of the defect.

From the above analysis of the knowledge about the vacancy in silicon it is apparent that a deeper understanding of its vibrational properties is required. This is important in three respects: (i) the response of the lattice to the Jahn-Teller forces or to external forces such as those induced by a stress, (ii) the vibrational contribution to the formation entropy, and (iii) the possibility of a softening of the vibration modes corresponding to local changes in force constants induced by the atomic displacements, which would correspond to an increase in the vibrational entropy. The aim of this work is thus to discuss in detail these problems. For this we use a valence-force-field Hamiltonian and apply a Green's-function approach[28] to treat the perturbation induced by the vacancy. This is in contrast with two previous treatments[16,18] where the lattice response to local forces was calculated using a cluster approach. Our results for the effective response force constant are intermediate between those found by Larkins and Stoneham[18] and those of Baraff, Kane, and Schlüter[16] (the ratio of these two sets of values being of order 2 to 3). This has some implications on the actual values of their parameters for the negative-$U$ center formed by $V^{2+}$, $V^{+}$, and $V^{0}$ since the Jahn-Teller energies are proportional to the inverse of these effective force constants.

We begin by defining the valence-force-field phonon Hamiltonian and its application to the perfect crystal. We also describe an approximate analytic solution, which will be very useful in the following, whose predictions are compared to the numerical results. In Sec. III we describe the perturbation induced by the vacancy and its treatment by the Green's-function method. Section IV presents the similar treatment in the approximate analytic model, showing very nice agreement with the exact treatment. Both models are applied in Sec. V to the calculation of the vibrational formation entropy for the undistorted vacancy. They are used in Sec. VI to determine the response of the lattice to forces on the nearest-neighbors. In Sec. VII we investigate the possibility of a softening of the phonon modes induced by local changes in force constants which can be due to the atomic displacements. We show that there can be a dramatic increase in the lattice response and in the formation entropy for small changes in the back bond force constants.

## II. THE PERFECT-CRYSTAL DESCRIPTION

In this section we present our perfect-crystal phonon Hamiltonian. It is based on a valence-force-field potential as was used by Larkins and Stoneham[18] and contains Keating's model[29] as a particular case. The general form of the potential energy for nuclear motion is taken to be

$$V=\tfrac{1}{2}k_r\sum_{i,j}(d_{ij})^2 + \sum_{ijk}\left[\tfrac{1}{2}k_\theta(r\,d\theta_{ijk})^2+k_{rr}d_{ij}d_{jk} + k_{r\theta}(r\,d\theta_{ijk})(d_{ij}+d_{jk})\right] . \tag{1}$$

In this expression $d_{ij}$ is the change in length of the bond between atoms $i$ and $j$, and $d\theta_{ijk}$ the change in angle between two adjacent bonds $ij$ and $jk$. The sum over $ij$ is performed on all distinct bonds while the sum over $ijk$ is made over all distinct pairs of bonds. It is well known[30] that such a short-range phonon Hamiltonian leads to a poor description of the transverse acoustical branches of the silicon phonon spectrum. A description of their characteristic flattening near the Brillouin-zone limits requires the inclusion of long-range interactions. However, the treatment of such interactions for point defects is a very difficult problem and for this reason we shall discard them here.

To discuss the phonon spectrum we proceed by successive steps. The first one corresponds to a fully analytic model incorporating the effect of $k_r$ and the average effect of the other terms in expression (1). It provides a very useful zeroth order description of the phonon density of states and allows an analytic calculation of all the vacancy parameters with a good accuracy. To illustrate the model let us first consider the case where only the stretching force constant $k_r$ is nonvanishing. This simplified situation has already been discussed,[31] but we rederive here the essential results in a different manner. The equations of motion are

$$M\omega^2\vec{u}_i=k_r\sum_j d_{ij}\vec{n}_{ji} , \tag{2}$$

where $M$ is the atomic mass, $\vec{n}_{ji}$ the unit vector from atom $j$ to $i$, and the sum is performed over the nearest neighbors of atom $i$. We can write the same equation for a nearest neighbor $k$ of atom $i$, write the difference $M\omega^2(\vec{u}_i-\vec{u}_k)$, and project it on the unit vector $\vec{n}_{ki}$, which leads to

$$M\omega^2 d_{ik}=k_r\left[\sum_j d_{ij}\vec{n}_{ji}\cdot\vec{n}_{ki}-\sum_l d_{kl}\vec{n}_{lk}\cdot\vec{n}_{ki}\right] , \tag{3}$$

where $l$ are the nearest neighbors of atom $k$. All scalar products $\vec{n}_{ji}\cdot\vec{n}_{ki}$ are equal to $-\frac{1}{3}$ except for

$\vec{n}_{ji}\cdot\vec{n}_{ji}$, which is unity, while the opposite is true for the $\vec{n}_{lk}\cdot\vec{n}_{kl}$. This allows us to rewrite Eq. (3) in the form

$$M\omega^2 d_{ik}=k_r\left[\tfrac{8}{3}d_{ik}-\tfrac{1}{3}\sum_j d_{ij}-\tfrac{1}{3}\sum_l d_{kl}\right] . \tag{4}$$

Introducing new quantities $S_i$ equal to $\sum_j d_{ij}$ this equation can be rewritten

$$\left[\frac{M\omega^2}{k_r}-\frac{8}{3}\right]d_{ik}=-\tfrac{1}{3}(S_i+S_k) , \tag{5}$$

which can now be summed over $k$, leading to

$$\left[\frac{M\omega^2}{k_r}-\frac{4}{3}\right]S_i=-\tfrac{1}{3}\sum_k S_k . \tag{6}$$

This equation is equivalent to the tight-binding $s$-band case on the same lattice, giving for the dispersion relation

$$\frac{M\omega^2}{k_r}=\frac{4-\phi}{3} , \tag{7}$$

where $\phi$ is the dispersion relation for the tight-binding $s$ band with unit interactions between nearest neighbors. General theorems show that $\phi$ is between $-4$ and 4 for the diamond lattice so that (7) defines a broad band lying between $\omega^2$ equal to zero and a maximum value of $\frac{8}{3}k_r/M$. This band corresponds to nonvanishing $S_i$ and thus contains one state per atom. Other solutions can be found, which now correspond to vanishing $S_i$. One of them is obtained for nonvanishing $d_{ik}$ (with all $S_i$, $S_k$ equal to zero) which from Eq. (5) leads to

$$\frac{M\omega^2}{k_r}=\frac{8}{3} . \tag{8}$$

This gives a flat band containing again one state per atom. Finally, there still exists another nontrivial solution for which not only the $S_i$ but also the $d_{ij}$ are zero. The condition that the $\vec{u}_i$ themselves be nonzero imposes from Eq. (2) another flat band, with one state per atom at $\omega^2$ equal to zero. The corresponding schematic density of states is pictured in Fig. 1.

