PHYSICAL REVIEW B VOLUME 17, NUMBER 2 15 JANUARY 1978

Local force variations due to substitution impurities in nine compounds with the zinc-blende structure

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(Received 15 August 1977)

A Green's-function technique and a rigid-ion model including general forces between nearest neighbors, next-nearest neighbors, and Coulomb forces were used to calculate the frequency of vibrational modes against the relative variation of forces between nearest neighbors $\Delta f/f$ for some isolated atomic substitutions in nine compounds possessing the zinc-blende structure: GaP, GaAs, GaSb, InSb, InAs, ZnSe, ZnTe, ZnS, CdTe. By comparison of these results with existing experimental data it was possible to determine $\Delta f/f$ for each particular case. For isoelectronic substitutions this quantity can be far from zero and reaches -53% in the case of B on Ga in GaP, still higher values being obtained for nonisoelectronic substitutions (for example, -87% for beryllium substituted on gallium in GaP). These values are found to depend largely on the force model adopted for the perfect crystal and especially on the way in which the forces between next-nearest neighbors are taken into account. No general correlation was observed between the size of the impurity compared with the atom it replaces and the $\Delta f/f$ values, which however are clearly related to the donor or acceptor situation of this impurity: for GaAs, where a term of comparison exists, our results agree quite well with those given by a recent model accounting for local charge and polarizability changes consistent with this situation.

I. INTRODUCTION

During the last fifteen years or so, a large amount of work has been devoted to the study of crystal lattices perturbed by a small impurity fraction. Most of this research concerns the vibrational modes of impurities deliberately introduced into compounds of zinc-blende structure, especially II-VI and III-V compounds for which very many experimental results are now available on localized-mode frequencies of isolated impurities; moreover, in most cases the dynamics of the perfect lattice is known, and various calculation methods have been developed where, by knowing the perfect-lattice dynamics and the vibrational frequencies of the defect, the perturbation may be determined. It is now possible therefore to obtain a general view of such perturbations, and this article is devoted to the comparative study of local force variations due to isolated atomic substitutions (T_d symmetry defect) in nine zinc-blende structure compounds: GaP, GaAs, GaSb, InP, InSb, ZnSe, ZnTe, ZnS, and CdTe. An exact knowledge of the perturbations introduced by these elementary defects is essential as a first approach towards the understanding of more complex point defects, for which some experimental results, relatively few but significant, now exist.[1-5] Such a study will be given later.

A vibrational mode of an isolated impurity in a crystal was first observed quite recently,[6] and so far most of the experimental results have been obtained by infrared spectroscopy (absorption or reflection) or by Raman spectroscopy (for compilation see Refs. 1, 7–9, and Table III). Together with all these numerous data concerning localized modes, some examples of gap modes[10,11] or band modes[12,13] are known. On the basis of these experimental results a series of attempts has been made to calculate the perturbation introduced in the lattice by the presence of the defect, and different models have been proposed. These include: (i) molecular models originally intended for alkali halides but difficult to apply to zinc-blende-type crystals[14-17]; (ii) diatomic linear-chain models[8,18,19]; (iii) models using variational methods[20]; models using a Green's-function technique.[21-23]

All these studies have shown that an isolated atomic substitution in a zinc-blende-type crystal cannot be reduced to a defect involving a local mass change only, and that it is necessary, especially in the case of a nonisoelectronic substitution, to account for a local modification of interatomic forces.[22,24] For instance, in a very recent article, Bellomonte proposed a model for GaAs by which the local change in forces can be predicted from the charge and polarizability variation.[25]

Of all these perturbation calcuation methods the most frequently used is that involving the Green's-function technique, which enables local short-range force changes to be introduced quite easily. It has the additional advantage of giving not only the localized modes but also all possible vibrational modes of the impurity (gap and band modes). This is the method used in the present work.

II. GREEN'S-FUNCTION METHOD

The condition necessary for the existence of a vibrational mode (localized, gap, or band) is that the real part of the secular determinant cancels out, i.e.,[21,23]

$$Re\,[\mathrm{Det}(I-g\cdot\delta l)]=0\,, \tag{1}$$

where g is a Green's-function matrix of the perfect crystal and δl a perturbation matrix which defines the defect and includes local modifications of both mass and forces. The dimension of the matrices g and δl is that of the "defect space," i.e., $3N\times 3N$, where N is the number of atoms which have their situation been changed by the presence of the defect.

The Green's functions are obtained from the eigenvalues and the eigenvectors of the Fourier matrix,[23] themselves calculated from a set of parameters characteristic of the force model adopted to describe the dynamic properties of the perfect crystal. In the present work, a rigid-ion model was used, accounting for the general interactions between nearest neighbors and next-nearest neighbors, and the Coulomb forces. This model, developed by Kunc[31] and possessing eleven adjustable parameters [known as rigid-ion model (RIM) 11 in Refs. 26 and 27], is not the most complete[28] but gives a correct account of inelastic neutron scattering results and elastic constant values for all III-V and II-VI compounds having the zinc-blende structure. Moreover the parameter-adjustment procedure is relatively easy.

The Green's functions involved in Eq. (1) were thus calculated with the sets of 11 parameters established by Kunc for ZnS, ZnSe, GaP, GaAs, and InSb,[29,30] and by Plumelle *et al.* for CdTe, ZnTe,[27] and InP.[26] For GaSb, it was possible to account satisfactorily (see Fig. 1 and Table I) for the neutronic results established by Farr *et al.*[57] with the set of parameters given in Table II, by performing successive adjustments at the characteristic points.[27] The perturbation matrix δl is defined by the mass of the substituted atom (known exactly) and the local interatomic force variation. The hypotheses adopted are those of Refs. 23 and 26, i.e., (i) only the force constants between nearest neighbors (called A and B in Refs. 26, 27, and 31) are liable to vary; (ii) moreover, these two force constants change in the same way, so that A and B become aA and aB respectively after perturbation. Thus the solutions of Eq. (1) depend on a single parameter, i.e., $t=1-a=-\Delta f/f$.

