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Vibrational Properties of Mixed CdS_xSe_{1-x}†

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An investigation of the effects of heavy doping has been carried out in the case of the system CdS_xSe_{1-x}. For CdS containing a low concentration of Se, the dopant acts as a heavy impurity and gives a gap mode at $\omega_{G\,E\parallel c} = 182.5$ cm^{-1} and $\omega_{G\,E\perp c} = 187$ cm^{-1}. An increase in the Se concentration brings into prominence two constituents of the ω_G band having, respectively, the character of a longitudinal mode $\omega_{LO}{}^G$ and a transverse mode $\omega_{TO}{}^G$. The frequencies $\omega_{LO}{}^G$ and $\omega_{TO}{}^G$ are dependent on the impurity concentration and tend toward the normal-mode frequencies of CdSe in the high-concentration limit. S in CdSe gives two localized modes, $\omega_{L\,E\parallel c} = 266.5$ cm^{-1} and $\omega_{L\,E\perp c} = 269$ cm^{-1}, whose frequencies are also concentration-dependent and at high S concentration reach the normal-mode frequencies for CdS. The localized-mode frequencies of S in CdSe and the resonance-mode frequencies of Se in CdS have been investigated by Green's-function techniques. A model assuming a random arrangement of impurities, developed by Elliott and Taylor, has been applied to the study of mixed CdS_xSe_{1-x}, using the now available CdS Green's function. Up to an impurity concentration of 20%, the calculated optical properties (such as the normal-mode and impurity-mode frequency shift, oscillator strength, and absorption coefficient) compare satisfactorily with the experimental data.

I. INTRODUCTION

Optical measurements in the region of normal-mode frequencies in a great number of ternary alloys have produced considerable theoretical interest. Different attempts to treat the vibrations of a disordered lattice are known: the very-low-concentration limit for substitutional impurities[1,2] has received wide experimental confirmation.[3] High impurity concentrations and alloys have been considered in a few recent investigations.[4,5]

The experimental results have been discussed mainly in terms of macroscopic theoretical approaches such as the random-element isodisplacement model in the cases of GaP_xAs_{1-x},[6] CdS_xSe_{1-x},[5] and ZnS_xSe_{1-x},[7] the short-range clustering model in the case of GaP_xAs_{1-x}, CdS_xSe_{1-x}, and $Ba_{1-x}Sr_xF_2$.[8] A virtual-crystal model has been applied to some ionic crystals such as $Ni_{1-x}Co_xO$,[9] $Ca_xSr_{1-x}F_2$, and $Ba_{1-x}Sr_xF_2$,[10] and a linear-chain model has been used to predict the behavior of $Na_{1-x}K_xCl$ [11] and CdS_xSe_{1-x}.[12]

The Green's-function technique used in the investigations of impurity vibrations has been recently introduced into the problem of vibrations in random dilute alloys[13]; similar theories have been developed by Langer,[14] Maradudin,[15] Takeno,[16] and Davies and Langer.[17] Taylor[18] has developed a self-consistent method within the multiple-scattering formalism of Lax[19] which extends the results obtained by Elliott and Taylor to crystals with large defect concentration. Since the Green's functions for CdS are now available,[20] it becomes possible to calculate the impurity-mode frequencies in the wurtzite-type crystals and to investigate the vibrational spectrum of their alloys.

After a brief summary of the Elliott-Taylor theory on the vibrations of random dilute alloys, we shall present here experimental results on localized and gap modes in CdS_xSe_{1-x}. The frequencies of these modes split with increasing x into a LO- and a TO-mode frequency tending toward the normal-mode optical frequencies of the pure crystal. The impurity-frequency,

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shifts and the optical absorption are discussed in terms of the Elliott-Taylor theory.