To test the usefulness of this simplified picture let us now investigate the situation where both $k_r$ and $k_\theta$ are nonvanishing, which is the case for which all numerical calculations of this work have been performed. In Fig. 2 we give the phonon dispersion curves obtained with the two force constants chosen to obtain the correct Raman frequency $\omega_M$ and a good overall fit to the elastic constants. Clearly, the elastic constants are correctly obtained but the flattening of the transverse acoustical modes is not described. The density of states is given in Fig. 3. Its shape is reminiscent of what we have obtained in our analytical model with $k_\theta=0$, the two flat bands being now shifted and broadened. However, to have some interest for what follows, the simplified model should produce the flat bands at positions which are the barycenters of the corresponding broadened bands. This can be made possible simply by adding to Eq. (2) the diagonal contribution to the dynamical matrix due to the bond bending terms in $k_\theta$. This contribution is equal to $\frac{28}{3}k_\theta/M$ and simply shifts the approximate density of states of Fig. 1. The shifted density of states is compared in Fig. 3 to the exact density of states, and one can see that

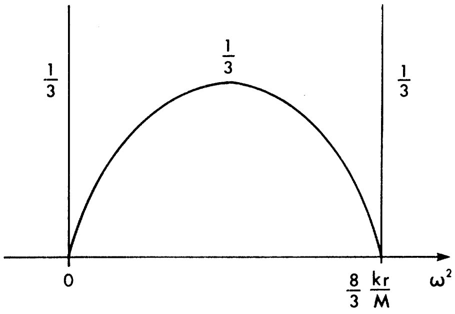

FIG. 1. Bulk phonon density of states for $k_\theta=0$ (schematic). The weight of each subband is given.

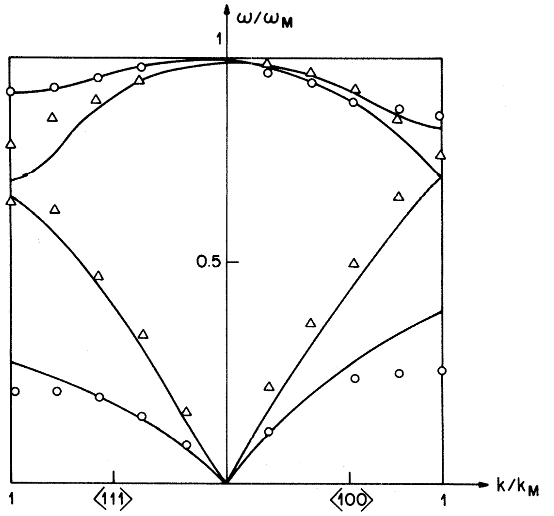

FIG. 2. Phonon dispersion curves corresponding to case (a) of Table I.

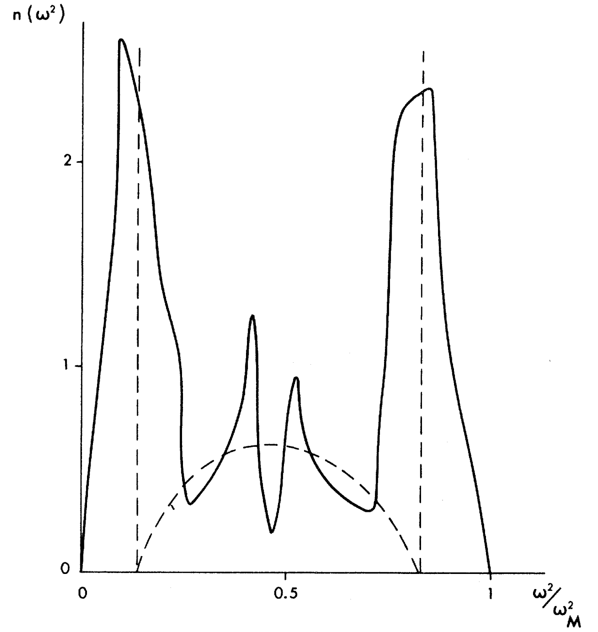

FIG. 3. Plot of the bulk density of states $n(\omega^2)$ for case (a) of Table I. The dashed lines correpond to the curve of Fig. 1 shifted by an amount equal to $\frac{28}{3}k\theta/M$ (see text).

now the flat bands can be considered as giving the average position of the calculated bands. This makes the analytical model much more meaningful, providing now an exact value for the first moment of the density of states.

To close this section we still have to consider the influence of the remaining terms in $k_{rr}$ and $k_{r\theta}$. The first is very easy to include since its contribution to the potential energy can be rewritten in the form

$$\tfrac{1}{2}k_{rr}\sum_i\left[\left(\sum_j d_{ij}\right)^2-\sum_j d_{ij}^2\right] . \tag{9}$$

The first term gives a contribution to the equation of motion (2) which is proportional to $\sum_j \vec{n}_{ij}$ and is thus zero in the perfect crystal. The second term simply adds to the bond-stretching term, changing the force constant from $k_r$ to $k_r-2k_{rr}$. It introduces no qualitative modification of the phonon dispersion curves.

The final effect corresponds to the term in $k_{r\theta}$. It will practically not affect the lowest acoustical band, since its wave functions are mainly built from combinations of atomic displacements with $d_{ij}$ equal to zero, as shown in the analytical model. This property is reflected in the values of the transverse acoustical frequencies at the Brillouin-zone limits $X$ and $L$, which are

$$\begin{aligned}\omega_{\mathrm{TA}}^2(X)&=12k_\theta/M\ ,\\ \omega_{\mathrm{TA}}^2(L)&=6k_\theta/M\ ,\end{aligned} \tag{10}$$

rigorously independent of $k_r$, $k_{rr}$, and $k_{r\theta}$. This is not true for the maximum phonon frequency $\omega_M$:

$$\omega_M^2=\frac{8}{3M}(k_r-2k_{rr}+8k_\theta-8\sqrt{2}k_{r\theta}) . \tag{11}$$

In this work we want to compare our results with those of Larkins and Stoneham[18] and Baraff, Kane, and Schlüter.[16] We give in Table I the force constants used by these authors as well as the two sets which we use in this work. In the same table are given the corresponding values of $\omega_M^2$ and $\omega_{\mathrm{TA}}^2(X)$.