The first hypothesis involves five atoms only: the substituted atom and its nearest neighbors alone have their situation changed by the defect so that the matrices g and δl take the dimension 15×15. The total representation then breaks up into irreducible representations as follows[23,24]:

$$\Gamma_{\mathrm{tot}}=A_1+E+F_1+3F_2\,. \tag{2}$$

The solutions of Eq. (1) belonging to these different irreducible representations were therefore worked out for t varying between +1 and −1, proceeding by Green's-function calculation as

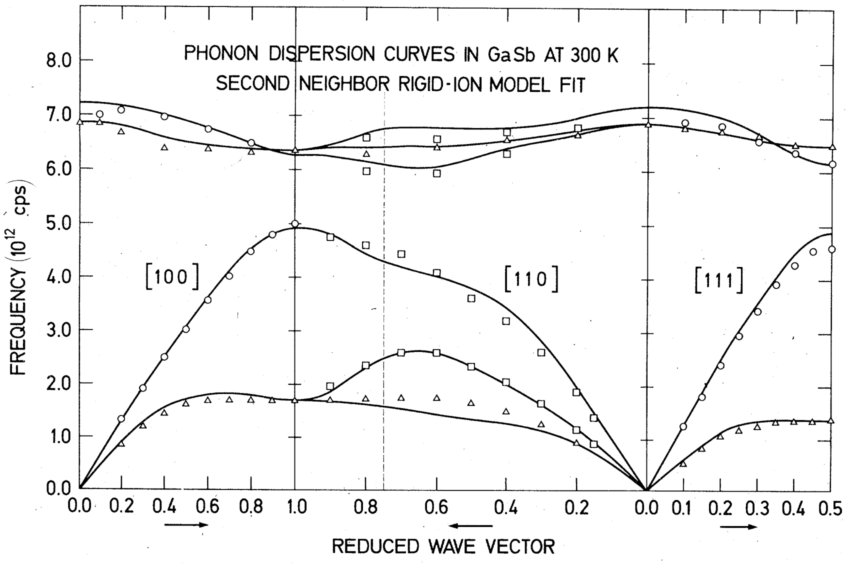

FIG. 1. Experimental results (Ref. 57) and phonon-scattering curves calculated with the eleven-parameter rigid-ion model (Ref. 31) for GaSb.

TABLE I. Experimental and calculated values for gallium antimonide. Frequency in 10^{12} cycles/sec.; C_{11}, C_{12}, C_{44} in 10^{11} dyn cm^{-2}.

	Gallium antimonide Experimental results	 Calculated results [a]
C_{11} [b]	8.839 ± 0.008	8.996
C_{12} [b]	4.033 ± 0.010	4.033
C_{44} [b]	4.316 ± 0.004	4.316
Γ (LO)	7.164 [c]	7.194
Γ (TO) [d]	6.87 ± 0.140	6.901
X (TO) [d]	6.36 ± 0.130	6.377
X (LO) [d]	6.35 ± 0.130	6.236
X (LA) [d]	4.99 ± 0.100	4.896
X (TA) [d]	1.698 ± 0.034	1.708
L (TO) [d]	6.480 ± 0.130	6.482
L (LO) [d]	6.150 ± 0.120	6.102
L (TA) [d]	1.368 ± 0.027	1.343
L (LA) [d]	4.600 ± 0.090	4.923

[a] Obtained with the eleven-parameter rigid-ion model and the force-constant values given in Table II.

[b] Reference 68.

[c] The experimental value of Γ(LO) is not given in Ref. 57. The extrapolated value 7.164 is taken on the assumption that the experimental Γ(LO)−Γ(TO) value is that obtained optically, i.e., 0.294 (Ref. 67).

[d] Reference 57.

described in Ref. 26.

In most cases, Eq. (1) only gives solutions corresponding to vibrational modes of F_2 symmetry, with which the present article deals exclusively. Table III gives, for localized modes of F_2 symmetry: (i) a compilation of experimental data on the frequencies of these modes; (ii) the $\Delta f/f$ values for which the solution of Eq. (1) coincides in each particular case with the experimental value; (iii) for comparison, the relative variations $\Delta\varphi/\varphi$ of the force constant associated with the radial (central) part of the interaction between nearest neighbors, calculated by Talwar *et al.*[22] using the same Green's-function technique but with a less elaborate rigid-ion model possessing only seven adjustable parameters [Rigid-ion model seven (RIM 7)].

TABLE II. Rigid-ion model, eleven-parameter version.[a]

Gallium antimonide
$a_0 = 3.04795$
$M_1 = 69.72$
$M_2 = 121.75$
$Z = 0.484$
$A = -0.356$
$B = -0.262$
$C_1 = -0.019$
$D_1 = -0.067$
$E_1 = +0.070$
$F_1 = +0.130$
$C_2 = -0.028$
$D_2 = +0.023$
$E_2 = -0.120$
$F_2 = -0.119$

[a] a_0 in Å; M_1, M_2 in a.m.u.; $A, B, \ldots, F_1, F_2$ in 10^5 dyn cm^{-1}. The parameters are defining the best eleven-parameter models (solid lines in Fig. 1).

Figs, 2–9 show the calculated localized-mode frequency variations versus t for different atomic substitutions, together with the corresponding experimental data.

III. RESULTS AND DISCUSSION

A. Isoelectronic substitutions

Table III shows that for isoelectronic substitutions the relative variation of forces between nearest neighbors, $\Delta f/f$, can take values quite different from zero (for example, −0.53 for B on Ga in GaP and +0.43 for P on Sb in InSb). A similar behavior, though much less pronouced (±0.2 maximum), appears in the results of Talwar *et al.*[22] (see $\Delta\varphi/\varphi$, Table III). In an earlier article, Gaur *et al.*[56] had calculated the localized-mode frequency for different isolated atomic substitutions in a set of II-VI and III-V compounds. Here again, Green's-function technique was used but with a rigid-ion model including only four adjustable parameters, and therefore, accounting very inadequately for the forces between next-nearest neighbors. These authors had assumed moreover that the force constants remain unchanged after perturbation on the basis of the isotopic-defect approximation, a hypothesis later justified in the case of isoelectronic substitutions by the fact that their calculated values for the localized mode frequencies are generally very close to the experimental values. Thus, the compared results of calculations by Gaur *et al.*[56], Talwar *et al.*,[22] and the present work show that for isoelectronic substitutions the more exactly the forces between next-nearest neighbors are taken into account the higher are the $\Delta f/f$ values obtained.

