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Lattice Dynamics of CsI Containing Impurity Ions

Bal K. Agrawal and P. N. Ram
Department of Physics, University of Allahabad, Allahabad, India
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A new effective force constant in crystals introduced earlier in the framework of a nearest-neighbor rigid-ion model of lattice dynamics has been calculated in a self-consistent manner. The present force constant is general in the sense that it can be evaluated for any frequency between zero and infinity. The effective force constants defined by the earlier workers are seen to be special cases of this force constant. The method is applied to determine force constants both at the positive-ion and at the negative-ion sites in CsI, which possesses a CsCl crystal structure. The eigenfrequencies and the eigenvectors for CsI obtained by Mahler in the breathing shell model have been utilized for evaluating the pertinent Green's functions. The results of the calculation of these Green's functions are also reported.

I. INTRODUCTION

Much experimental and theoretical work on the dynamical properties of imperfect alkali halides has been done in recent years. Most of the investigations were directed toward the study of the behavior of impurity ions in alkali halides having a rock-salt structure, although the dynamical response due to some impurities in CsCl structure has been investigated in some experiments, e.g., far-infrared absorption due to U centers in cesium halides[1,2] and due to monovalent cations in CsI[3] and CsCl[4] or due to the molecular ions OH^- and OD^- in CsBr and CsI,[5] but no elaborate attempt has been made to understand the data theoretically. In order to study the various dynamical properties of an imperfect crystal, a detailed knowledge of the lattice vibrations is required. It is therefore useful to make a systematic study of the vibrational Green's functions of these crystals.

In order to understand the various defect properties in the framework of the nearest-neighbor approximation, the lattice Green's functions have been computed for both the anion and cation impurities in CsI. These Green's functions have been utilized to study the resonance and the localized modes due to impurities. After using the experimentally observed frequencies of the resonance or the localized modes, a new self-consistent method has been evolved to determine the earlier defined[6] nearest-neighbor effective force constant for a host lattice. The method has been applied to the case of CsI using the positive and the negative impurity ions as probes. The results are compared with the values of the force constants calculated by other methods which are, in fact, special cases of the present method.

In Sec. II, the defect model is described and two special cases of the new force constant are discussed. The numerical results are obtained in Sec. III and are discussed in Sec. IV.

TABLE I. Perfect-lattice Green's functions used in Secs. II and III. $g_{ij}(l,\ l',\ z) \equiv g_{ij}(n_1,\ n_2,\ n_3)$, where the difference in the lattice vectors $(\vec{R}_l - \vec{R}_{l'})$ is denoted by $(n_1,\ n_2,\ n_3)\frac{1}{2}a$ and a stands for the edge of the unit cube.

Symbol	$g_{ij}(n_1,\ n_2,\ n_3)$
$g_1^\pm$	$g_{xx}(0,\ 0,\ 0)$
$g_2^\pm$	$g_{xx}(1,\ 1,\ 1)$
$g_3^\pm$	$g_{xy}(1,\ 1,\ 1)$
$g_4^\pm$	$g_{xx}(2,\ -2,\ 0)$
$g_5^\pm$	$g_{zz}(2,\ -2,\ 0)$
$g_6^\pm$	$g_{xy}(2,\ -2,\ 0)$
$g_7^\pm$	$g_{xx}(2,\ 2,\ 2)$
$g_8^\pm$	$g_{xy}(2,\ 2,\ 2)$
$g_9^\pm$	$g_{xx}(2,\ 0,\ 0)$
$g_{10}^\pm$	$g_{yy}(2,\ 0,\ 0)$