## III. GREEN'S-FUNCTION TREATMENT OF THE VACANCY

We describe here the basic principles of our numerical computation. We have taken a model including only two force constants $k_r$ and $k_\theta$, whose numerical values are given in Table I. Let us first derive the potential $U$ describing the perturbation

TABLE I. Values of the force constants in the three models in units of the experimental value of $k_M=M\omega_M^2$ equal to 27.935 eV/Å$^2$. The two last columns give the theoretical values of $M\omega_M^2$ and $M\omega_{\mathrm{TA}}^2(X)$ deduced from these force constants. Choice (a) gives a good overall fit to experiment. Choice (b) corresponds to the same value of $k_r$ but $k_\theta$ is chosen to fit $\omega_{\mathrm{TA}}^2(X)$ given by Eq. (10).

| | $k_r$ | $k_\theta$ | $k_{rr}$ | $k_{r\theta}$ | $M\omega_M^2$ | $M\omega_{\mathrm{TA}}^2(X)$ |
|---|---|---|---|---|---|---|
| Larkins and Stoneham, Ref. 18 | 0.332 | 0.0066 | 0.006 | 0.009 | 0.724 | 0.079 |
| Baraff, Kane, and Schlüter, Ref. 16 | 0.351 | 0.007 | 0.0009 | 0.0025 | 1.006 | 0.0842 |
| This work (a) | 0.261 | 0.0143 | 0 | 0 | 1.001 | 0.1716 |
| (b) | 0.261 | 0.0071 | 0 | 0 | 0.847 | 0.0852 |

created by the vacancy on the phonon Hamiltonian. For this we can rewrite quite generally the perfect-crystal potential energy $V$ in the form

$$V=\frac{1}{2}\sum_{\substack{ij\\ \alpha\beta}}{}' A_{ij}^{\alpha\beta}(u_i^\alpha-u_j^\alpha)(u_i^\beta-u_j^\beta) + \frac{1}{2}\sum_{\substack{ijk\\ \alpha\beta}} B_{ijk}^{\alpha\beta}(u_i^\alpha-u_j^\alpha)(u_k^\beta-u_j^\beta) \qquad (12)$$

in which $u_i^\alpha$ is the $\alpha$th component of the $i$th atom displacement; the $A_{ij}^{\alpha\beta}$ and $B_{ijk}^{\alpha\beta}$ are force constants related in a simple manner to the $k_r$, $k_\theta$ defined previously. One possible choice for defining the perturbation induced by the vacancy is to suppress from expression (12) all terms involving the atom which has been removed to create the vacancy. This will be the case in this work and corresponds in our valence-force-field description to removing the stretching force constants between this atom and its neighbors, but keeping the angular terms between the backbonds and the broken bonds. Another choice could have been to suppress these angular terms but this does not affect much the results as was discussed in Ref. 16.

With these conventions the perturbation matrix extends up to second-nearest neighbors of the missing atom, i.e., its size is 51×51. To treat it we use the Green's-functions formalism and introduce the resolvent operators $G^0$ and $G$, respectively, for the perfect and perturbed system, defined by

$$G_0=\lim_{\eta\to 0+}(\omega^2-D_0+i\eta)^{-1}\,. \qquad (13)$$

$$G=\lim_{\eta\to 0+}(\omega^2-D_0-U+i\eta)^{-1}\,,$$

where $D_0$ is the perfect-crystal dynamical matrix. The first thing to do is to calculate the 51×51 matrix of $G_0$ in the basis of the displacements of the atom to be removed, its first-and second-nearest neighbors. From this we then calculate the change $\delta N(\omega^2)$ in the total number of states with squared frequency smaller than $\omega^2$, as given by

$$\delta N_U(\omega^2)=-\frac{1}{\pi}\tan^{-1}\frac{\operatorname{Im}\det(I-G_0U)}{\operatorname{Re}\det(I-G_0U)}\,, \qquad (14)$$

where Im and Re stand for the imaginary and real part of the determinant of $I-G_0U$. In practice, we consider a system with a constant number of atoms, where the missing atom is placed on a kink at the surface. In this case the change $\delta N(\omega^2)$ in the total number of states can be written

$$\delta N(\omega^2)=N_0(\omega^2)+\delta N_U(\omega^2)\,, \qquad (15)$$

where $N_0(\omega^2)$ is the corresponding quantity for a bulk atom, since putting the atom on a kink is strictly equivalent to increasing the number of bulk atoms by one. We give the numerical result for $\delta N(\omega^2)$ in Fig. 4 versus the frequencies in units of $\omega_M$. This result will be discussed in detail in the next section.

Other quantities of interest for the following are the perturbed Green's functions (the matrix elements of $G$) in the vicinity of the defect, since they give the lattice response. They are discussed in Sec. VI. Finally, there is a possibility that localized vibrational modes can appear. If so, they are solutions of the equation

$$\det(I-G_0U)=0\,, \qquad (16)$$

a determinant whose size is the same as the $U$ matrix, i.e., 51×51 in our case.

## IV. ANALYTIC MODEL FOR THE VACANCY

We now describe an analytic calculation whose principle is similar to that discussed for the perfect crystal. The basis of this comes from the fact that $k_r$ is much greater than $k_\theta$, as shown in Table I. The first step is then to consider $k_r$ alone, introducing the effect of $k_\theta$ later on in some average manner. In this limit the elements of the dynami-

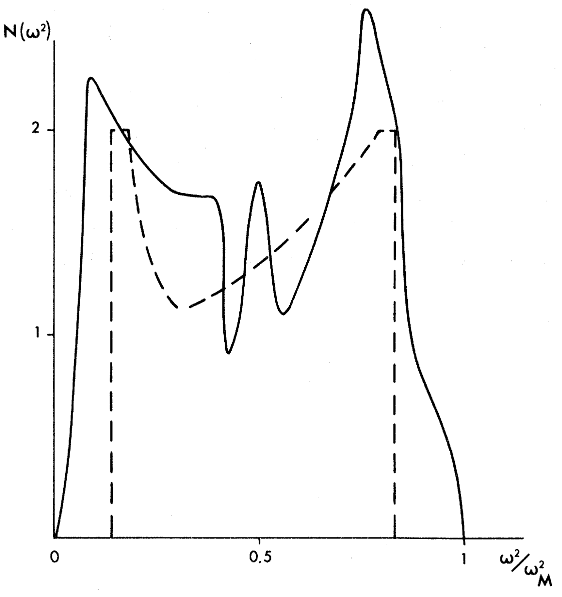

FIG. 4. Plot of $\delta N(\omega^2)$ for case (a) of Table I. The dashed line corresponds to the analytic description.

cal matrix are

$$D_{ij}^{\alpha\beta}=-k_r X_{ij}^{\alpha} X_{ij}^{\beta} \text{ for } i\neq j\ ,$$
$$D_{ii}^{\alpha\beta}=k_r \sum_j X_{ij}^{\alpha} X_{ij}^{\beta}\ , \tag{17}$$

where $i$ and $j$ stand for the atoms, $\alpha$ and $\beta$ the components of the atomic displacements, and $X_{ij}^{\alpha}$ is the $\alpha$th component of the unit vector $\vec{n}_{ij}$ defined above.