At this level three comments can be made:

(a) When the substituted atom is very light it may be assumed that in the localized mode it vibrates alone, the other atoms of the lattice remaining almost still. Under these conditions the recoil force due to short-range forces exerted on the substituted atom for an elementary displacement along the x axis depends only on the force constants appearing on the diagonals of coupling matrices between nearest neighbors (A) and next-nearest neighbors (F_i and C_i)[31] and is written, bearing in mind the change in A ($A \to aA$)

TABLE III. Localized-mode frequency for isolated substitutional impurities in some II-VI and III-V compounds possessing the zinc-blende structure.

Compound [a]	Experimental results [b] (cm^{-1})	$\Delta\varphi/\varphi$ [c]	$\Delta f/f=-t$ (Present work)	Ref.
$\underline{\mathrm{Ga}}\mathrm{P}$:^{9}Be	527		−0.87	32
$\underline{\mathrm{Ga}}\mathrm{P}$:^{10}B	592.7	+0.18	−0.53	33
$\underline{\mathrm{Ga}}\mathrm{P}$:^{11}B	570	+0.18	−0.53	33
$\underline{\mathrm{Ga}}\mathrm{P}$:Al	444.7	+0.19	−0.23	34
$\underline{\mathrm{Ga}}\mathrm{P}$:^{28}Si	464.9	+0.39	−0.08	34, 35
$\underline{\mathrm{Ga}}\mathrm{P}$:^{29}Si	461.1	+0.39	−0.08	34, 35
$\underline{\mathrm{Ga}}\mathrm{P}$:^{30}Si	456.6	+0.39	−0.08	34, 35
$\mathrm{Ga}\underline{\mathrm{P}}$:^{12}C	606.2	+0.21	+0.37	36
$\mathrm{Ga}\underline{\mathrm{P}}$:^{14}C	564	+0.21	+0.37	36
$\mathrm{Ga}\underline{\mathrm{P}}$:^{14}N	495.8 (488)	−0.15	−0.03	37
$\mathrm{Ga}\underline{\mathrm{P}}$:^{15}N	480.3 (472)	−0.15	−0.03	37
$\mathrm{Ga}\underline{\mathrm{P}}$:O	464	−0.13	~0	34
$\underline{\mathrm{Ga}}\mathrm{As}$:^{9}Be	482		−0.63	38
$\underline{\mathrm{Ga}}\mathrm{As}$:^{10}B	540.2	+0.09	−0.33	33
$\underline{\mathrm{Ga}}\mathrm{As}$:^{11}B	517.0	+0.09	−0.33	33
$\underline{\mathrm{Ga}}\mathrm{As}$:^{24}Mg	331		−0.5	39
$\underline{\mathrm{Ga}}\mathrm{As}$:^{25}Mg	326		−0.5	39
$\underline{\mathrm{Ga}}\mathrm{As}$:^{26}Mg	321.5		−0.5	39
$\underline{\mathrm{Ga}}\mathrm{As}$:^{27}Al	362	+0.05	−0.18	40
$\underline{\mathrm{Ga}}\mathrm{As}$:^{28}Si	384	+0.23	+0.03	41
$\underline{\mathrm{Ga}}\mathrm{As}$:^{30}Si	374	+0.23	+0.03	41
$\mathrm{Ga}\underline{\mathrm{As}}$:^{12}C	582.4	+0.40	+0.61	33
$\mathrm{Ga}\underline{\mathrm{As}}$:^{13}C	561.2	+0.40	+0.61	33
$\mathrm{Ga}\underline{\mathrm{As}}$:^{28}Si	399	+0.39	+0.54	41
$\mathrm{Ga}\underline{\mathrm{As}}$:^{30}Si	389	+0.39	+0.54	41
$\mathrm{Ga}\underline{\mathrm{As}}$:^{31}P	355	+0.18	+0.31	40
$\underline{\mathrm{Ga}}\mathrm{Sb}$:Al	316.7	+0.012	+0.15	42
$\mathrm{Ga}\underline{\mathrm{Sb}}$:P	324	+0.18	−0.28	43
$\mathrm{Ga}\underline{\mathrm{Sb}}$:As	240	−0.017	−0.14	43
$\underline{\mathrm{In}}\mathrm{Sb}$:Al	296	−0.04	−0.3	44
$\underline{\mathrm{In}}\mathrm{Sb}$:Ga	196	−0.08	−0.3	43
$\mathrm{In}\underline{\mathrm{Sb}}$:P	293	+0.19	+0.43	8
$\mathrm{In}\underline{\mathrm{Sb}}$:As	200	+0.008	+0.18	43
$\underline{\mathrm{In}}\mathrm{P}$:^{11}B	522.8		+0.25	45
$\underline{\mathrm{Zn}}\mathrm{Se}$:^{6}Li	412		−0.97	46, 48
$\underline{\mathrm{Zn}}\mathrm{Se}$:^{7}Li	383		−0.97	46, 48
$\underline{\mathrm{Zn}}\mathrm{Se}$:Be	450	−0.13	−0.50	47, 48
$\underline{\mathrm{Zn}}\mathrm{Se}$:^{24}Mg	352	+0.20	+0.05	48
$\underline{\mathrm{Zn}}\mathrm{Se}$:^{25}Mg	345	+0.19	+0.05	48
$\underline{\mathrm{Zn}}\mathrm{Se}$:^{26}Mg	334	+0.19	+0.05	48
$\underline{\mathrm{Zn}}\mathrm{Se}$:Al	359	+0.38	+0.30	49, 48
$\mathrm{Zn}\underline{\mathrm{Se}}$:^{32}S	295	+0.05	+0.23	43
$\underline{\mathrm{Zn}}\mathrm{Te}$:Be	415	−0.08	+0.12	50, 51
$\underline{\mathrm{Zn}}\mathrm{Te}$:^{24}Mg	270		+0.10	d
$\underline{\mathrm{Zn}}\mathrm{Te}$:^{25}Mg	265		+0.10	d
$\underline{\mathrm{Zn}}\mathrm{Te}$:^{26}Mg	260.5		+0.10	d
$\underline{\mathrm{Zn}}\mathrm{Te}$:Al	313	+0.52	+0.51	47, 48
$\mathrm{Zn}\underline{\mathrm{Te}}$:^{32}S	269	−0.09	−0.24	43
$\underline{\mathrm{Zn}}\mathrm{S}$:Be	490	+0.16	+0.1	50
$\underline{\mathrm{Zn}}\mathrm{S}$:^{24}Mg	380	+0.07	+0.2	43
$\underline{\mathrm{Zn}}\mathrm{S}$:^{25}Mg	377.5	+0.07	+0.2	43
$\underline{\mathrm{Zn}}\mathrm{S}$:^{26}Mg	374	+0.07	+0.2	43
$\underline{\mathrm{Zn}}\mathrm{S}$:Al	438	+0.58	+0.76	48