II. PERTURBATION MODEL

The nearest-meighbor perturbation model for a substitutional impurity in a solid of CsCl strucure has been discussed in an earlier paper.[6] Except for the cases of more comples defects such as a defect with an off-center configuration or a molecular impurity ion, the cubic point-group symmetry of the defect site is preserved for the case of a substitutional impurity. The perturbation matrix $P(\omega^2)$ and the Green's-function matrix $g(z) = (L_0 - zI)^{-1}$ can be easily block diagonalized according to the different irreducible representations pertaining to the point group O_h. As defined in Ref. 6, the perturbed phonon propagator $g(z)$ can be expressed in terms of the unperturbed ones. The elements $g_\mu^\pm$ used in the present calculations are presented in Table I. The elements of the perturbation matrix $P(\omega^2)$ in its general form have been discussed in detail in Ref. 6. The perturbation due to a single impurity is characterized completely by three parameters ϵ, λ, and λ'. Here $\epsilon = \Delta M/M_\pm$ is the mass-change parameter, and λ and λ' represent the changes in the nearest-neighbor central and noncentral force constants, respectively. The upper or lower sign (±) on the Green's functions and M specifies the quantities for the positive or negative impurity ions, respectively.

The present model will give a meaningful picture of the physical situation of the defect problem, if we are able to specify satisfactorily the parameters λ and λ'. In the rigid-ion picture of the host lattice, the assumption of a nearest-neighbor interaction in the present case presents no conceptual difficulty, but when we consider a deformation dipole model or a shell model for the host-lattice dynamics, the situation becomes complex. In order to cope with this difficulty, the parameters λ and λ' must be considered as effective changes in nearest-neighbor central and noncentral force constants.

As the noncentral-force-constant changes are, in general, an order of magnitude smaller than the central ones, in the alkali halides we assume that $\lambda' = 0$. The presumption that the noncentral component of the force constant is much smaller than the central one, particularly in CsI, is supported by the fact that the value of the elastic constant C_{44} is not much different from that of C_{12} in CsI.[7] Also, it has been observed[8] that the assumption $\lambda' = 0$ works well in reproducing the frequency of the low-lying resonant mode with a reasonable changed central force constant. The effective nearest-neighbor force constant for the host lattice is defined for the optically active F_{1u} symmetry modes. By using the relations among the different lattice Green's functions, the calculation is greatly simplified if we restrict ourselves only to the changes in the central forces. In fact, only one Green's function, i.e., $g_1^\pm$, is required in the calculation if one knows the value of the effective central force constant. Conversely, we may use this relation to compute the effective nearest-neighbor central force constant for the host lattice.

The frequencies of a resonance or a localized mode in the irreducible representation Γ are determined by

$$\mathrm{Re} D_\Gamma(z) = 0, \tag{1}$$

where the determinant $D_\Gamma(z)$ is the resonance denominator appearing in the irreducible representation Γ. For central-force-constant changes only, the perturbation affects only the modes which transform according to the irreducible representations A_{1g}, A_{2u}, F_{2g}, and F_{1u}. For these irreducible representations we have[6]

$$D_{A_{1g}}(z) = 1 + \chi\lambda(g_1^\mp - 2g_4^\pm + g_5^\pm + 2g_6^\pm - g_7^\pm - 2g_8^\pm - g_9^\pm + 2g_{10}^\pm), \tag{2}$$

$$D_{A_{2u}}(z) = 1 + \chi\lambda(g_1^\mp - 2g_4^\pm + g_5^\pm + 2g_6^\pm + g_7^\pm + 2g_8^\pm + g_9^\pm - 2g_{10}^\pm), \tag{3}$$

$$D_{F_{2g}}(z) = 1 + \tfrac{1}{3}\chi\lambda(3g_1^\mp + 2g_4^\pm - g_5^\pm - 3g_7^\pm - 2g_6^\pm - 6g_8^\pm + g_9^\pm - 2g_{10}^\pm), \tag{4}$$

and

$$D_{F_{1u}}(z) = (1 - \epsilon\omega^2 g_1^\pm)[1 + \tfrac{1}{3}\chi\lambda(3g_1^\mp + 2g_4^\pm - g_5^\pm - 2g_6^\pm + 3g_7^\pm + 6g_8^\pm - g_9^\pm + 2g_{10}^\pm)] + \tfrac{8}{3}\lambda[g_1^\pm - 2(\sqrt{\chi})(g_2 + 2g_3^\pm) + \chi\epsilon\omega^2 \times (g_2 + 2g_3^\pm)^2], \tag{5}$$

where $\chi = M_\pm/M_\mp$ is the ratio of ionic masses at the two sublattices. Of these representations, the only important resonance mode corresponds to the F_{1u} irreducible representation which may occur in the whole frequency interval *ranging* from zero to infinity. The perturbations due to the A_{1g} and F_{2g} symmetry components of $P(\omega^2)$ are expected to give rise to resonance modes only in the gap region, if it exists. No local mode or well-defined low-lying resonance modes are expected to occur in these symmetry motions.[9]