In this model we first attempt to calculate the Green's-function matrix $G$ on the atom 0 of Fig. 5, which is connected to a Bethe lattice which has the same coordination as the diamond lattice but with no closed loops of atoms. The situation of this atom is similar to the one for the nearest neighbors of the vacancy in this model, and for the quantities to be calculated later the replacement of the true lattice by a Bethe lattice is not a serious approximation. To calculate $G$ we use the following technique: We define an unperturbed system with resolvent $G_0$ corresponding to broken bonds (i.e., $k_r=0$) between the atom 0 and its nearest neighbors $i=1-3$. We can thus relate $G$ to $G_0$ through Dyson's equation

$$G=G_0+G_0 W G\ , \tag{18}$$

where $W$ is the perturbation, i.e., the part of the dynamical matrix corresponding to the stretching force constants of the bonds $0-i$. We intend to calculate the $3\times 3$ submatrix $(G)_{00}$ of $G$ in the basis of the displacements of atom 0, knowing from (17) that $W$ has only elements on 0, between 0 and $i$, and finally on atoms $i$. It is also clear that $(G_0)_{00}$ is disconnected from the other matrix elements of $G_0$.

We can then write in matrix form

$$G_{00}=(G_0)_{00}+(G_0)_{00}\left[W_{00}G_{00}+\sum_i W_{0i}G_{i0}\right]\ , \tag{19}$$

$$G_{i0}=(G_0)_{ii}(W_{ii}G_{i0}+W_{i0}G_{00})\ , \tag{20}$$

where all the matrices are $3\times 3$. To get $G_{00}$ we can thus extract $G_{i0}$ from (20) and inject it into (19) to get the matrix relation

$$(G)_{00}=\left[(G_0)_{00}^{-1}-W_{00}-\sum_{i=1}^{3} W_{0i}[(G_0)_{ii}^{-1}-W_{ii}]^{-1}W_{i0}\right]^{-1}\ . \tag{21}$$

If we choose a local system of coordinates on each atom defined in the same manner, it is clear that the matrix $(G)_{00}$ must be identical to each matrix $(G_0)_{ii}$. Equation (21) thus defines a nonlinear system of equations for the unknown elements of $(G)_{00}$. Its general solution is numerical but fortunately, in our case, the $C_{3v}$ local symmetry allows us to separate it into three quadratic independent equations. For this we use the local coordinates of Fig. 5, where $\vec{x}$ is along the symmetry axis and $\vec{y}$ and $\vec{z}$ are perpendicular to it. With such local axes of coordinates, the system of equations (21) is diagonal and separates into two equations

$$G_{xx}=\frac{1-G_{xx}}{\omega^2-\frac{1}{3}-\omega^2 G_{xx}} \tag{22}$$

and

$$G_{yy}=G_{zz}=\frac{1-G_{xx}}{\omega^2(1-G_{xx})-\frac{4}{3}}\ , \tag{23}$$

where, for simplicity, the squared frequencies are expressed in units of $k_r/M$ and $G$ in units of $M/k_r$. Equation (22) is quadratic in $G_{xx}$ and can be solved to give

$$G_{xx}=\frac{1}{2}+\frac{1}{3\omega^2}+\frac{\theta}{2\omega^2}[(\omega^2-\tfrac{4}{3})^2-\tfrac{4}{3}]^{1/2}\ ,$$
$$\theta=-1 \text{ for } \omega^2>\frac{2}{\sqrt{3}}+\frac{4}{3}\ ,$$
$$\theta=+1 \text{ for } \omega^2<-\frac{2}{\sqrt{3}}+\frac{4}{3}\ , \tag{24}$$
$$G_{xx}=\frac{1}{2}+\frac{1}{3\omega^2}-\frac{i}{2\omega^2}[\tfrac{4}{3}-(\omega^2-\tfrac{4}{3})^2]^{1/2}$$
$$\text{for } \frac{4}{3}-\frac{2}{\sqrt{3}}<\omega^2<\frac{4}{3}+\frac{2}{\sqrt{3}}\ ,$$

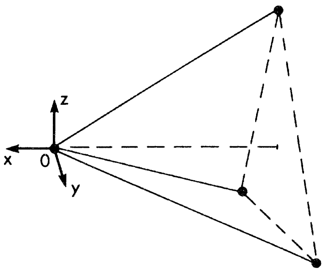

FIG. 5. Local system of axes on the nearest neighbors of the vacancy.

which then allows the determination of $G_{yy}$ through Eq. (23). Both Green's functions are plotted in Fig. 6. They exhibit delta functions at $\omega^2=0$ and $\omega^2=\frac{8}{3}$ (in units of $k_r/M$) whose weight is explicitly given in Fig. 6.

Once $G_{xx}$ and $G_{yy}$ are known, it is possible to calculate $\delta N_U$ simply by connecting one atom to four Bethe lattices. In our simple description $\delta N_U(\omega^2)$ is simply a function of $G_{xx}$ which takes the form

$$\delta N_U(\omega^2)=\frac{1}{\pi}\left[3\tan^{-1}\left[1-G_{xx}-\frac{4}{3\omega^2}\right]+\tan^{-1}(1-G_{xx})\right] \tag{25}$$

in which the determination of $\tan^{-1}$ has to be properly chosen. Once this is done it is possible to determine the total change $\delta N(\omega^2)$ defined in (15) by realizing that the bulk diagonal matrix element of the Green's function, in this model, is equal to $G_{yy}$. This gives for $N_0(\omega^2)$

$$N_0(\omega^2)=-\frac{1}{\pi}\int_{4/3}^{\omega^2}-\frac{2}{\sqrt{3}}\operatorname{Im}G_{yy}(\omega^2)d\omega^2 \,. \tag{26}$$

All these expressions are analytic but will not be reproduced here. They allow a simple calculation of $\delta N(\omega^2)$ which is reproduced in Fig. 4 (shifted by an amount equal to $\frac{28}{3}k_\theta/M$) where it is compared to the exact curve. The agreement is very good showing that the dominant part of $\delta N(\omega^2)$ corresponds to gaining two states in the lower flat band ($\omega^2=28/3Mk_\theta$) and losing them in the upper one ($\omega^2=\frac{8}{3}k_r/M+\frac{28}{3}k_\theta/M$).

The reason for this shift of $\frac{28}{3}k_\theta/M$ of the whole band comes, as for the perfect crystal, from the contribution of the angular term to the diagonal elements of the dynamical matrix. If these are assumed to be identical in the perturbed and unperturbed system, then $\delta N(\omega^2)$ is rigorously shifted by $\frac{28}{3}k_\theta/M$. However, this is not strictly correct since the diagonal terms on the nearest neighbors of the vacancy are found to be different from those in the bulk: For the $\vec{x}$ displacement it is still $\frac{28}{3}k_\theta/M$, but becomes $\frac{16}{3}k_\theta/M$ for the $\vec{y}$ and $\vec{z}$ displacements. This induces extra contribution $\delta N'(\omega^2)$ to the change in total number of states, given by

$$\delta N'(\omega^2)=-\frac{8}{\pi}\tan^{-1}\frac{4\frac{k_\theta}{M}I_{yy}}{1+\frac{4k_\theta}{M}R_{yy}} \,. \tag{27}$$

The major feature of $\delta N'(\omega^2)$ comes from the existence of a pole in the denominator of (27) corresponding to a shift of the lower flat band to lower $\omega^2$ by an amount given by $\frac{4}{3}k_\theta/M$ to an excellent approximation (this is exact to first order).