II. THEORETICAL CONSIDERATIONS

A. Impurity Frequencies

For a perfect crystal, the normal-mode frequencies are given by the solutions of the secular equation:

$$|M\omega^2-\Phi|=0, \tag{1}$$

where Φ is the potential-energy matrix for the perfect crystal formed by atoms with mass M. If C is the local perturbation matrix, the secular equation for the perturbed crystal is

$$|M\omega^2-\Phi-C|=0. \tag{2}$$

One can define a matrix G whose coefficients are the Green's functions of the crystal:

$$G(M\omega^2-\Phi-C)=I-GC. \tag{3}$$

The impurity-mode frequencies are given by the solutions of the secular equation

$$|I-G(\omega)C(\omega)|=0. \tag{4}$$

The matrix elements of the Green's function $G(\omega)$ may be obtained from the phonon eigenvectors $\boldsymbol{\sigma}(j\mathbf{q})$ and eigenfrequencies $\omega^2(j\mathbf{q})$:

$$G_{\alpha k\alpha' k'}(\mathbf{l}\mathbf{l}'\omega^2)=\sum\frac{\boldsymbol{\sigma}_{\alpha k}(j\mathbf{q})\boldsymbol{\sigma}_{\alpha' k'}{}^*(j\mathbf{q})e^{i\mathbf{q}\cdot(r\mathbf{l}-r\mathbf{l}')}}{NM_k{}^{1/2}M_{k'}{}^{1/2}[\omega^2-\omega^2(j\mathbf{q})]}. \tag{5}$$

The α's are the Cartesian coordinates, the k's label the ions.

The Green's function can be expanded into real and imaginary parts:

$$\lim_{\varphi\to 0} G(\omega+i\varphi)=G'(\omega)+i\pi\nu(\omega)/2\omega, \tag{6}$$

which are related by the Kramers-Kronig relation

$$G'(\omega)=\int_0^{\omega_M}\frac{\nu(\omega')d\omega'}{\omega^2-\omega'^2}, \tag{7}$$

where $\nu(\omega)$ is the density of modes.

When a light substitutional impurity is introduced, a localized mode may appear at $\omega>\omega_M$. The localized-mode frequencies are given by the solutions of

$$\epsilon\omega^2G'(\omega)=1, \tag{8}$$

where ϵ is the positive-mass parameter

$$\epsilon=1-M'/M.$$

When a heavy-mass impurity is introduced, a band resonance may appear at $\omega<\omega_M$. The resonance-mode frequencies related to the imaginary part of the imperfect-crystal Green's function are given by the solutions of

$$\epsilon\omega^2G'(\omega)=1,$$

where ϵ is the negative-mass parameter.

B. Vibration of Alloys

The theory used to interpret our experimental results is that developed by Elliott and Taylor[13] concerning the vibrational properties of an isotropic cubic crystal containing impurities in small concentration. In the present work we are concerned with hexagonal crystals. The application of this theory is an approximation which is justified by the fact that the anisotropy introduced by the hexagonal structure does not constitute an important deviation from the cubic structure, as far as the vibrational properties are concerned: The splitting of the optical mode due to the hexagonal symmetry is only a 2% effect. The Green's function of a crystal containing one impurity on site i is given by

$$\bar{G}=G+GXG,$$

where

$$X=C_i(I-GC_i)^{-1} \tag{9}$$

is a matrix having the dimensions of the C_i impurity matrix.

For a concentration of c of randomly distributed impurities, $\bar{G}$ is written

$$\bar{G}=G+cGX'G, \tag{10}$$

where

$$X'=C[I-(1-c)GC]^{-1}. \tag{11}$$

The imaginary part of the Green's function is then

$$\mathrm{Im}G_j(\mathbf{q}\omega)=\frac{\omega^2\Gamma(\omega)}{\{\omega^2[1-\Delta(\omega)]-\omega^2(j\mathbf{q})\}^2+[\omega^2\Gamma(\omega)]^2}, \tag{12}$$

where $\Delta(\omega)$ is the frequency shift and $\Gamma(\omega)$ is the damping coefficient in the spectral region of allowed frequencies. $\omega^2\Delta(\omega)$ and $\omega^2\Gamma(\omega)$ are, respectively, the real and the imaginary part of X'.