Using the relations among different lattice Green's functions as given in the Appendix of Ref. 6, the resonance denominator in the F_{1u} mode may further be reduced to the simple form

$$D_{F_{1u}}(z) = (1+\beta)(1 - \epsilon\omega^2 g_1^\pm) + \beta(1+\epsilon)(3\omega^2/8\eta)(1 + \omega^2 g_1^\pm), \tag{6}$$

where $\eta = \gamma/M_\pm$, γ being the nearest-neighbor central force constant in the pure crystal and $\beta = \lambda/\eta$ the relative change in the force constant due to the impurity ion. By using Eqs. (5) and (6) for the resonance denominator in the F_{1u} symmetry mode, one can calculate the nearest-neighbor central force constant for the pure lattice if one knows the values of the various Green's functions for the experimentally observed resonance- or localized-mode frequency.

We now consider two limiting cases.

(a) *Low-frequency resonances*. In the limiting case $\omega \to 0$, the resonance denominator (6) simplifies to

$$D_{F_{1u}}(z) \simeq 1 + \beta. \tag{7}$$

Thus for a resonance appearing at very low frequency we have

$$\beta \simeq -1, \quad \text{i.e.,} \quad \eta \simeq -\lambda. \tag{8}$$

This implies a complete decoupling of the impurity from the host lattice. This is the effective force constant defined earlier by Benedek and Nardelli.[10]

(b) *High-frequency localized modes*. For a high-frequency localized mode such as a U-center mode appearing due to a light H⁻ ion, the resonance denominator gives approximately

$$\eta \simeq -\lambda(1+\tfrac{3}{8}M_i\omega_L^2), \qquad (9)$$

where $M_i = 1+\epsilon$ is the relative mass of the impurity ions with respect to the host-ion mass and is very small. Equation (9) may be rewritten as

$$\tfrac{8}{3}(\eta+\lambda) \simeq -\beta M_i \omega_L^2 . \qquad (10)$$

The effective force constant by which the impurity is coupled to the host lattice is $\frac{8}{3}(\eta+\lambda)$. It may be noted from Eq. (10) that the effect of the vibrating host lattice on the highly localized impurity motion is approximately contained in β, the relative-force-constant change around the impurity. Klein[11] has defined an effective force constant in the high-frequency region by utilizing the U-center localized mode after neglecting the contributions of the symmetry motions involving the neighboring host-lattice ions of the impurity in the F_{1u} irreducible representation. As the U-center mode is highly localized in space, only the symmetry coordinate containing the motion of the impurity is expected to give reasonable results.

III. NUMERICAL RESULTS

A. Green's-Function Matrix Elements

In order to calculate the complex-valued Green's functions appearing in Eqs. (2)–(6), a detailed knowledge of the frequencies and polarization vectors of the normal modes of the pure crystal should be known. The necessary data for the eigenfrequencies and the polarization vectors were supplied to us by Mahler,[12] who has studied the lattice dynamics of CsI at 4.2 °K using the breathing shell model.[13] In this calculation, a set of the eigenfrequencies $\omega_{k,s}$ and the polarization vectors $\vec{e}(\pm|\vec{k},s)$ were chosen for 2744 distinct points distributed uniformly in the first Brillouin zone (BZ). These points are produced by selecting 120 points in the irreducible $\frac{1}{48}$ part of the first BZ.