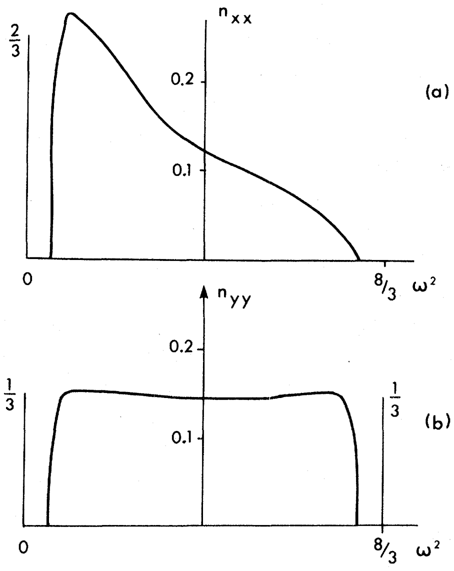

FIG. 6. Densities of states $n_{xx}$ and $n_{yy}$ corresponding to the Green's functions $G_{xx}$ and $G_{yy}$. All quantities are in reduced units of $k_r/M$.

## V. THE VIBRATIONAL ENTROPY OF THE VACANCY

In this section we calculate the change in entropy $S_F$ induced by the formation of the vacancy. The high temperature expression of $S_F$ is given by[32,33]

$$S_F=-k\left[\sum_{\alpha'}\ln\omega_{\alpha'}-\sum_{\alpha}\ln\omega_\alpha\right] , \tag{28}$$

where the $\omega_{\alpha'}$ and $\omega_\alpha$ are the vibration frequencies of the perturbed and perfect crystal, respectively. This expression can be written in integral form as

$$S_F=-\frac{k}{2}\int\ln\omega^2\left[\sum_{\alpha'}\delta(\omega^2-\omega_{\alpha'}^2)-\sum_{\alpha}\delta(\omega^2-\omega_\alpha^2)\right]d\omega^2 \tag{29}$$

or equivalently

$$S_F=-\frac{k}{2}\int \ln\omega^2\delta n(\omega^2)d\omega^2\ , \tag{30}$$

where $\delta n(\omega^2)$ is the change in density of states for the eigenvalues $\omega^2$ of the dynamical matrix. For numerical use with the Green's-functions method, it is convenient to integrate this expression by parts, which gives

$$\frac{S_F}{k}=\frac{1}{2}\int \frac{\delta N(\omega^2)}{\omega^2}d\omega^2\ , \tag{31}$$

where in our case $\delta N(\omega^2)$ is defined by Eq. (15) and can be expressed in terms of Green's functions through (14).

The numerical value of $S_F$ can be calculated readily from the change in total number of states $\delta N(\omega^2)$ pictured in Fig. 4 and determined from our complete Green's-functions calculations. We obtain for $S_F$ values of $2.8k$ and $3.3k$ [corresponding to case (a) and (b) of Table I], much larger than the usually expected value of $1.5k$ deduced from simple Einstein models. To understand the origin of this difference we now explore different approximations to the calculation of $S_F$.

Let us first consider the Einstein model[27,33] which corresponds to the replacement of the dynamical matrix by its diagonal part. In this description $S_F$ is given by

$$\frac{S_f}{k}=-\frac{1}{2}\sum_{i,\alpha}\frac{d'_{i\alpha,i\alpha}}{d_{i\alpha,i\alpha}}\ , \tag{32}$$

where $d_{i\alpha,i\alpha}$ and $d'_{i\alpha,i\alpha}$ are the unperturbed and perturbed diagonal elements for atom $i$ and for the $\alpha$th component of the displacement. In the perfect crystal $d_{i\alpha,i\alpha}$ is simply equal to $\frac{4}{3}k_r/M+\frac{28}{3}k_\theta/M$ for any couple $i,\alpha$. Only the nearest neighbors of the vacancy contribute to (32), for which $d'_{i\alpha,i\alpha}$ is given by

$$d_{ix,ix}=\frac{k_r+28k_\theta}{3M}\ ,$$
$$d_{iy,iy}=d_{iz,iz}=\frac{4k_r+16k_\theta}{3M}\ , \tag{33}$$

in the local atomic basis of Fig. 5. This gives for the entropy $S_F$ a value

$$\frac{S_F}{k}=2\left[\ln\frac{4k_r+28k_\theta}{k_r+28k_\theta}+2\ln\frac{4k_r+28k_\theta}{4k_r+16k_\theta}\right]\ , \tag{34}$$

which using the numerical values of Table I leads to $S_F/k$ equal to 2.07 [case (a)] and 2.27 [case (b)], which are not too bad when compared to the exact numbers.

To do better requires the use of the analytical approximation to the Green's function which we developed in the preceding section, giving approximate forms of $\delta N(\omega^2)$ or $\delta n(\omega^2)$ to be used in expression (31) or (30). For this we proceed by steps, incorporating different contributions to $S_F$ by decreasing order of magnitude. As we discussed in the last section the main contribution to the $\delta N(\omega^2)$ given in Fig. 4 corresponds for $\delta n(\omega^2)$ to a delta function of weight 2 at $\omega^2$ equal to $\frac{28}{3}k_\theta/M$ and another one of weight $-2$ at $(8k_r+28k_\theta)/3M$. Injecting this into (30) gives a contribution to $S_F/k$ given by $\ln(8k_r+28k_\theta)/28k_\theta$, numerically equal to 1.83 [case (a)] and 2.44 [case (b)]. This contribution only concerns displacements of the neighbors of the vacancy along the local axes $\vec{x}$. It thus gives an improved value of the first term in (34) whose contribution was 1.56 in case (a). If we keep an Einstein model for the $\vec{y}$ and $\vec{z}$ displacements, then the total entropy would be increased in case (a) by 0.27, giving 2.34.