TABLE III. *(Continued)*

Compound[a]	Experimental results[b] (cm^{-1})	$\Delta\varphi/\varphi$[c]	$\Delta f/f=-t$ (Present work)	Ref.
Cd<u>Te</u>:^{7}Li	275		−1.08	52
<u>Cd</u>Te:Be	391 (381)	−0.05	−0.5	53, 54
<u>Cd</u>Te:^{24}Mg	249	−0.12	−0.36	53
<u>Cd</u>Te:^{25}Mg	245	−0.12	−0.36	53
<u>Cd</u>Te:^{26}Mg	241	−0.12	−0.36	53
<u>Cd</u>Te:Al	299		+0.23	55
Cd<u>Te</u>:^{32}S	248.6	−0.04	+0.38	53
Cd<u>Te</u>:^{34}S	244.1	−0.04	+0.38	53
Cd<u>Te</u>:Se	170	−0.02	+0.10	52
Cd<u>Te</u>:P	322		+1.15	69

[a] The atom replaced is underlined.

[b] The values in parentheses are not accounted for in the calculation.

[c] Values calculated by Talwar *et al.* (Ref. 22) using a rigid-ion model with seven adjustable parameters.

[d] Experimental values obtained during the present work.

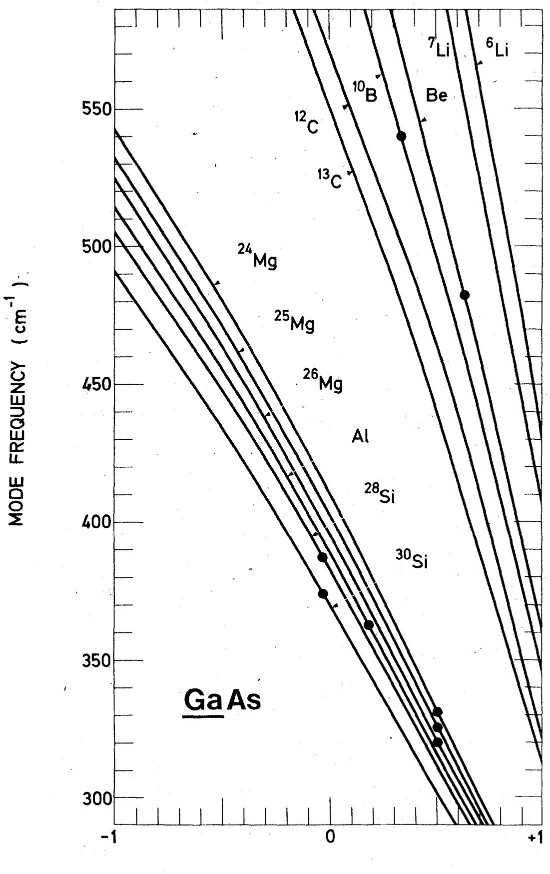

FIG. 2. GaAs—Calculated frequencies of the F_2 localized mode for various substitutions on Ga as a function of the force-constant defect. ● is experimental results (Refs. 33 and 38–41).

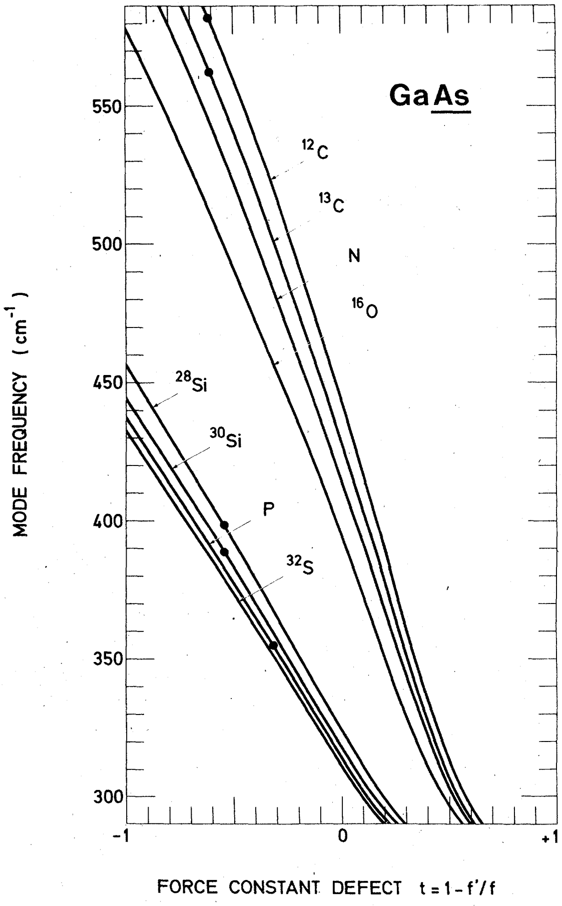

FIG. 3. GaAs—Calculated frequencies of the F_2 localized mode for various substitutions on As as a function of the force-constant defect. ● is experimental results (Refs. 33, 40, and 41).