A staggered bin averaging procedure is followed in the machine computation of the Green's functions. The Green's function is separated into real and imaginary parts as

$$G(\omega^2) = \sum_k \frac{f(k)}{\omega_k^2 - \omega^2 - 2i\Delta\omega}$$

$$= p\sum_k \frac{f(k)}{\omega_k^2 - \omega^2} + i\pi\sum_k f(k)\delta(\omega_k^2-\omega^2). \qquad (11)$$

First, the expressions $\sum_k f(k)\delta(\omega_k-\omega)$ are calculated and the histograms are obtained for the various Green's functions. To carry out the actual integration for the real part of the Green's functions at low frequencies, the method of Maradudin[14] has been followed. We may write

$$\mathrm{Re}G(\omega^2) = \int_0^{\omega_m} d\omega' \,\frac{QT(\omega') - QT(\omega)}{\omega'^2-\omega^2} - \frac{QT(\omega)}{2\omega}\ln\frac{\omega_m+\omega}{\omega_m-\omega}\,, \qquad (12)$$

where $QT(\omega) = \sum_k f(k)\delta(\omega_k-\omega)$ and ω_m is the maximum frequency of the lattice. The imaginary part in terms of $QT(\omega)$ is given by

$$\mathrm{Im}G(\omega^2) = (\pi/2\omega)\,QT(\omega). \qquad (13)$$

The whole frequency range is divided into 60 equal bins and the histograms are calculated at the center of each bin. Since the mesh points have finite size, the increment in the frequency used in the actual integration should be finite. The value of the increment in the frequency is chosen in such a way that the spurious fluctuations appearing in the Green's functions are minimized. The value 0.6 in the units of the bin width is found to be appropriate in the present calculations.

For the defect model considered here, in all only ten Green's functions are needed for a particular impurity. The value of the element $g_2^{\pm}$ ($=g_2$) remains the same for the case of a positive or a negative impurity ion. The real and imaginary parts of the 19 Green's functions, which are pertinent in the

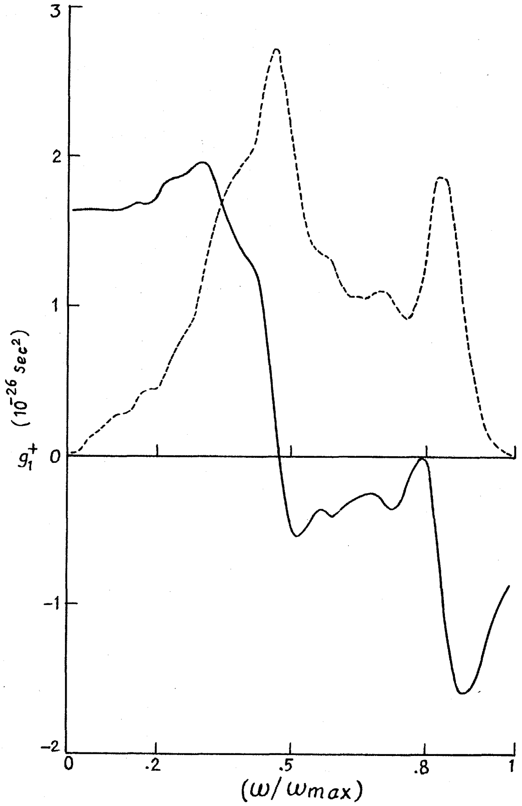

FIG. 1. Green's function g_1^+ (solid curve, real part; dashed curve, imaginary part).