$$\lim_{\Phi\to 0} X_j'(\omega+i\Phi)=\omega^2(\Delta(\omega)-i\Gamma(\omega))$$
$$=\frac{c\epsilon\omega^2[\alpha(\omega)-i\beta(\omega)]}{\alpha^2(\omega)+\beta^2(\omega)}, \tag{13}$$

which are related to the density of states by

$$\alpha(\omega)-i\beta(\omega)=1-(1-c)\epsilon\omega^2$$
$$\times\left(P\int\frac{\nu(\omega')d\omega'}{\omega^2-\omega'^2}+\frac{i\pi\nu(\omega)}{2\omega}\right). \tag{14}$$

In the case of a diatomic crystal, the density of states must be that appropriate to the displacement of the substituted ion. Therefore, the density of states $\nu(\omega)$ in the Elliott-Taylor paper is in the present work the

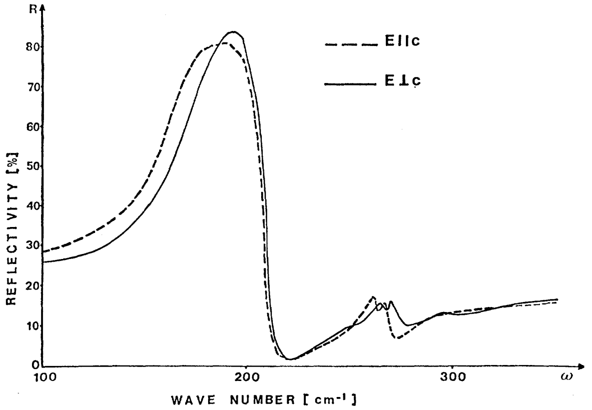

FIG. 1. Infrared reflectivity spectrum of CdSe with 0.5% S, for light polarized parallel and perpendicular to the c axis.

corresponding imaginary part of the nonperturbed lattice Green's function. We use the calculated values of $\nu(\omega)$ given by Nusimovici, Balkanski, and Birman.[20]

It should be emphasized that although the theory given in Ref. 13 is appropriate only to a cubic crystal, the unperturbed density of states is nevertheless taken to be that of hexagonal CdS. Therefore, some of the effects arising from the hexagonal symmetry will nevertheless be included in the present theoretical treatment.

At small c, $\Delta(\omega)$ and $\Gamma(\omega)$ in Eq. (12) are small, so that there is a peak near $\omega=\omega_{\mathrm{TO}}$. In addition, a second peak is found near the resonance position, where $1-(1-c)\epsilon\omega^2G(\omega)\rightarrow 0$ and $\Delta(\omega)$ becomes large.

The strength of the impurity mode is

$$\frac{c\pi\omega_l^2}{2(\omega_l^2-\omega_{\mathrm{TO}}^2)^2}\frac{1}{B(\omega_l)}, \tag{15}$$

with

$$B(\omega_l)=\int_0^\infty \frac{\omega'^2\nu(\omega')d\omega'}{(\omega_l^2-\omega'^2)^2}. \tag{16}$$

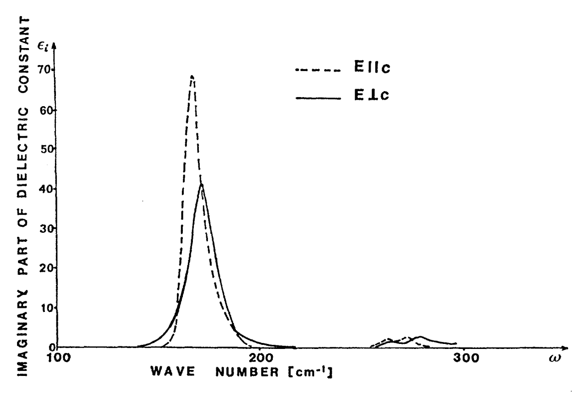

FIG. 2. Imaginary part of the dielectric constant of CdSe with 0.5% S, for light polarized parallel and perpendicular to the c axis.

III. EXPERIMENTAL RESULTS

A. Experimental Procedure

The reflectivity measurements were performed on a far-infrared vacuum spectrometer *CODERG*. The reflectivity was taken point by point, comparing the reflectivity of a mirror with that of the crystal. The resolution is 1 cm^{-1} in the entire range studied.