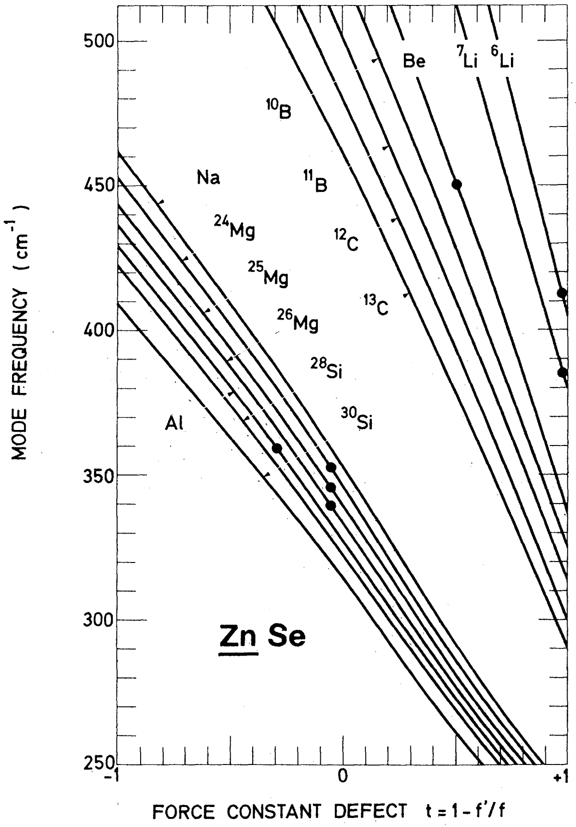

FIG. 4. ZnSe—Calculated frequencies of the F_2 localized mode for various substitutions on Zn as a function of the force-constant defect. ● is experimental results (Refs. 46–49).

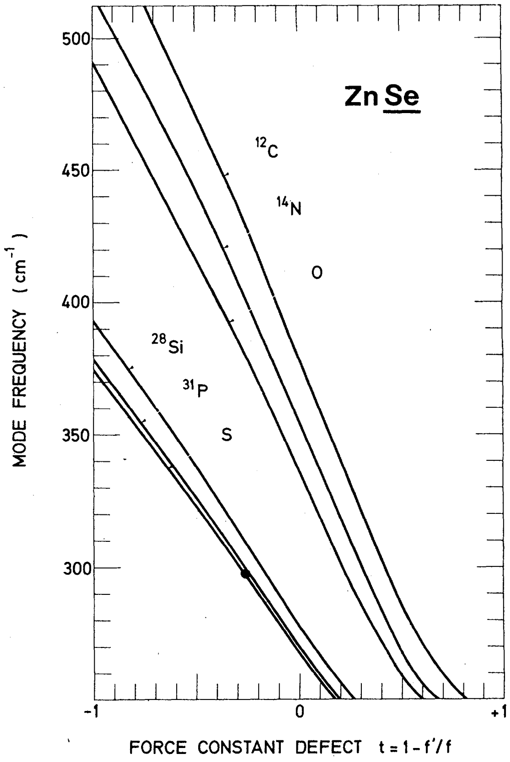

FIG. 5. ZnSe—Calculated frequencies of the F_2 localized mode for various substitutions on Se as a function of the force-constant defect. ● is experimental results (Ref. 43).

due to the defect and given by the present calculation,[26,29]

$$F = 4aA + 4F_i + 8C_i\,,$$

where $i = 1.2$ is the substituted atom number in the unit cell. The localized mode frequency is then given by the expression $\omega_c = 2\pi(F/M_i')^{1/2}$, with M_i' the mass of the impurity. The frequencies calculated by this equation are fairly close to the experimental values (Table IV) which confirms the fact that the impurity vibrates alone. Under these conditions the force constant B, which is not a diagonal term of the coupling matrix between nearest neighbors, is not involved in the calculation and the hypothesis that it varies in the same way as $A(B\rightarrow aB)$ hardly affects the calculated frequency of the localized mode.

(b) Table IV also shows that in the case of very light substituted atoms a certain correlation exists between the calculated $\Delta f/f$ values and the relative magnitude of forces between next-nearest and nearest neighbors defined by the ratio $(F_i + 2C_i)/A$. This correlation has no physical meaning *a priori* but explains why, when forces between next-nearest neighbors are underestimated or neglected as in the case of Ref. 56 for example, the calculation gives $\Delta f/f$ values around 0.

(c) In view of comment (a), it is possible to estimate the force variations to which the full calculation would lead if the three force constants A, F_i, C_i, were all assumed to vary in the same way i.e., $A\rightarrow a'A, F_i\rightarrow a'F_i, C_i\rightarrow a'C_i$. Under such conditions the result would be

$$F = 4aA + 4F_i + 8C_i = a'(4A + 4F_i + 8C_i)\,.$$

The relative force variations $\Delta f'/f = a' - 1$ thus calculated are given in Table IV. These values are somewhat lower than the corresponding $\Delta f/f$ values but still remain quite different from 0. This implies that our results depend little on the hypotheses adopted for the type of short-range force variation but that, even for isoelectronic substitutions, the mass-defect approximation alone without force variation is inadequate.

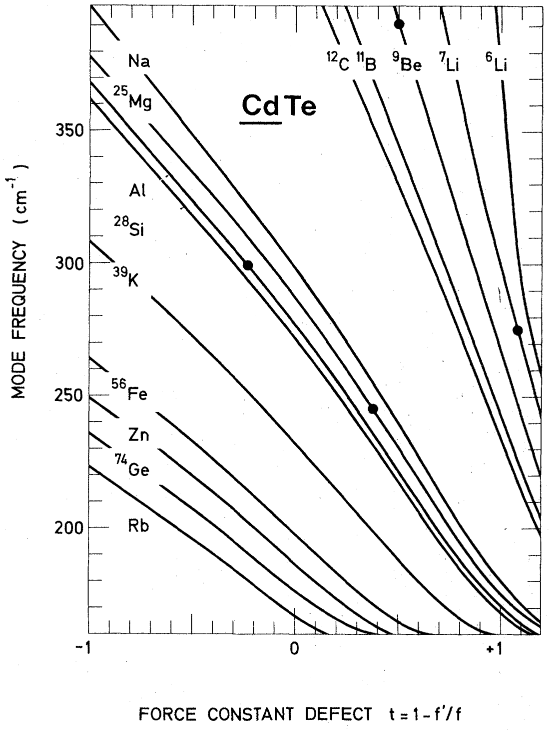

FIG. 6. CdTe—Calculated frequencies of the F_2 localized mode for various substitutions on Cd as a function of the force-constant defect. ● is experimental results (Refs. 52–55).

