Assignment of features in the observed two-phonon Raman scattering can be satisfactorily carried out using the calculated values of phonon frequencies at critical points. The model has been applied to a calculation of lattice dynamics of imperfect wurtzite lattices; results for frequencies of resonant and localized modes in a crystal of CdS with mass substituted impurities are given in an accompanying paper.

Work applying the model to BeO, for which some experimental dispersion curves have been reported, is under way as a direct test of the model. Results and a comparison with experiment have been given elsewhere.[5]

APPENDIX

TABLE V. Lorentz matrix for vanishing wave vectors in wurtzite structure. $\mathbf{B}_2$ corresponds to a wave vector perpendicular to the *c* axis. $\mathbf{B}_1$ corresponds to a vanishing wave vector parallel to the *c* axis.

i	j	$B_{1ij}v_a$	$B_{2ij}v_a$	i	j	$B_{1ij}v_a$	$B_{2ij}v_a$
1	1	3.8012	−2.4823	3	6	−0.5632	5.7110
4	4	3.8012	−2.4823	9	12	−0.5632	5.7110
7	7	3.8012	−2.4823	1	7	−1.5063	−7.7881
10	10	3.8012	−2.4823	4	10	−1.5063	−7.7881
2	2	3.8012	3.8012	2	8	−1.5063	−1.5063
5	5	3.8012	3.8012	5	11	−1.5063	−1.5063
8	8	3.8012	3.8012	3	9	3.1126	9.2944
11	11	3.8012	3.8012	6	12	3.1126	9.2944
3	3	−7.6024	−1.3189	4	7	5.5941	−0.6918
6	6	−7.6024	−1.3189	1	10	5.5941	−0.6918
9	9	−7.6024	−1.3189	5	8	5.5941	5.5941
12	12	−7.6024	−1.3189	2	11	5.5941	5.5941
1	4	0.2866	−5.9976	6	9	−11.1882	−4.8023
7	10	0.2866	−5.9976	3	12	−11.1882	−4.8023
2	5	0.2866	0.2866				
8	11	0.2866	0.2866				

Let dipole moment

$$\mathbf{p}(l,\kappa)=\mathbf{p}_\kappa e^{i\eta\cdot\mathbf{R}_l} \tag{A1}$$

be at the site of ion (l,κ), then the field at ion $(0,\kappa')$ can be expressed by

$$\mathbf{E}_{\kappa'}=\mathbf{B}_{\kappa\kappa'}(\boldsymbol{\eta})\mathbf{P}_\kappa. \tag{A2}$$

The matrix $\mathbf{B}(\boldsymbol{\eta})$ composed of the blocks $\mathbf{B}_{\kappa\kappa'}(\boldsymbol{\eta})$ defined by (A2) is the Lorentz matrix. This matrix is discontinuous for $\boldsymbol{\eta}\rightarrow 0$, and it has two limits $\mathbf{B}_1(0)$ and $\mathbf{B}_2(0)$ if $\boldsymbol{\eta}$ goes, respectively, to zero parallel or perpendicular to the crystal *c* axis. The elements of $\mathbf{B}_1(0)$ and $\mathbf{B}_2(0)$ have been computed and are given in Table V.

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Vibrations of a Mass Defect in Cadmium Sulfide†

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A Green's-function technique is used to study the vibrations of a substitutional impurity in CdS. Three cases have been investigated, corresponding to localized modes, gap modes, and in-band resonant modes. The theoretical results are in close agreement with experimental results for the gap mode of vibration of a Se impurity substituted for the S ion and the resonant mode of a Mn impurity substituted for the Cd ion in CdS.

I. INTRODUCTION AND METHOD

WE have calculated the frequency spectrum of the vibrations of an imperfect CdS (wurtzite) crystal containing isolated substitutional mass defects at the Cd or S site. We have used the results of our