The next contribution comes from $\delta N'(\omega^2)$ given by Eq. (27), i.e., from the diagonal perturbation $-4k_\theta/M$ on the $y$ and $z$ displacements of the nearest neighbors of vacancy. This gives the second term in (34) when using the Einstein model. To go beyond we should use the detailed form given by (27). However, as we have seen, the main feature of the change in density of states $\delta n'(\omega^2)$ [(equal to $(d/d\omega^2)\delta N'(\omega^2)$] is a delta function of weight 8 at $24k_\theta/3M$ and another one of weight $-8$ at $\frac{28}{3}k_\theta/M$ (position of the perfect-crystal flat band). To complete this picture of $\delta n'(\omega^2)$ we use an Einstein approximation for the remaining contribution, i.e., we add two other delta functions of weight $+8$ and $-8$ at positions determined in such a way that the first moments of the local density of states (i.e., the sum of the diagonal terms) are preserved. The total first moment of $\delta n'(\omega^2)$ is $-32k_\theta/M$ (eight times the diagonal perturbation $-4k_\theta/M$) to which the two delta functions discussed above contribute by an amount equal to $-32k_\theta/3M$. This leaves $-64k_\theta/3M$ for the two other delta functions. We position the one with weight $-8$ at the barycenter of the broad band and the upper flat band of Fig. 8, i.e., $(6k_r+28k_\theta)/3M$. Then the delta function with weight $+8$ must lie at $(6k_r+20k_\theta)/3M$. Summing all the contributions, we obtain for $S_F/k$ in this redefined model a value of

$$\frac{S_F}{k}=\ln\frac{8k_r+28k_\theta}{28k_\theta}+4\left[\ln\tfrac{28}{24}+\ln\frac{6k_r+28k_\theta}{6k_r+20k_\theta}\right], \qquad (35)$$

which is equal to 2.68 in case (a) and to 3.19 in case (b) of Table I. This is within a few percent of the exact values and shows that our simple description contains the essential contributions.

## VI. RESPONSE OF THE LATTICE TO FORCES

In this section we want to determine the effect of forces applied on the atoms in the vicinity of the vacancy site. These forces can be of electronic origin, i.e., due to the creation of the vacancy, or also to externally applied stresses. If we call $F_i^\alpha$ the $\alpha$th component of the force on the $i$th atom, then the lattice energy becomes

$$E=-\sum_{i,\alpha}F_i^\alpha u_i^\alpha+\tfrac{1}{2}\sum_{\substack{ij\\ \alpha\beta}}K_{i,j}^{\alpha,\beta}u_i^\alpha u_j^\beta \qquad (36)$$

to second order in the atomic displacements. The $K_{ij}^{\alpha\beta}$ is the matrix of force constants for the system containing a vacancy. To find the stable atomic positions we must minimize $E$ with respect to all $u_i^\alpha$, which gives for the stable positions

$$u_i^\alpha=\sum_{j\beta}(K^{-1})_{i,j}^{\alpha,\beta}F_j^\beta \qquad (37)$$

and minimum energy

$$E_m=-\tfrac{1}{2}\sum_{\substack{ij\\ \alpha\beta}}(K^{-1})_{i,j}^{\alpha,\beta}F_i^\alpha F_j^\beta\ . \qquad (38)$$

Then the response of the lattice is completely determined by the knowledge of the inverse force-constant matrix $K^{-1}$ which for a system of identical atoms with mass $M$ is related to the dynamical matrix $D$ by $(MD)^{-1}$. This can be expressed in terms of the Green's functions defined in (13) by

$$K^{-1}=-\frac{1}{M}G(\omega^2=0)\ . \qquad (39)$$

The calculation of the lattice response reduces to the determination of the Green's functions at zero frequency. Under matrix form, this gives

$$\begin{aligned}\vec{u}&=-\frac{1}{M}\underline{G}(\omega^2=0)\cdot\vec{F}\ ,\\ E_m&=-\frac{1}{2M}\vec{F}\cdot\underline{G}(\omega^2=0)\cdot\vec{F}\ .\end{aligned} \qquad (40)$$

In many cases one can find a suitable basis such that $\vec{F}$ has only one nonvanishing component $F_0$.

Using the same basis set for the displacements we obtain

$$\begin{aligned}u_0&=-\frac{1}{M}G_{00}(\omega^2=0)F_0\ ,\\ E_m&=-\frac{1}{2M}G_{00}(\omega^2=0)F_0^2\ ,\end{aligned} \qquad (41)$$

which is the same formal answer as for a system with only one degree of freedom, in which case the energy would be

$$E=-F_0u_0+\frac{K_0}{2}u_0^2 \qquad (42)$$

leading after minimization, to

$$u_0=\frac{F_0}{K_0},\quad E_{\min}=-\tfrac{1}{2}K_0F_0^2\ . \qquad (43)$$

$K_0$ has the meaning of an effective force constant for the displacement $u_0$, which from the comparison of (41) and (43) can be defined as

$$K_0=-\frac{M}{G_{00}(\omega^2=0)}\ . \qquad (44)$$

This concept of effective force constant describing the lattice response to local forces in terms of the corresponding local displacements is very interesting in practice. It can be used for the vacancy in silicon for instance. In this case one can define symmetry displacements which are combinations of the nearest neighbor's atomic displacements. Usually, one considers the breathing mode $Q_A$ and the tetragonal mode $Q_E$ pictured in Fig. 7 (their detailed expression is given in Refs. 4, 18, and 34; note that these definitions differ by a factor of 2 from that used in Ref. 16). We can define in the same way symmetry forces $F_A$ and $F_E$ which have been calculated by different authors.[4,16,18,35,36] Such forces and displacements being of different symmetry can be treated independently and the problem reduces to the previous formulation leading to Eqs. (41)–(44). We have then to calculate two different effective force constants $k_A$ and $k_E$, given by Eq. (44) in terms of the corresponding Green's functions $G_{Q_A,Q_A}(\omega^2=0)$ and $G_{Q_E,Q_E}(\omega^2=0)$. We have calculated these Green's functions numerically, and the results for $k_A$ and $k_E$ are reproduced in Table II, where they are compared to those of previous calculations (for this we have taken the same convention as in Ref. 16,

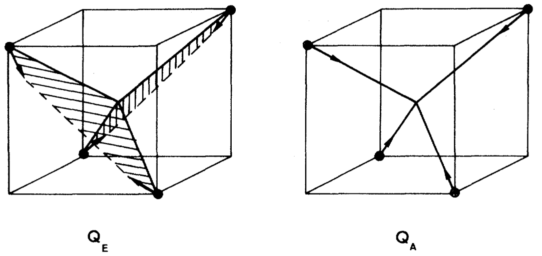

FIG. 7. Symmetry modes $Q_A$ and $Q_E$ around the vacancy.

where $k_A$ and $k_E$ are given by the ratio of the total force to the displacement of one neighbor of the vacancy). The main conclusion is that $k_A$ and $k_E$ are practically proportional to $\omega_{\mathrm{TA}}^2(X)$ (this was also noted in Ref. 16). In case (b) where $\omega_{\mathrm{TA}}(X)$ is given the same value as in both cluster calculations, we find effective force constants lying between those found by Larkins and Stoneham[18] and Baraff, Kane, and Schlüter.[16]