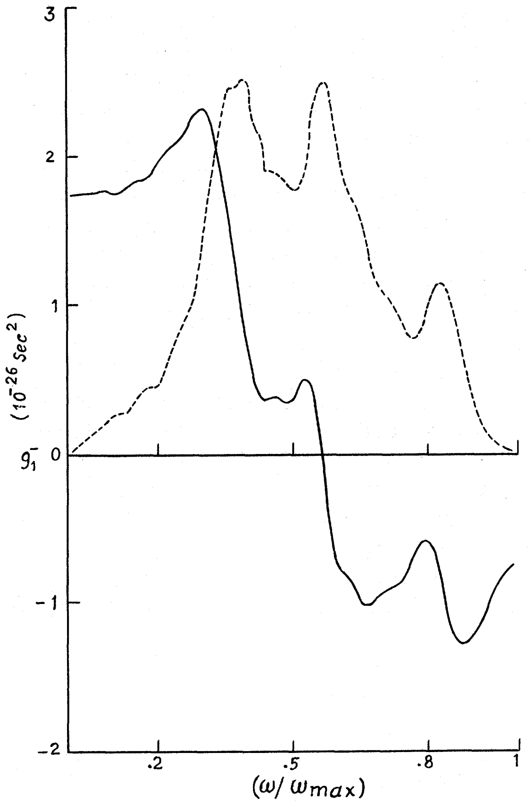

FIG. 2. Green's function g_1^- (solid curve, real part; dashed curve, imaginary part).

framework of the nearest-neighbor approximation, are plotted in Figs. 1-7.

B. Effective Force Constant

As discussed in Sec. II, the effective nearest-neighbor central force constant can be evaluated by using the resonance or the localized-mode frequencies. Recently, Genzel *et al.*[3] have measured the impurity-induced infrared absorption in CsI. There appears a resonance at 14.1 cm^{-1} in the case of CsI doped with Tl$^+$. It has been used to determine the change in the nearest-neighbor central force constant λ by using Eq. (5). This effective force constant is defined in the framework of the rigid-ion model for the host lattice considering only nearest-neighbor interactions. The change in the central force constant is -0.325×10^{26} sec^{-2}. Using this value for λ in Eq. (6), the nearest-neighbor effective force constant ($=\frac{8}{3}\eta$) is 0.92×10^{26} sec^{-2}.

The case of the substitutional negative impurity ion is furnished by the local-mode absorption due to *U* centers in cesium halides observed by Dötsch and Mitra.[2] For the local-mode frequency in CsI, the values of the Green's-function matrix elements in units of (rad/sec)$^{-2}$ are

$$g_1^+(\omega_l^2) = -3.6250\times 10^{-28},$$

$$g_1^-(\omega_l^2) = -3.6081\times 10^{-28},$$

$$g_2(\omega_l^2) = 1.5434\times 10^{-30},$$

$$g_3^-(\omega_l^2) = 1.4133\times 10^{-30},$$

$$g_4^-(\omega_l^2) = -0.55401\times 10^{-30},$$

$$g_5^-(\omega_l^2) = 0.13845\times 10^{-30},$$

$$g_6^-(\omega_l^2) = -0.19255\times 10^{-30},$$

$$g_7^-(\omega_l^2) = -0.19981\times 10^{-30},$$

$$g_8^-(\omega_l^2) = -0.53986\times 10^{-31},$$

$$g_9^-(\omega_l^2) = 2.9529\times 10^{-30},$$

$$g_{10}^-(\omega_l^2) = -0.46863\times 10^{-30}.$$

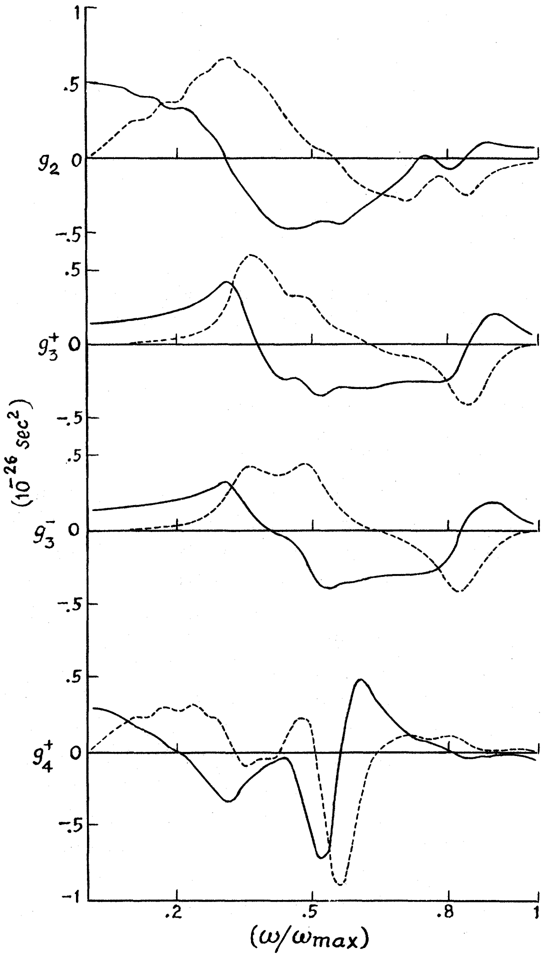

FIG. 3. Green's functions g_2, g_3^+, g_3^-, and g_4^+ (solid curve, real part; dashed curve, imaginary part).