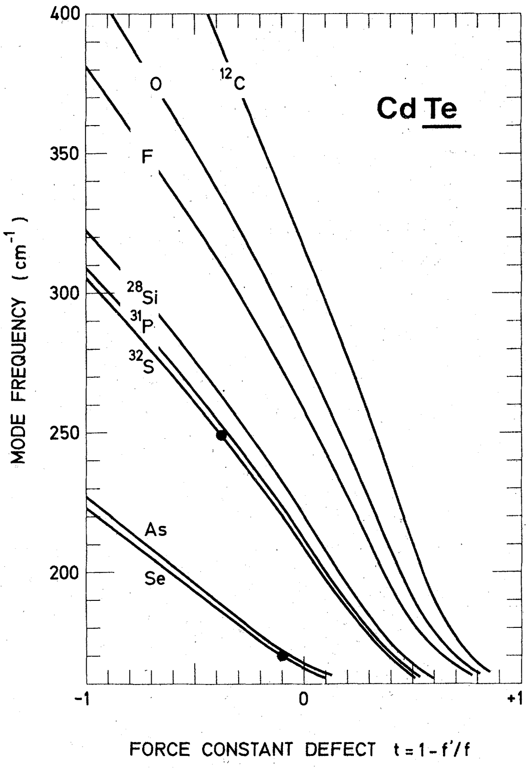

FIG. 7. CdTe—Calculated frequencies of the F_2 localized mode for various substitutions on Te as a function of the force-constant defect. ● is experimental results (Refs. 52 and 53).

B. General case including nonisoelectronic substitutions

On Table III can be seen a large $\Delta f/f$ variation, averaging 20%–30% when we pass from an isoelectronic to a nonisoelectronic substitution of comparable mass; for example, in III-V compounds for the pairs B-Be, Al-Si (GaP, GaAs); Al-Mg (GaAs); N-C (GaP); P-C, P-Si (GaAs), but also in the II-VI compounds Be-Li (ZnSe, CdTe); Mg-Al (ZnSe, ZnTe, ZnS, CdTe). (See Table III, the notation B-Be, Al-Si (GaP, GaAs) means that B or Be, Al or Si are substituted on Ga in GaP or GaAs.) Moreover the sign of this variation is correlated unambiguously with the situation (donor or acceptor) of the nonisoelectronic impurity with respect to that of the atom it replaces. On analyzing Gaur's work,[56] Grimm[58] also found a relationship, for III-V compounds, between the relative short-range force variation which must be considered in order to account for the experimental data and the donor or acceptor situation of the impurity in substitutional site, i.e. using our notations: (i) $\Delta f/f \simeq 0$ for an isoelectronic substitution, (ii) $\Delta f/f \simeq +0.25$ for a single donor on site III or a single acceptor on site V, and (iii) $\Delta f/f \simeq -0.25$ for a single acceptor on site III, (iv) $\Delta f/f \simeq +0.40$ for a double acceptor on site V, and (v) $\Delta f/f \simeq -0.52$ for a double donor on site III. Thus, the relative force constant variation is directly dependent on the charge difference between the defect and its neighbors.[58] The results obtained in the present article are very similar on condition that account is taken of the force-constant variations with respect to those which must be introduced for an isoelectronic substitution of comparable mass, for example in the case of GaAs,

$$\delta\left(\frac{\Delta f}{f}\right)^{\rm Si}_{\rm Al} = \frac{\Delta f({\rm Si}) - \Delta f({\rm Al})}{f} = \frac{f'({\rm Si}) - f'({\rm Al})}{f} = +0.21$$

for a single donor on site III, and

$$\delta\left(\frac{\Delta f}{f}\right)^{\rm Mg}_{\rm Al} = \frac{f'({\rm Mg}) - f'({\rm Al})}{f} = -0.32$$

for a single acceptor on site III.

The case of multiple acceptors has been neglected here, especially that of lithium on a site III in III-V compounds. Recent studies[59] in fact have shown that lithium does not exist as an isolated impurity in GaAs, in contradiction to earlier work where the bands at 406 and 379 cm^{-1} were

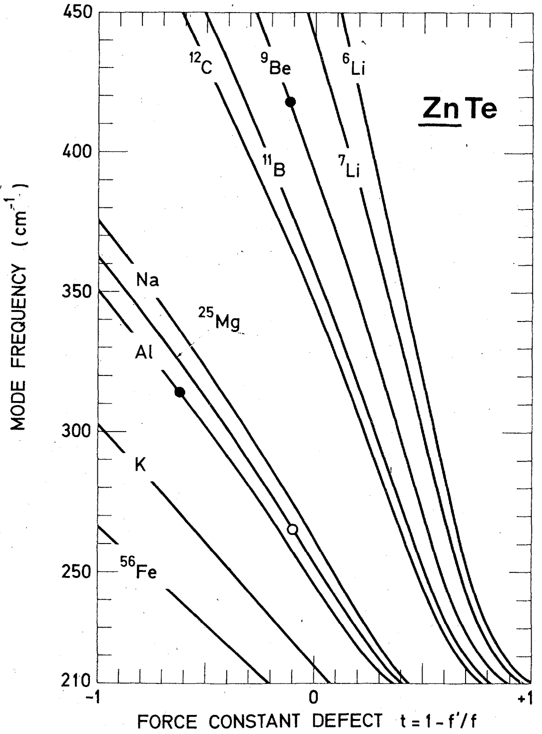

FIG. 8. ZnTe—Calculated frequencies of the F_2 localized mode for various substitutions on Zn as a function of the force-constant defect. ● is experimental results (Refs. 47, 48, 50, and 51). ○ is experimental result obtained during the present work.