To have a little more insight into that result let us again use the analytical version of our Green's-function treatment. In this approximation there is no interaction between the nearest neighbors of the vacancy. For each of these neighbors the Green's function involved in the $Q_A$ mode is simply $G_{xx}(\omega^2)$ (since $\vec{x}$ is the radial displacement of this atom towards the vacancy), but where $\omega^2$ has been shifted by the diagonal part of the angular term. This one is equal to $\frac{28}{3}k_\theta/M$, the same value as in the perfect crystal [see Eq. (33)]. The corresponding density of states is given in Fig. 6(a). In this model we can estimate $k_A$ to be given by

$$k_A=-4M/G_A(\omega^2=0)\ , \tag{45}$$

where $G_A(\omega^2)$ is given by Eq. (24) where $\omega^2$ is replaced by $\omega^2-28k_\theta/3M$. This leads for $k_A$ to

$$\frac{k_A}{k_r}=4\Bigg/\left\{\frac{1}{2}-\frac{k_r}{28k_\theta}-\left[\left[\frac{1}{2}+\frac{k_r}{14k_\theta}\right]^2-3\left[\frac{k_r}{28k_\theta}\right]^2\right]^{1/2}\right\}. \tag{46}$$

With the numerical values taken from Table I, this gives 18.71 eV/Å$^2$for $k_A$ in case (a) and 9.92 eV/Å$^2$ in case (b), both values being about a factor of 2 too high, when compared to the numerical results of Table II.

TABLE II. Values of the effective force constants $k_A$ and $k_E$ (defined in the text) in eV/Å$^2$.

| | $k_A$ | $k_E$ |
|---|---|---|
| Larkins and Stoneham, Ref. 18 | 3.72 | 5.08 |
| Baraff, Kane, and Schlüter, Ref. 16 | 7.47 | 14.81 |
| This work (a) | 10.24 | 17.2 |
| (b) | 4.69 | 9.34 |

We can understand the reason for this discrepancy by noticing that the main contribution to $G_A(\omega^2)$ near $\omega^2=0$ comes from the delta function of weight $\frac{2}{3}$ at $\omega^2=\frac{28}{3}\,k_\theta/M$ (i.e., the pole $\omega^2=0$ in $G_{xx}$). Retaining only this contribution would lead for $G_A(\omega^2)$ to a value equal to

$$G_A(\omega^2)\simeq\frac{2}{3}\,\frac{1}{\omega^2-\frac{28}{3}k_\theta/M}\ . \tag{47}$$

This expression injected into (45) leads for $k_A$ to values equal to 22.37 eV/Å$^2$ and 11.18 eV/Å$^2$ close to the values obtained by Eq. (46), showing that (47) contains the essential term. However, broadening effects will enhance this contribution. A reasonable estimate of this can be obtained by replacing the delta function by an elliptical density of states extending from $\omega^2=0$ to $\omega^2=\frac{56}{3}k_\theta/M$. In such a case the contribution to $G_A(\omega^2=0)$ is enhanced by a factor of 2. If we use (47) multiplied by this factor we obtain for $k_A$ given by (45) the very simple expression

$$k_A\simeq 28k_\theta\ , \tag{48}$$

which gives 11.18 eV/Å$^2$ for case (a) and 5.6 eV/Å$^2$ for case (b), explaining very nicely the order of magnitude obtained in Table II.

We can do the same sort of treatment for $k_E$, the effective force constant for tetragonal modes. The basic Green's function for such a displacement perpendicular to the broken bonds is now $G_{yy}(\omega^2)$ defined by Eqs. (23) and (24). To obtain the correct Green's function $G_E(\omega^2)$ entering the definition of $k_E$ through

$$k_E=-4M/G_E(\omega^2=0)\ , \tag{49}$$

we have first to shift the whole spectrum for $\omega^2$ by $\frac{28}{3}k_\theta/M$, as usual. However, we have also to account for the change in diagonal term on the neighbors of the vacancy from this value to $\frac{16}{3}k_\theta/M$ [see Eq. (33)].

This allows us to write

$$G_E(\omega^2)=\frac{G_{yy}(\omega^2-\frac{28}{3}k_\theta/M)}{1+4(k_\theta/M)G_{yy}(\omega^2-\frac{28}{3}k_\theta/M)} \ . \tag{50}$$

The imaginary part of $G_{yy}(\omega^2)$ (corresponding to the bulk density of states) has been given in Fig. 6(b). There is now a flat band of weight $\frac{1}{3}$ at $\omega^2=0$ which will give the main contribution to $G_E(\omega^2)$. In this approximation, $G_E(\omega^2)$ is given near $\omega^2=0$ by

$$G_E(\omega^2)\simeq\frac{1}{3}\frac{1}{\omega^2-8k_\theta/M} \ . \tag{51}$$

Again this will be increased by broadening effects, for which we take the same enhancement factor of two as before for $G_E(\omega^2=0)$. Using twice the value given by (51) into (49) finally gives

$$k_E\simeq 48k_\theta \ . \tag{52}$$

This gives numerical values of 19.17 and 9.6 eV in cases (a) and (b), respectively, again in very good agreement with the exact values of Table II.

We have thus obtained a very simple and accurate description of the response of the lattice which directly relates the effective force constants to the bond-bending force constant $k_\theta$. This clearly illustrates the sensitivity of $k_A$ and $k_E$ to the description of the transverse acoustic phonon branch.

## VII. THE INFLUENCE OF LOCAL CHANGES IN FORCE CONSTANTS

Forces applied on the nearest neighbors of the vacancy change the equilibrium positions of the atoms. Such forces can be internal, e.g., due to electronic redistribution (such as the Jahn-Teller forces), or externally applied forces. In all cases they induce changes in bond lengths in the vicinity of the defect. This results in local modifications of the force constants. When these force constants are lowered, the response of the lattice becomes softer and at the same time the vibration entropy increases. It is thus interesting to know the behavior of the phonon frequencies for such local changes in force constants and to study quantitatively the corresponding increase in the formation entropy.

To investigate this problem, we consider here a simple case where the three backbonds of each neighbor of the vacancy are affected in the same way, the change in the force constant matrix between each first nearest and second-nearest neighbors being taken as

$$\delta K_{12}=+\delta k\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} . \tag{53}$$

The translational invariance imposes diagonal force-constant matrices $\delta K_{11}$ on the nearest neighbors and $\delta K_{22}$ on the second-nearest neighbors, respectively, equal to $-3\delta k$ and $-\delta k$ times the $3\times 3$ unit matrix. The effective force constant $k_A$ and the formation entropy $S_F$ can be calculated as functions of $\delta k$. For $\delta k>0$ (which corresponds to a decrease of the backbond force constants), it is found that $k_A$ tends to decrease with increasing $\delta k$, while the reverse is true for $S_F$. At a critical value $\delta k_c$, $k_A$ vanishes and $S_F$ tends to infinity, which obviously corresponds to the appearance of localized states at $\omega^2<0$. The numerical calculation of this effect shows that $\delta k_c$ is equal to about 15% of the radial force constant $k_r$ in case (a) and only to 4% of this value in case (b), which obviously is a condition which can be very easily fulfilled.