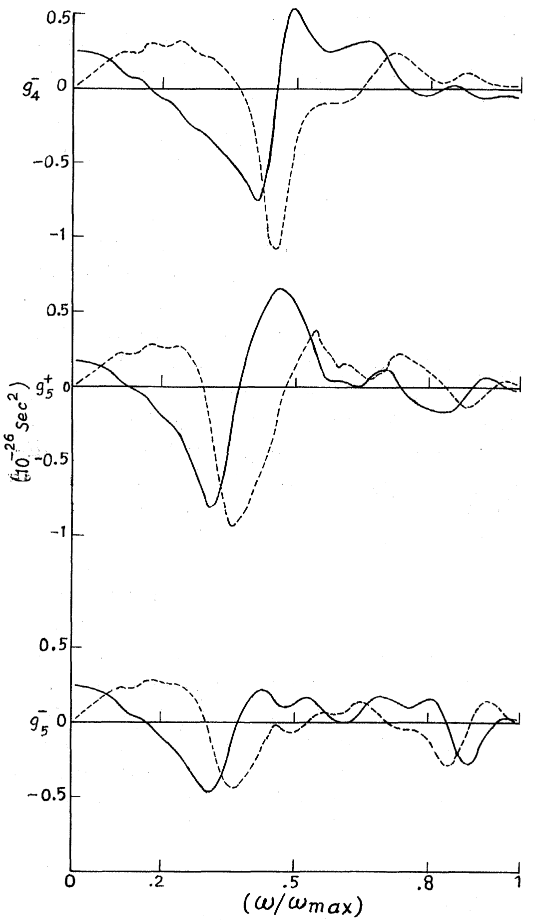

FIG. 4. Green's functions g_4^-, g_5^+, and g_5^- (solid curve, real part; dashed curve, imaginary part).

The local-mode frequency is

$$\omega_l = 5.33074\times 10^{13}\ \text{rad/sec}.$$

The change in the effective central force constant $\frac{8}{3}\lambda$ calculated from Eq. (5) is -0.48×10^{26} sec^{-2} and the value of the nearest-neighbor effective force constant from Eq. (6) is 0.693×10^{26} sec^{-2}.

Now we calculate the value of the force constants for the two special cases (a) and (b) discussed in Sec. II at both the lattice sites occupied by the positive ion and the sites occupied by the negative impurity ion. The values of the force constants derived in these different ways are presented in Table II. The values of the force constants computed by Benedek and Nardelli[15] in the deformation dipole model are also shown in Table II. It must be noted that in their calculation the authors used van der Waals forces which were actually determined for a rock-salt structure.

IV. DISCUSSION

From Table II we note that for the case of the positive-ion site, the value of the force constant determined by Eq. (6) using the frequency of a low-lying resonance node due to a heavy small-sized Tl^+ in CsI is very near to the value obtained in Benedek and Nardelli's approximation given by Eq. (8). The agreement is seen to be very close, which might result from the fact that the comparatively much smaller Tl^+ occupies the site of the larger-sized Cs^+ ion and consequently nearly a perfect decoupling of the impurity ion from the host lattice is observed. A very large change in the force constant, i.e., 94%, also supports this assumption. Further, the present value in the breathing shell model is in complete agreement with the value calculated by Benedek and Nardelli[15] in Hardy's deformation dipole model. This is a very interesting result in view of the fact that two quite different sophisticated models for the lattice dynamics of the host crystal have been used in the calculations. For the case of the negative-impurity-ion site (U center), again the value obtained from Eq. (6) is very near to a value