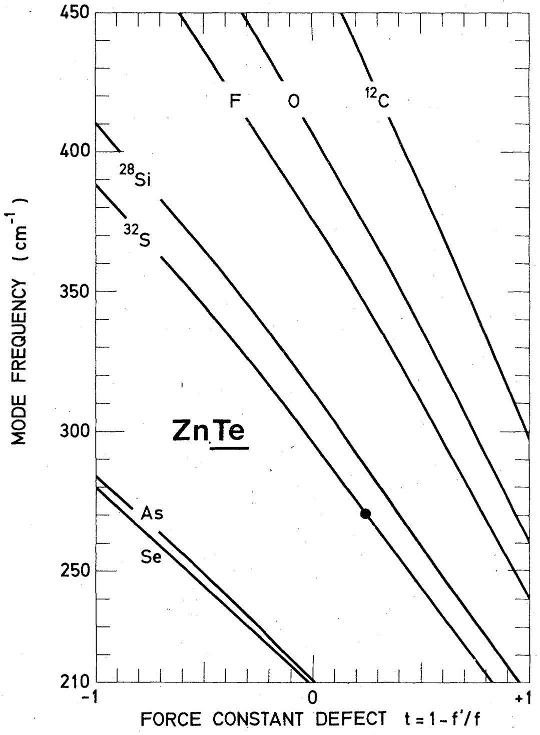

FIG. 9. ZnTe—Calculated frequencies of the F_2 localized mode for various substitutions on Te as a function of the force-constant defect. ● is experimental results (Ref. 43).

assigned, respectively, to ^{6}Li and ^{7}Li substituted on gallium.[60,61]

In addition, an important but not surprising result emerges from the present work: This empirical rule applies not only to III-V compounds but to all the experimental results obtained on II-VI compounds.

Bellomonte[62] recently proposed a physical model to determine the charges and polarizabilities of the impurity and its nearest neighbors, together with their effect on the modification of forces between nearest neighbors (denoted $\Delta\alpha$). This model was applied to the case of GaAs, and gives

TABLE IV. Case of very light impurities. Values of $\Delta f/f$ obtained in the present calculation; ratio of diagonal second neighbors forces on first neighbors forces: $-(\mathrm{Fi}+2\mathrm{Li}/A)$; localized mode frequencies we calculated as if the impurity vibrates alone and $\Delta f'/f$ obtained in the case of the first and second neighbor forces are modified in the same amount.

System	$\Delta f/f$	$-(F_i+2C_i)/A$	Experimental localized-mode frequency (cm^{-1})	ω_c (cm^{-1}) [a]	$\Delta f'/f$ [b]
GaP:^{10}B	−0.53	−0.63	592.7	581	−0.32
GaAs:^{10}B	−0.33	−0.37	540.2	537	−0.24
InP:^{11}B	+0.25	+0.066	522.8	516	+0.27
InSb:^{27}Al	−0.30	−0.44	296	289	−0.21
GaSb:^{31}P	−0.28	−0.49	324	307	−0.19
ZnSe:^{9}Be	−0.50	−0.53	450	447	−0.33
ZnTe:^{9}Be	+0.12	+0.15	415	404	+0.14
ZnS:^{9}Be	+0.10	+0.17	490	448	+0.12
CdTe:^{9}Be	−0.50	−0.44	391	377	−0.35
CdTe:^{32}S	+0.26	+0.19	248	213	+0.07
ZnTe:^{32}S	−0.24	−0.37	269	260	−0.15

[a] ω_c is the localized-mode frequency calculated from the expression: $\omega_c = 2\pi(-F/M'_i)^{1/2}$, where M'_i is the mass of the substituted atom and $F = 4aA + 4F_i + 8C_i$.

[b] $\Delta f'/f$ is defined by $\Delta f'/f = [(4aA + 4F_i + 8C_i)/(4A + 4F_i + 8C_i)] - 1$ see Sec. III A c.

$\Delta\alpha$ values closer to our results than to those of Talwar *et al.*[22] for local charge and polarizability values consistent with physical grounds: $\Delta\alpha$ is negative for Al, Mg, B on Ga and positive for Si, C, P on As in particular.

To explain the large force reduction in the case B on Ga, ($\Delta\alpha = -0.578.10^4$ dyn/cm), also observed in the present work ($\Delta f/f = -0.33$), Bellomonte suggests a possible size effect since the covalent radius of boron (0.88 Å) is appreciably smaller than that of the gallium it replaces (1.26 Å).[25] The considerable decrease in f also observed when boron substitutes gallium in GaP ($\Delta f/f = -0.53$) should not be related in our opinion to the size of the substitute ion: for instance the substitution B on In in InP leads this time to $\Delta f/f = +0.25$. Moreover for atoms such as carbon and nitrogen, even smaller than boron atoms, no relationship exists between the calculated $\Delta f/f$ values and the covalent radius: the short-range force modification is not clearly understood but should in our opinion be connected with local charge and polarizability changes rather than to atomic size factors.

C. Individual results

1. ZnTe

(a) Oxygen and tellurium are isoelectronic and the presence of oxygen as a substitute for tellurium is to be expected here. This impurity was studied mainly because of the intense fluorescence produced even at 300 °K, attributed to the deep electronic center formed by oxygen substituted for tellurium.[63] No experimental data are yet available on the vibrational modes of oxygen in ZnTe. If the short-range force-constant variation $\Delta f/f$ is assumed to be the same for O on Te as that found in the case of S on Te, i.e., -0.24, we obtain for oxygen, using the curves of Fig. 9, an energy of 375 cm^{-1} for the localized mode. This energy lies on the side of a two-phonon additive band of intensity almost independent of temperature. Thus the characteristic absorption of the crystal is high at this energy, whatever the experimental conditions, and observations can only be carried out on large quantities of oxygen, probably more than some 10^{17} cm^{-3}. We studied some samples of ZnTe doped with oxygen by Schneider according to an original method[64] and no vibrational transition was observed in the 375-cm^{-1} region, although the presence of oxygen in the tellurium site is proved by electronic transitions quite visible at 4 °K in the region of 2 eV. This result is understandable if it is considered that electronic transitions are much more intense than vibrational transitions, and also illustrates the difficulty of introducing large amounts of oxygen in the form of isolated substitutions in ZnTe.