The real and imaginary parts of the dielectric constant are deduced from the optical constants by means of the Kramers-Kronig relations. The optical-mode frequencies are given by

$$\omega_{\mathrm{TO}}=\epsilon_{i\,\max}=2nk_{\max},$$
$$\omega_{\mathrm{LO}}=\mathrm{Im}(-1/\epsilon)_{\max}=[2nk/(n^2+k^2)]_{\max}.$$

B. Low Impurity Concentration

1. S Replacing Se in CdSe

S ($M=32$) replaces Se ($M=79$) in CdSe. The mass parameter $\epsilon=(M_{\mathrm{Se}}-M_{\mathrm{S}})/M_{\mathrm{S}}=0.595$ is positive, and localized modes are expected at frequencies higher than the LO-mode frequencies of pure CdSe.

Figure 1 gives the reflectivity spectrum of CdSe containing 0.5% S, for $E\|c$ and $E\perp c$. The main reflectivity band is the CdSe reststrahl; the reflectivity peaks due to S are located at frequencies higher than the LO-mode frequency of pure CdSe.

Figure 2 gives the imaginary part of the dielectric constants. For each polarization two types of oscillators can be observed: (1) the TO mode of pure CdSe, whose frequencies are

$$\omega_{\mathrm{TO}\ \mathbf{E}\|c}=166.5\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{TO}\ \mathbf{E}\perp c}=169\ \mathrm{cm}^{-1},$$

and (2) the localized-mode frequencies of S in CdSe.

In both polarizations, two localized modes are seen, which are labeled ω_{TO_1} and ω_{TO_2}:

$$\omega_{\mathrm{TO}_1\ \mathbf{E}\|c}{}^{\mathrm{loc}}=262\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{TO}_1\ \mathbf{E}\perp c}{}^{\mathrm{loc}}=263\ \mathrm{cm}^{-1},$$
$$\omega_{\mathrm{TO}_2\ \mathbf{E}\|c}{}^{\mathrm{loc}}=266.5\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{TO}_2\ \mathbf{E}\perp c}{}^{\mathrm{loc}}=269\ \mathrm{cm}^{-1}.$$

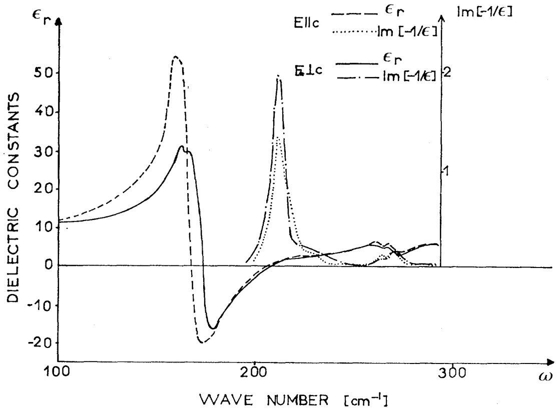

FIG. 3. Real part of the dielectric constant and imaginary part of minus the inverse of the dielectric constant of CdSe with 0.5% S, for $\mathbf{E}\perp c$ and $\mathbf{E}\|c$.

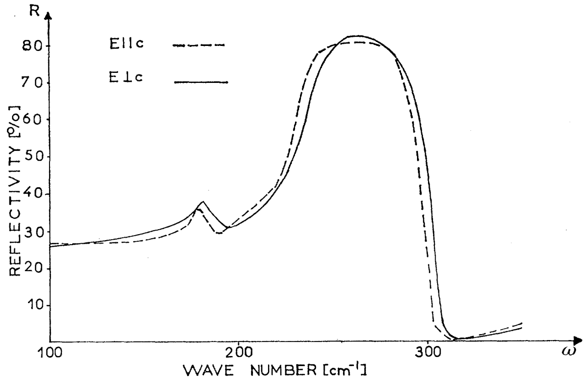

FIG. 4. Infrared reflectivity spectrum of CdS with 1.5% Se, for light polarized parallel and perpendicular to the c axis.