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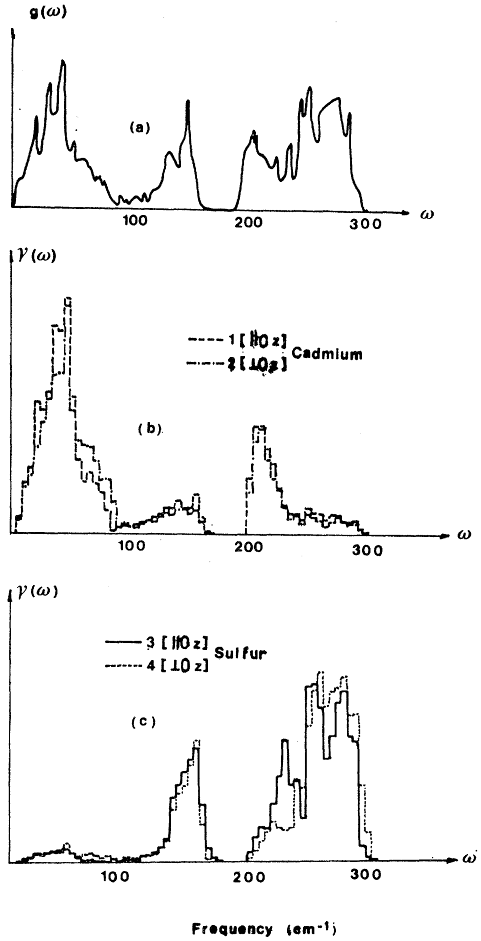

FIG. 1. Density of modes and imaginary part of the Green's functions of the nonperturbed crystal. The one-phonon density of modes is illustrated (a). The histograms (b) and (c) correspond to the vibrations of the heavy and the light ion, respectively. The vibrations of the heavy ion are predominent for low-frequency modes, and the vibrations of the light ion are predominent for the high-frequency modes.

calculation of the normal-mode frequency spectrum of perfect CdS based upon an improved model, as reported in an accompanying paper.[1]

The method used to compute the perturbed frequencies of the imperfect lattice is originally due to Lifshitz[2]; it has been developed by Elliott[3] and Dawber and Elliott[4] for a study of perturbed cubic crystals with a Debye spectrum of vibration assumed for the perfect lattice. It has also been used for [5,6] other cubic crystals with alkali-halide structures. Previously, we reported on preliminary results of a calculation of local and resonant modes in an imperfect CdS crystal[7]; it was based on our earlier work on lattice dynamics in CdS.[8]

We shall assume that the reader is familiar with the general theory of the method, and also with our previous papers; thus we present only a brief summary of our work. In CdS (wurtzite), the unit cell contains four atoms in the basis, which are labeled $\kappa=1$, 2, 3, and 4; respectively, Cd I, Cd II, S I, S II. We assume that a single mass defect of mass M' is present replacing the mass M_κ originally at site κ, and we define a parameter

$$\epsilon_\kappa=(M_\kappa-M')/M_\kappa. \qquad (1.1)$$

The force constants are assumed unchanged in the perturbed lattice.

If we define the matrix Green's function $g_{\kappa\kappa',ll',\alpha\alpha'}(\omega)$ in terms of the eigenvectors $\mathbf{e}_\kappa(\boldsymbol{\eta}/j)$ of the perfect lattice, and the corresponding eigenfrequencies $\omega(\boldsymbol{\eta}/j)$, we have

$$g_{\kappa\kappa',ll',\alpha\alpha'}(\omega)=\frac{1}{N}\sum_{j\eta}(M_\kappa M_{\kappa'})^{-1/2}\times\frac{e_\kappa^*(\boldsymbol{\eta}/j)\cdot\mathbf{e}_{\kappa'}(\boldsymbol{\eta}/j)e^{2i\pi\boldsymbol{\eta}\cdot(\mathbf{R}_l-\mathbf{R}_{l'})}}{\omega^2-\omega^2(\boldsymbol{\eta}/j)}, \qquad (1.2)$$

where $\mathbf{R}_l$ is a lattice vector in the crystal, and α, α' are Cartesian indices ($\alpha=x, y, z$). In the spectral region of the normal modes, it is necessary to define an auxiliary distribution $\nu(\omega)$ by incorporating a small imaginary part in the real frequency ω. Then we have

$$\lim_{\Phi\to0} g(\omega+i\Phi)=g'(\omega)+(i\pi/2\omega)\nu(\omega). \qquad (1.3)$$