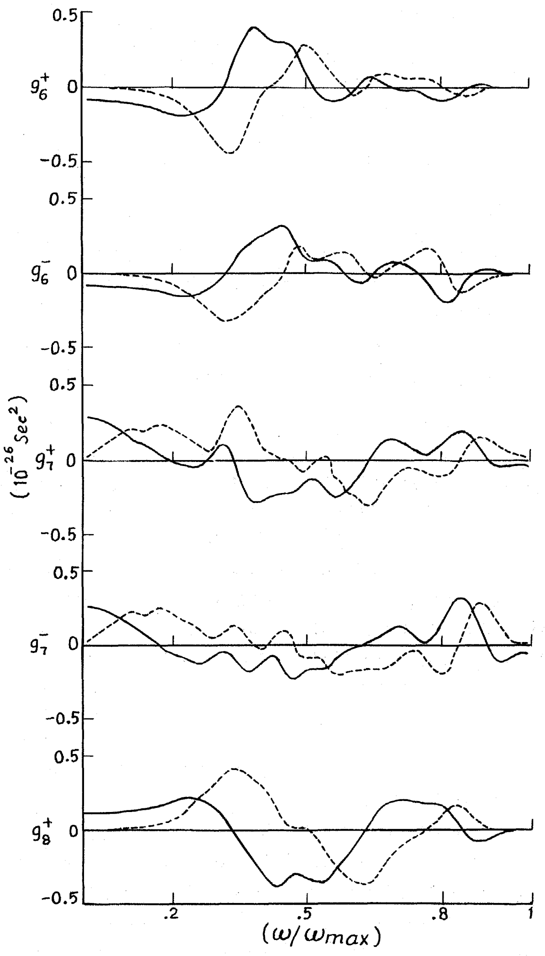

FIG. 5. Green's functions g_6^+, g_6^-, g_7^+, g_7^-, and g_8^+ (solid curve, real part; dashed curve, imaginary part).

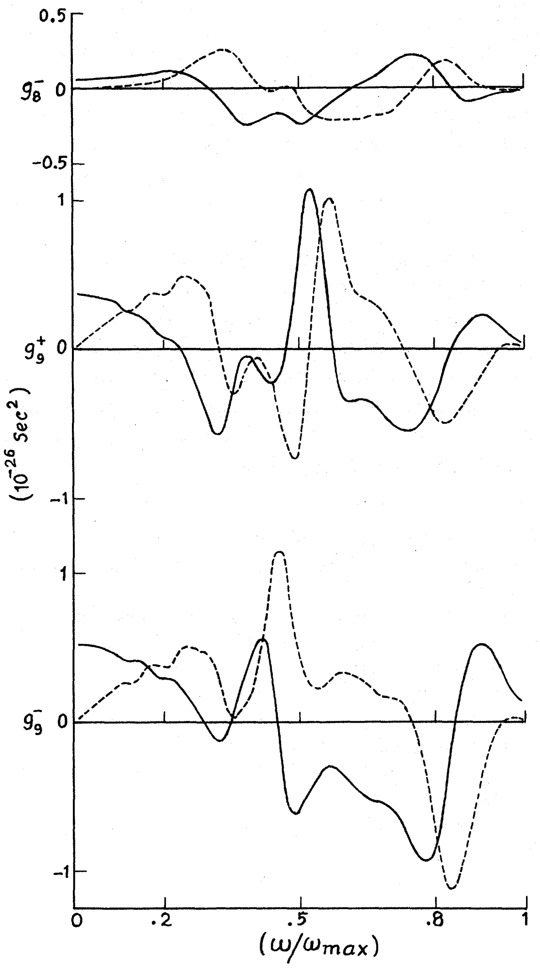

FIG. 6. Green's functions g_8^-, g_9^+, and g_9^- (solid curve, real part; dashed curve, imaginary part).