(b) The work of Vodop'yanov *et al.*[65] includes mention of a gap mode at 153 cm^{-1} for cadmium as substitute on zinc. In fact, the existence of a phonon gap is foreseen by the model we use Ref. 26 between 151 and 172 cm^{-1} for ZnTe. Moreover, our results point in the case of Cd on Zn to the presence of a gap mode for which the resonance frequency varies with $\Delta f/f$ almost linearly between 151 and 170 cm^{-1} for $\Delta f/f$ between -0.15 and $+0.30$, the experimental value 154 cm^{-1} corresponding to about $\Delta f/f = -0.1$. This result is comparable to the $\Delta f/f$ values obtained for Be on Te (+0.12) and Mg on Te (+0.10), which means that isoelectronic substitutions of quite different masses lead here to similar $\Delta f/f$ values.

2. CdTe

(a) The case of beryllium in CdTe was studied by Hayes *et al.*[54] who observed, apart from the localized mode of beryllium substituted on the cadmium site at 391 cm^{-1}, a narrow absorption peak in the far infrared at 61 cm^{-1} which they identified as a band mode, this peak also reappearing in the sideband between 391 and 560 cm^{-1}. They used a "Shell"-type model to determine the density of states and their results show a low density of one-phonon states around 60 cm^{-1} consistent with a narrow-line band mode. These experimental data were analyzed by Talwar *et al.*,[66] using a seven-parameter rigid-ion model and a Green's-function technique accounting for changes of mass and of forces between nearest neighbors. They found no band mode whatever the variation in these forces. Since, in addition, their model supplied an accumulation of one-phonon states around 60 cm^{-1}, they proposed an extra absorption due to an impurity-activated one-phonon mechanism. The force model which we used and which accounts very satisfactorily for the CdTe-dispersion curves gives on the contrary a very low one-phonon-state density more or less constant between 55 and 80 cm^{-1},[27] and therefore, Talwar's explanation must be ruled out. On the other hand, and here our results agree with those of Talwar, we find no band mode, whatever the force constant variation between nearest neighbors, and consequently, Hayes results are still inexplicable. It is possible however that the defect responsible for the peak at 61 cm^{-1} is more complex than a berryllium atom in isolated substitution; this point will be examined in a later paper.

(b) The situation of zinc in CdTe has been studied by Vodop'yanov.[65] For high zinc concentrations, around 5–10 at.%, two transitions appear at 167 and 175 cm^{-1}, respectively, due to the splitting of the triply degenerated F_2 mode of the isolated impurity. They lie in the intrinsic band and are only observable when the zinc concentration is very high. Plotted on Fig. 6 these energy values lead to $\Delta f/f$ values around -0.25, quite close to that found for the isoelectronic substitution of magnesium on the cadmium site.

(c) In a very recent article,[69] Dutt and Spitzer observed a vibrational band at 322 cm^{-1} in CdTe containing phosphorus as acceptor with a tetrahedral site symmetry. This band is assigned by the authors to P on Te (*a priori* single acceptor) or possibly *P* is an interstitial site (multiple acceptor).

The vibrational frequency of interstitial phosphorus is not at present predictable by calculation; moreover, adopting the P on Te hypothesis we find: $\Delta f/f = 1.15$ (outside Fig. 7) for 322 cm^{-1}. The $\Delta f/f$ increase (0.77) with respect to the case of isoelectronic substitution S on Te ($\Delta f/f = +0.38$), due to the acceptor situation of phosphorus, is abnormally high for a single acceptor in site VI. Such a hypothesis therefore seems improbable, but this result is not significant enough in our opinion to exclude it definitively and assume that the band at 322 cm^{-1} is due to phosphorus in the interstitial site.

3. *GaAs*

In a very recent article, Laithwaite *et al.*[13] observed, in GaAs samples doped with silicon by the LEC method (liquid-encapsulation Czochralski) but also containing boron, an absorption peak at 123 cm^{-1} analyzed as the resultant of a band mode reflecting by its narrow width the low density of states at this energy.[31] They also noted that the intensity of this peak is related to the boron and silicon concentrations. We analyzed these data by calculating the band-mode frequencies and observed amongst other things that a band mode only exists for a light atom substitution if the impurity is on the As site.

Under these conditions B on As gives rise to a band mode between 127 and 140 cm^{-1} for $\Delta f/f$ varying from 0 to +1. Since $\Delta f/f = +0.31$ for the case of the isoelectronic substitution P on As, the substitution B on As where boron is a double acceptor on a site *V* should lead to $\Delta f/f$ values distinctly higher than 0.31, i.e., to resonance frequencies between about 135 and 140 cm^{-1}. These values are still in keeping with the mode frequency observed at 123 cm^{-1}, but one of Laithwaite's results is that the antistructure B on As is highly improbable. On the other hand, a band mode at 130 cm^{-1} is obtained in the case of Si on As for $\Delta f/f = +0.54$, which accounts also for the localized-mode frequency. It is therefore more likely to assign the peak observed by Laithwaite to silicon on an arsenic site.

IV. CONCLUSION

From a rigid-ion model including general forces between nearest and next-nearest neighbors and Coulomb forces we used a Green's-function technique accounting for mass changes and variations of forces between nearest neighbors to determine these variations in the case of isolated substitutional impurities in II-VI and III-V compounds. The use of a model which takes precise account of forces between next-nearest neighbors leads to $\Delta f/f$ values quite different from zero even in the case of isoelectronic impurities. Our results show, moreover, that the force modification is bound up mainly with the donor or acceptor situation of the impurity with respect to the atom it replaces, and apparently bears no relationship to the impurity size. For the case of GaAs, where a term of comparison exists, our results are fairly close to those obtainable by an independent method[62] accounting for local charge and polarizability changes consistent with physical bases. In addition, our results on band or gap modes contribute some details of information on certain existing experimental data.

ACKNOWLEDGMENTS

We wish to thank Dr. B. Schaub of the Laboratoire d'Electronique et de Technologie de l'Informatique in Grenoble who supplied us with the magnesium-doped ZnTe samples, and Dr. M. Schneider of the Centre National de la Recherche Scientifique in Meudon Bellevue (Laboratoire de Physique des Solides) who provided the oxygen-doped ZnTe samples.

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