The function $g'(\omega)$ is equal to the Green's function $g(\omega)$ for every frequency different from an eigenfrequency of vibration of the perfect lattice and is equal to zero otherwise. The distribution $\nu(\omega)$ is given by

$$\nu_{\kappa\kappa',ll',\alpha\alpha'}(\omega)=\frac{1}{N}\sum_{j\eta}(M_\kappa M_{\kappa'})^{-1/2}\mathbf{e}_{\kappa,\alpha}^*(\boldsymbol{\eta}/j)\cdot\mathbf{e}_{\kappa',\alpha'}(\boldsymbol{\eta}/j)e^{-2i\pi\boldsymbol{\eta}\cdot(\mathbf{R}_l-\mathbf{R}_{l'})}\delta[\omega-\omega(\boldsymbol{\eta}/j)]. \qquad (1.4)$$

With the assumptions of no change in force constant, the frequencies of the perturbed crystal can be obtained from the complex imperfect-crystal Green's functions g^{imp}, which is conveniently defined as

$$\lim_{\Phi\to0} g_i^{imp}(\omega+i\Phi)=\frac{g_i'(\omega)+\frac{1}{2}i\pi\nu_i(\omega)}{1-\epsilon\omega^2g_i'(\omega)+\frac{1}{2}\epsilon i\pi\nu_i(\omega)}. \qquad (1.5a)$$

The functions $g'(\omega)$ and $\nu(\omega)$ of Eq. (1.5a) are defined in

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[1] M. A. Nusimovici, M. Balkanski, and J. L. Birman, preceding paper, Phys. Rev. B **1**, 595 (1969).

[2] E. M. Lifshitz, Nuovo Cimento Suppl. 3, 716 (1956).

[3] R. J. Elliott, Phil. Mag. **1**, 298 (1956).

[4] P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **A261**, 222 (1963).

[5] R. F. Wallis and A. A. Maradudin, Progr. Theoret. Phys. (Kyoto) **24**, 1055 (1960).

[6] S. S. Jaswal, Phys. Rev. **137**, 302 (1965); S. S. Jaswal and D. J. Montgomery, Phys. Rev. **135A**, 1257 (1967).

[7] P. Pfeuty, J. L. Birman, M. A. Nusimovici, and M. Balkanski, in *Proceedings of the International Conference on Localized Excitations in Solids, Irvine, California, 1967* Edited by R. Wallis (Plenum Press, Inc., New York, 1968), pp. 210–217.

[8] M. A. Nusimovici and J. L. Birman, Phys. Rev. **156**, 925 (1967).