We can again understand very simply the values obtained for $\delta k_c$ using arguments similar to those developed in the preceding section. The critical value $\delta k_c$ is obtained when a localized state appears, i.e., in the case considered, when

$$G_A(\omega^2=0)=-\frac{M}{3\delta k_c} \ , \tag{54}$$

since the most important part of the perturbation corresponds to the diagonal term on the nearest neighbors. If we use for $G_A(\omega^2)$ the approximate form (47) with an enhancement factor of 2, we obtain for (54)

$$\delta k_c=\frac{7}{3}k_\theta \ , \tag{55}$$

which gives for $k_c/k_r$ 12.7% in case (a) and 6.3% in case (b), in good agreement with the exact value. The minor differences are due to the neglect of the other terms in the perturbation.

The corresponding curve for the formation entropy $S_F$, in case (a), is plotted in Fig. 8. The entropy first increases linearly and then diverges at a value $\delta k$ equal to $\delta k_c$. An important conclusion is thus that the entropy can take high values, much larger than the currently observed one which is about $1.5k$. This is still more true in case (b), and there is no reason that the vacancy could not ac-

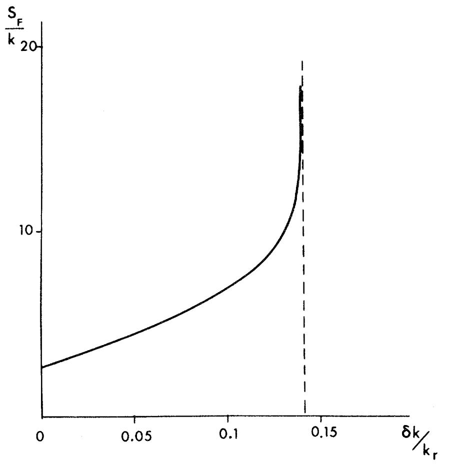

FIG. 8. Formation entropy $S_F$ vs the relative change in force constant $\delta k/k_r$.

count for the observed high-temperature value of $10-15k$.

A definite proof of this effect would require a much deeper analysis of the local changes in force constants. This could be done, for instance, by including the anharmonic terms in the radial potential of the twelve nearest neighbors' backbonds. The response to forces could then be analyzed as before but with position-dependent force constants. Such a calculation is not simple and is beyond the scope of the present work. However, one can anticipate that for some applied forces there will be an enhancement of the displacements with respect to these of the linear theory (e.g., a reduction in the effective response). This would result in an increase of the formation entropy $S_F$ which can be quite important as we have just shown.

## VII. CONCLUSION

We have shown in this paper that the lattice response near the vacancy in silicon is very soft. This means that the effective force constants describing the response to applied forces are low and that the vibration entropy is larger than usual. The reason for this comes from the low-lying transverse acoustical branches which are fairly sensitive to perturbations. A good example of this behavior is provided by the influence of local changes in force constants which are found to be capable of producing important increases in the response and in the formation entropy.

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[*] LA 253, CNRS.

[1] C. A. Coulson and M. J. Kearsley, Proc. R. Soc. London Ser. A 241, 433 (1957).

[2] G. D. Watkins, J. Phys. Soc. Jpn. Suppl. II, p. 22 (1963).

[3] G. D. Watkins, in *Effet des Rayonnements sur les Semiconducteurs* (Dunod, Paris, 1964), p. 97.

[4] J. Friedel, M. Lannoo, and G. Leman, Phys. Rev. 164, 1056 (1967).

[5] F. P. Larkins, J. Phys. Chem. Solids 32, 965 (1971)

[6] G. D. Watkins and R. P. Messmer, Phys. Rev. Lett. 32, 1244 (1974).

[7] R. P. Messmer, in *Lattice Defects in Semiconductors,* Proceedings of the International Conference on Lattice Defects in Semiconductors, Freiburg, Germany, 1974 (IOP, London, 1975), p. 44.

[8] M. Lanoo, in *Defects and Radiation Damage in Semiconductors,* Proceedings of the International Conference on Radiation Effects in Semiconductors, Nice, 1978, edited by J. Albany (IOP, London, 1979), p. 1.

[9] M. Lanoo, G. A. Baraff, and M. Shlüter, Phys. Rev. B 24, 955 (1981).

[10] G. A. Baraff and M. Schlüter, Phys. Rev. Lett. 41, 892 (1978).

[11] G. A. Baraff and M. Schlüter, Phys. Rev. B 19, 4965 (1979).

[12] J. Bernholc, N. Lipari, and S. T. Pantelides, Phys. Rev. Lett. 41, 895 (1978).

[13] S. G. Louie, M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1654 (1976).

[14] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. Lett. 43, 956 (1979).

[15] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B 21, 3563 (1980).

[16] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B 21, 5662 (1980).

[17] G. D. Watkins and J. R. Troxell, Phys. Rev. Lett. 44, 593 (1980).

[18] F. P. Larkins and A. M. Stoneham, J. Phys. C 4, 143 (1971).

[19] A. Seeger and M. L. Swanson, in *Lattice Defects in Semiconductors,* edited by R. R. Hasiguti (University of Tokyo Press and The Pennslyvania State University Press, Tokyo and Philadelphia, 1968), p. 93

[20] A. Seeger and K. P. Chik, Phys. Status Solidi 29, 455 (1968).

[21] A. Seeger, in *Radiation Effects in Semiconductors,* edited by J. W. Corbett and G. D. Watkins (Gordon and Breach, New York, 1971), p. 29.

[22] R. F. Peart, Phys. Status Solidi 15, K119 (1966).
[23] R. N. Goshtagore, Phys. Rev. Lett. 16, 890 (1966).
[24] B. J. Masters, Solid State Commun. 9, 283 (1971).
[25] J. A. Van Vechten and C. D. Thurmond, Phys. Rev. B 14, 3539 (1976).
[26] J. A. Van Vechten and C. D. Thurmond, Phys. Rev. B 14, 3551 (1976).
[27] M. Lannoo and J. C. Bourgoin, Solid State Commun. 32, 913 (1979).
[28] G. Allan and M. Lannoo, in *Radiation Effects in Semiconductors* (IOP, London, 1981), Chap. 2, p. 163.
[29] P. N. Keating, Phys. Rev. 145, 637 (1966).
[30] F. Herman, J. Phys. Chem. Solids 8, 405 (1959).
[31] D. Weaire and R. Alben, Phys. Rev. Lett. 29, 1505 (1972).
[32] L. Salter, Proc. R. Soc. London Ser. A 233, 418 (1956).
[33] L. Dobrzynski and J. Friedel, Surf. Sci. 12, 649 (1968).
[34] M. Lannoo, Ann. Phys. (Paris) 6, (1968).
[35] N. O. Lipari, J. Bernholc, and S. T. Pantelides, Phys. Rev. Lett. 43, 1354 (1979).
[36] M. Jaros, C. O. Rodrigues, and S. Brand, Phys. Rev. B 19, 3137 (1979).