The appearance of two peaks for each polarization is surprising, but the experiment indicates such a structure without any ambiguity. The low-energy peaks may be attributed to clusters of S in CdSe, and the high-energy peaks are the localized modes of substitutional S in CdSe.[21]

The LO-mode frequencies are deduced either from $\epsilon_r=0$ or from $\mathrm{Im}(-1/\epsilon)=\max$. As shown in Fig. 3, two sets of LO modes can be seen:

(1) those of pure CdSe, whose frequencies are

$$\omega_{\mathrm{LO}\ \mathrm{E}\|c}=210\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{LO}\ \mathrm{E}\perp c}=212\ \mathrm{cm}^{-1};$$

(2) those of S in CdSe, whose frequencies are

$$\omega_{\mathrm{LO}_1\ \mathrm{E}\|c}{}^{\mathrm{loc}}=262.5\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{LO}_1\ \mathrm{E}\perp c}{}^{\mathrm{loc}}=263.5\ \mathrm{cm}^{-1},$$
$$\omega_{\mathrm{LO}_2\ \mathrm{E}\|c}{}^{\mathrm{loc}}=268.5\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{LO}_2\ \mathrm{E}\perp c}{}^{\mathrm{loc}}=270.5\ \mathrm{cm}^{-1}.$$

$\omega_{\mathrm{LO}_1}{}^{\mathrm{loc}}$ and $\omega_{\mathrm{LO}_2}{}^{\mathrm{loc}}$, respectively, correspond to $\omega_{\mathrm{TO}_1}{}^{\mathrm{loc}}$ and $\omega_{\mathrm{TO}_2}{}^{\mathrm{loc}}$.

To calculate the localized-mode frequencies of substitutional S in CdSe, we take the CdS Green's functions of Ref. 20 and make the assumption that the CdSe density of states is that obtained from CdS after scaling the frequency by substituting for ω_{LO} of CdS the ω_{LO} of CdSe. The calculated frequencies are then

$$\omega_{\mathrm{L}\ \mathrm{E}\|c}=266\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{L}\ \mathrm{E}\perp c}=271\ \mathrm{cm}^{-1},$$

values which are in close agreement with the experimental frequencies,

$$\omega_{\mathrm{TO}_2\ \mathrm{E}\|c}{}^{\mathrm{loc}}=266.5\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{TO}_2\ \mathrm{E}\perp c}{}^{\mathrm{loc}}=269\ \mathrm{cm}^{-1}.$$

2. *Se Replacing S in CdS*

Se ($M=79$) replaces S ($M=32$) in CdS. The mass parameter $\epsilon=-1.47$ is then negative, so that a resonance mode or a gap mode is expected.

The reflectivity spectrum of CdS containing 1.5% Se is shown in Fig. 4, for **E**$\|c$ and **E**$\perp c$. The main reflectivity band is the CdS reststrahl; the reflectivity peaks due to Se are located at frequencies lower than the ω_{TO} frequencies of CdS.

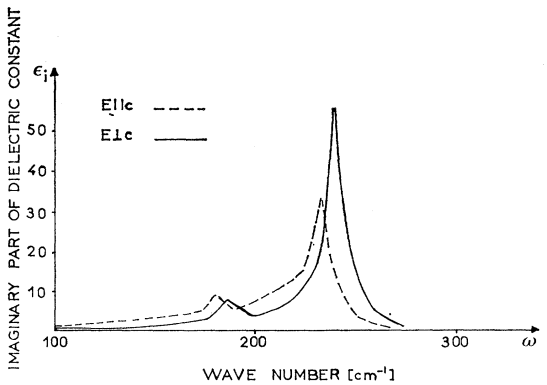

FIG. 5. Imaginary part of the dielectric constant of CdS with 1.5% Se for light polarized parallel and perpendicular to the c axis.