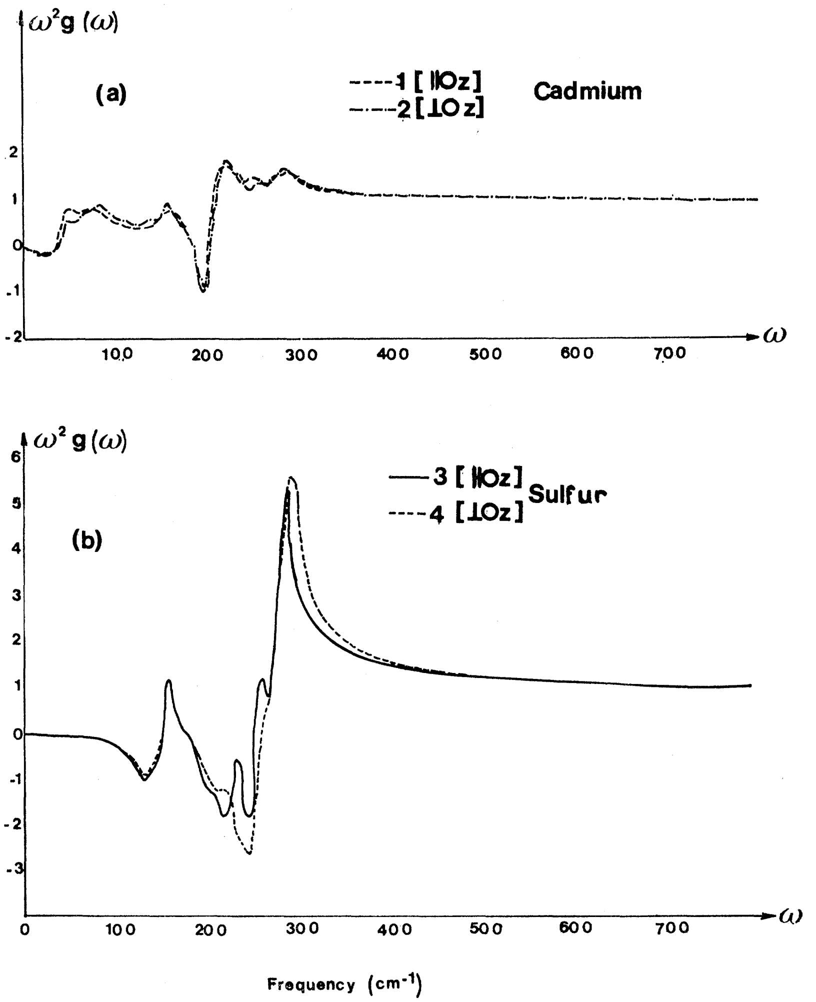

FIG. 2. Real parts of the Green's functions of the perfect crystal of CdS. The curves (a) correspond to the heavy ion and the curves (b) correspond to the light ion.

(1.3) and (1.4) from the perfect crystal eigenvectors and eigenfrequencies.

A localized mode or a gap mode of the imperfect crystal will arise if the real part of (1.5a) has a pole at ω_L, or if

$$\epsilon_\kappa \omega^2 g_i'(\omega_L) = 1\,. \tag{1.5b}$$

A localized mode or a gap mode arises in a spectral region where $\nu(\omega)$ identically vanishes. The imperfect-crystal Green's function is real and has a pole at ω_L only if

$$\epsilon_\kappa \omega^2 g_i'(\omega_L) = 1\,. \tag{1.6}$$

A resonant or band mode of the imperfect crystal will arise if the imaginary part of (1.4) is very large for a frequency ω_R, i.e., if

$$\epsilon_\kappa \omega^2 g_i'(\omega_R) = 1 \tag{1.7}$$

and

$$\nu_i(\omega_R) \neq 0\,. \tag{1.8}$$

II. CALCULATIONS, COMPARISON, AND EXPERIMENTS

Using eigenvectors and eigenvalues from the calculation of normal modes of CdS,[1] we have computed the matrix Green's functions (1.3), (1.4):

$$g_2 = g_{11,00,xx}(\omega) = g_{22,00,xx}(\omega) = g_{11,00,yy}(\omega) = g_{22,00,yy}(\omega)\,, \tag{2.1}$$

$$g_1 = g_{11,00,zz}(\omega) = g_{22,00,z}(\omega)\,, \tag{2.2}$$

$$g_4(\omega) = g_{33,00,xx}(\omega) = g_{44,00,xx}(\omega) = g_{33,00,yy}(\omega) = g_{44,00,yy}(\omega)\,, \tag{2.3}$$

$$g_3(\omega) = g_{33,00,zz}(\omega) = g_{44,00,zz}(\omega)\,. \tag{2.4}$$

The density of normal modes of vibration of CdS has been calculated elsewhere[1] and is given in Fig. 1(a). On Figs. 1(b) and 1(c), we give, respectively, the histograms corresponding to the distributions $\nu_1(\omega)$, $\nu_2(\omega)$, $\nu_3(\omega)$, and $\nu_4(\omega)$. Those distributions correspond, respectively, to the motions parallel and perpendicular

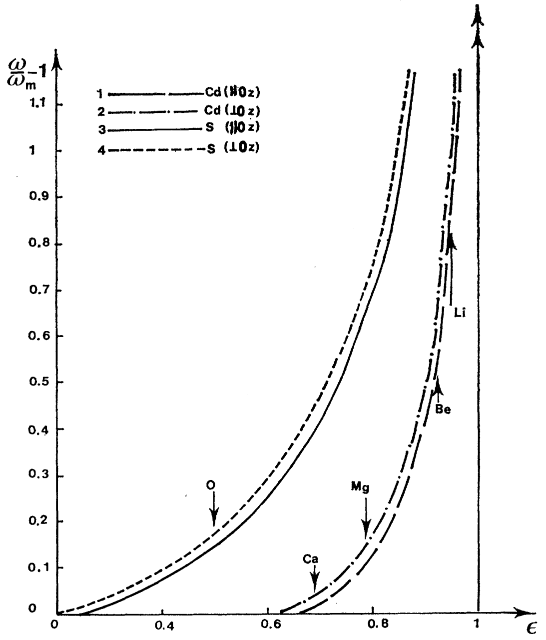

FIG. 3. Variation of a localized-mode frequency as a function of $\epsilon_\kappa=(M_\kappa-M')/M_\kappa$.