calculated in Klein's approximation. In fact, the discrepancy lies within 4%, which is not very surprising, since a very-high-frequency localized mode due to the U center has been employed in this determination. The U-center mode is highly localized in space, and is practically independent of the two remaining symmetry motions of the neighboring host ions. This result helps us a lot in future calculations concerning the U-center localized modes, as one can safely ignore the contributions of the symmetry motions of the neighboring ions in the F_{1u} irreducible representation and get rid of very cumbersome matrices of large dimensions. But a large discrepancy is observed between this value of the force constant and that obtained in Benedek and Nardelli's approximation. This is due to the fact that the decrease in the force constant is only about 67.5% and consequently the H^- ion is not completely decoupled from the host lattice. Similarly, our value is totally different from that obtained in the framework of Hardy's deformation dipole model, where the force constant is defined only for the case of a low-lying resonant mode. It is obvious that the low-frequency resonance approximation is inapplicable to the case of a high-frequency localized mode.

V. CONCLUSIONS

A new self-consistent method for determining the force constant for a crystal has been evolved by employing the two different forms of the resonance denominator in the F_{1u} irreducible representation. This effective central force constant for the crystal lattice has been introduced in the rigid-ion model of lattice dynamics in the nearest-neighbor approximation. The force constant is determined in a self-consistent manner by using the results of a realistic calculation of a resonance- or localized-mode frequency and is applicable to all frequencies between zero and infinity. The earlier effective force constants introduced by Benedek and Nardelli and by Klein are seen to be special cases of the present one. The present value of the force constant, using the frequency of the low-lying resonant mode due to the positive impurity ion in the breathing shell model, is in complete agreement with that obtained in the deformation dipole model for host-lattice dynamics. The method can successfully be used for

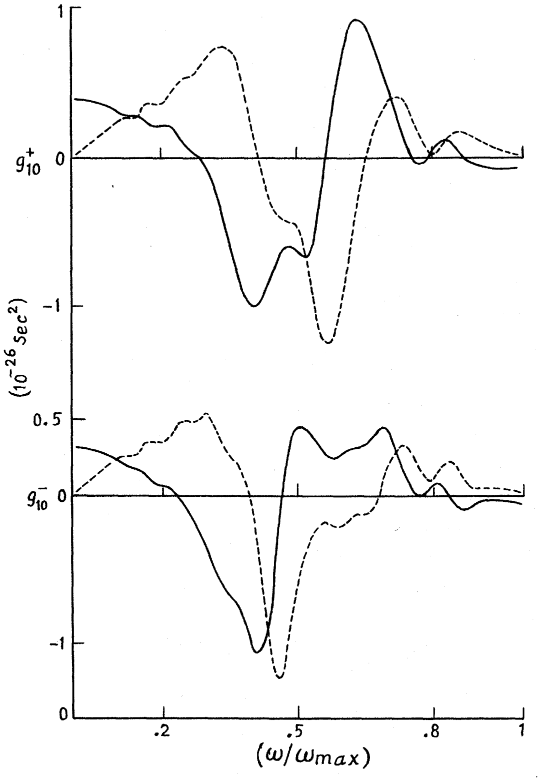

FIG. 7. Green's functions g_{10}^+ and g_{10}^- (solid curve, real part; dashed curve, imaginary part).

TABLE II. Values of the nearest-neighbor effective force constants for the two sublattices in pure CsI calculated in different approximations in units of 10^{26} sec^{-2}.

Lattice site	$\frac{8}{3}\lambda^{a}$	$\frac{8}{3}\eta^{a}$	$\phi_{\mathrm{eff}}/M_{\pm}{}^{b}$	$f^{\pm}/M_{\pm}{}^{c}$	$f^{*}/M_{\pm}{}^{d}$
$+ve$	−0.87	0.92	···	1.02	0.893
$-ve$	−0.48	0.693	0.719	0.95	0.935

[a] Values using Eqs. (5) and (6).

[b] Values in Klein's approximation.

[c] Values using Eq. (8).

[d] Values obtained in the deformation dipole model (Ref. 15).

the determination of the effective force constant in crystals by using an impurity as a probe. Although the present effective nearest-neighbor force constant introduced in the framework of the defect model is physically meaningful, a quantum-mechanical calculation of the force constant similar to Wood and Gilbert's[16] would improve the situation.

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