to the c axis of Cd and S ions. They measure the contributions of each of those degrees of freedom to the density of modes in Fig. 1(a). The distributions $\nu_1(\omega)$ and $\nu_2(\omega)$ corresponding to the vibration of the heavy ion are prominent for the modes of low frequency, whereas, on the contrary, the distributions $\nu_3(\omega)$ and $\nu_4(\omega)$ corresponding to the vibrations of the light ion are prominent for high frequencies. The differences between the distributions $\nu_1(\omega)$ and $\nu_2(\omega)$ on the one hand and the distributions $\nu_3(\omega)$ and $\nu_4(\omega)$ on the other hand are due to the crystal anisotropy. They cannot be explained by some elementary considerations of the normal modes of the perfect lattice.

Localized Modes

Let us first consider a light mass defect. In this case the quantity ϵ_κ defined by Eq. (1.1) is positive. The frequencies of localized modes are then calculated for any ϵ. The localized mode frequencies are different if the substituted ion is an anion or a cation. Owing to the axial anisotropy of the crystal, the frequencies are different also for modes polarized parallel or perpendicular to the c axis. The maximum frequency of the normal modes is ω_M.

Figure 3 shows the variations of the quantity (ω/ω_M-1) as a function of ϵ_κ. Note that the localized mode does not appear for arbitrary light substitutional impurity; ϵ_κ has to be larger than 0.23 if the substituted ion is S, and larger than 0.65 is the substituted ion is Cd, for such a mode to exist.

When ϵ_κ is large enough there are two localized modes, a singlet corresponding to the representation Γ_1 of the group C_{3v}, and a doublet corresponding to the representation Γ_3. The frequency of the doublet is smaller than the frequency of the singlet, and for very light impurities the difference between those frequencies can be large, especially if the substituted ion is the cation.

For very light impurities $\epsilon_\kappa\rightarrow 1$, the frequencies of localized modes go to infinity, and this is in fact quite obvious. If the impurity is very light it behaves as a harmonic oscillator with a vanishing mass. This result can also be deduced from the asymptotic form of the Green's functions,

$$g_{\kappa\kappa,00,\alpha\alpha'}=\frac{1}{N}\sum_{j\eta}\frac{1}{M_\kappa}\frac{\mathbf{e}_{\kappa,\alpha}{}^*(\boldsymbol{\eta}/j)\cdot\mathbf{e}_{\kappa,\alpha'}(\boldsymbol{\eta}/j)}{\omega^2}. \quad (2.5)$$

Since the eigenvectors of the dynamical matrix are orthonormal, the limit of the right-hand side of the relation (2.5) is

$$g_{\kappa\kappa,00,\alpha\alpha'}=1/M_\kappa\omega^2, \quad (2.6)$$

corresponding to $\epsilon_\kappa\rightarrow 1$.

In Table I we summarize our calculated results for frequencies of local modes for several mass substitutions (or impurities). The corresponding values of ν are indicated in Fig. 3. (Recall that the highest frequency of the perfect-CdS-lattice modes is $\omega_{\text{LO}}=302$ cm^{-1}.)

For positive values of ϵ smaller than the values previously indicated, the impurity is lighter than the substituted ion but will behave like a heavy impurity and may show a resonant mode of vibration.

None of the experimental results available correspond to a light substitutional impurity without change of the force constants. Therefore, the present theory cannot be compared with the experiment for localized modes.

Gap Modes: Theory and Experiments

When the mass of the substitutional impurity is large enough, the impurity may produce a gap mode if its frequency is in the gap of the density of modes [Fig. 1(a)]. The frequency of that mode can be calculated from Eqs. (1.5). We calculated explicitly the frequency of the gap mode of Se in CdS. In this case the parameter ϵ_κ is -1.5. By using the calculated Green's functions in the relation (2.5), we obtain two frequencies 187 and

TABLE I. Frequencies of localized modes.

Impurity	Substituted ion	M'	ϵ_κ	Frequency (cm^{-1}) parallel to c axis	Frequency (cm^{-1}) perpendicular to c axis
Li	Cd	7	0.94	541	588
Be	Cd	9	0.92	487	520
Mg	Cd	24	0.79	334	345
Ca	Cd	40	0.68	303	310
O	S	16	0.50	345	355

192 cm^{-1}, corresponding to the resonant modes of Se, respectively, polarized parallel and perpendicular to the crystal c axis.

The infrared spectrum of CdS containing Se has been studied by several authors[8–11] very recently. Reflectivity experiments on CdS containing 1.5% of Se have been done by Beserman.[12] The absorption coefficient obtained by a Kramers-Krönig inversion of the reflectivity shows maxima for the frequencies of 188 and 184 cm^{-1} corresponding, respectively, to polarizations of the incident light parallel and perpendicular to the crystal c axis. This result is in agreement with that of Lucovsky *et al.*[13] and Parrish *et al.*[11]

Our theoretically calculated values differ from the measured values by less than 5 cm^{-1}; also, the anisotropy splitting calculated (5 cm^{-1}) and measured (4 cm^{-1}) are in close agreement.

Resonant Modes: Theory and Experiments

Let us consider two cases of impurities substituted to a Cd ion in CdS, Zn and Mn. Zinc corresponds to $\epsilon=0.425$, and Mn corresponds to $\epsilon=0.513$, both being smaller than the critical value of 0.65 above which a local mode of vibration exists.

Equation (1.6) has no roots if $\epsilon=0.425$. Therefore there is no resonant mode of vibration of Zn in CdS. This result is a contradiction with the one obtained from Jaswal's[6] calculations predicting a mode at 170 cm^{-1}. Experiments[14] show, at very low temperature, a very weak band with an intensity much too small to be the one of a resonant or a gap mode of Zn in CdS. Equation (1.6) has several roots for $\epsilon=0.513$, but the only ones in a spectral region where $\nu(\omega)$ is small arise for frequencies of 284 and 289 cm^{-1} corresponding, respectively, to vibrations parallel and perpendicular to the crystal axis. These results are in good agreement with recent experiments by Beserman,[15] who found absorption bands at 278 and 283 cm^{-1}.

III. CONCLUSION

The lattice-dynamic model previously used for the lattice dynamics of CdS together with the Green's-function theory of the vibrations of imperfect CdS crystals have been used to compute the frequencies of local and resonant modes due to various mass defect substitutions in CdS.

No reports of measured values of local modes for light impurities in CdS are available against which theoretical predictions can be compared.

A gap mode with properties very similar to a local mode has been observed for a Se impurity. In the case of Se in CdS, calculated values of 192 and 188 cm^{-1} are in close accord with measured values of 188 and 184 cm^{-1}.

Theoretical results show resonant modes for Mn in CdS, and the calculated values of 284 and 289 cm^{-1} are in close accord with measured values of 278 and 283 cm^{-1}.[15]

The theory shows that neither resonant nor local mode can be expected for a Zn impurity in CdS. This fundamental difference in behavior between Se and Zn impurities in CdS may be related to the observed difference between the vibrational spectra of mixed $Cd_{1-x}Zn_xS$ and $CdS_{1-x}Se_x$. The Zn in $Cd_{1-x}Zn_xS$ does not show any local or resonant mode for $x \to 0$, and the reflection spectrum of $Cd_xZn_{1-x}S$ shows only one restrahlen band.[13] Se in $CdS_{1-x}Se_x$ shows gap modes for $x \to 0$, and the reflection spectrum of the mixed crystal shows two restrhalen bands corresponding, respectively, to CdS and CdSe.[10,12]

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[9] M. Balkanski, R. Beserman, and J. M. Besson, Solid State Commun. **4**, 201 (1966).

[10] H. N. Verleur and A. S. Barker, Jr., Phys. Rev. **155**, 750 (1967).

[11] J. F. Parrish, C. H. Perry, O. Brafman, I. F. Chang, and S. S. Mitra, in *Proceedings of the International Conference II-VI Semiconducting Compounds, Providence, 1967*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), pp. 1164–1184.

[12] R. Beserman, thése de Doctorat d'Etat, Faculté des Sciences, University of Paris, Paris, France, 1968 (unpublished).

[13] D. G. Lucovsky, E. Lind, and E. A. Davis, Ref. 11, pp. 1150–1163.

[14] I. G. Nolt, R. A. Westwig, R. W. Alexander Jr., and A. J. Sievers, Phys. Rev. **157**, 730 (1967).

[15] R. Beserman (private communication).