As shown in Fig. 5, the imaginary part of the dielectric constant exhibits two oscillators for each polarization. These are the TO modes of pure CdS, with frequencies

$$\omega_{\mathrm{TO}\ \mathrm{E}\|c}=233\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{TO}\ \mathrm{E}\perp c}=239.5\ \mathrm{cm}^{-1},$$

and the gap modes of Se, with frequencies

$$\omega_{\mathrm{TO}\ \mathrm{E}\|c}{}^{G}=182.5\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{TO}\ \mathrm{E}\perp c}{}^{G}=187\ \mathrm{cm}^{-1}.$$

Figure 6 gives the real part of the dielectric constant and the imaginary part of $(-1/\epsilon)$. Two sets of LO modes can be seen as those of pure CdS:

$$\omega_{\mathrm{LO}\ \mathrm{E}\|c}=301\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{LO}\ \mathrm{E}\perp c}=304.5\ \mathrm{cm}^{-1},$$

and those of the gap modes due to Se:

$$\omega_{\mathrm{LO}\ \mathrm{E}\|c}{}^{G}=186\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{LO}\ \mathrm{E}\perp c}{}^{G}=190\ \mathrm{cm}^{-1}.$$

The gap-mode frequencies have been calculated from the CdS Green's function by Nusimovici *et al.*,[20] by

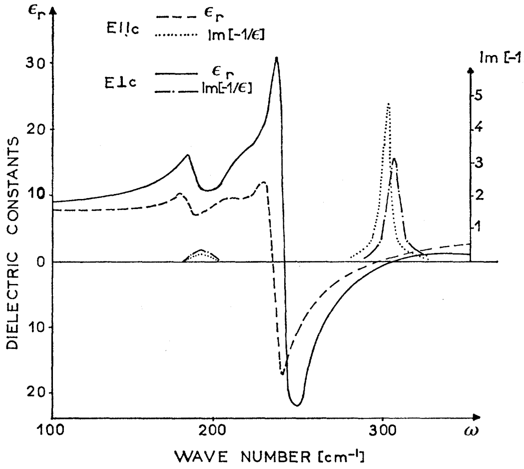

FIG. 6. Real part of the dielectric constant and imaginary part of minus the inverse of the dielectric constant of CdS with 0.5% Se, for **E**$\perp c$ and **E**$\|c$.

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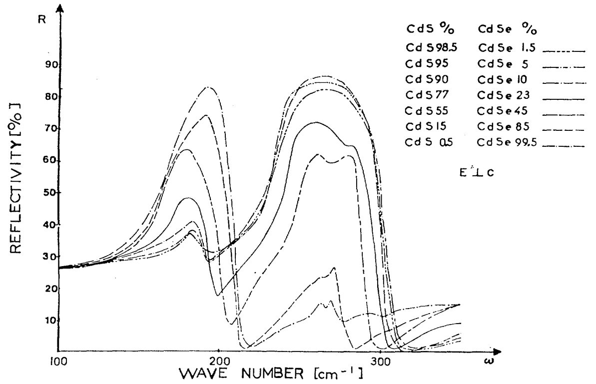

FIG. 7. Reflectivity spectra of mixed CdS_xSe_{1-x} for $\mathbf{E}\perp c$.

solving the set of equations $\epsilon\omega^2G'(\omega)=1$. The frequencies deduced from these equations are

$$\omega_{G\ \mathbf{E}\parallel c}=191\ \mathrm{cm}^{-1},\quad \omega_{G\ \mathbf{E}\perp c}=195\ \mathrm{cm}^{-1}.$$

These values are in good agreement with the experimental frequencies deduced from the infrared reflectivity spectrum with the help of the Kramers-Kronig relations:

$$\omega_{\mathrm{TO}\ \mathbf{E}\parallel c}{}^{G}=182.5\ \mathrm{cm}^{-1},\quad \omega_{\mathrm{TO}\ \mathbf{E}\perp c}{}^{G}=187\ \mathrm{cm}^{-1}.$$

C. Mixed Crystals of CdS_xSe_{1-x}

With increasing concentration of Se, the magnitude of the reflectivity peak increases as shown in Fig. 7 for $\mathbf{E}\perp c$.

The optical-mode frequencies are deduced by Kramers-Kronig relations from the reflectivity spectrum. The Se gap mode in CdS splits apart into two optical modes, having, respectively, the character of a TO and a LO mode. The frequencies of these two modes separate continuously from each other with increasing concentration, and attain the limiting values ω_{TO} and ω_{LO} of pure CdSe. The S local mode in CdSe has the same behavior with increasing concentration of S in CdS_xSe_{1-x}.

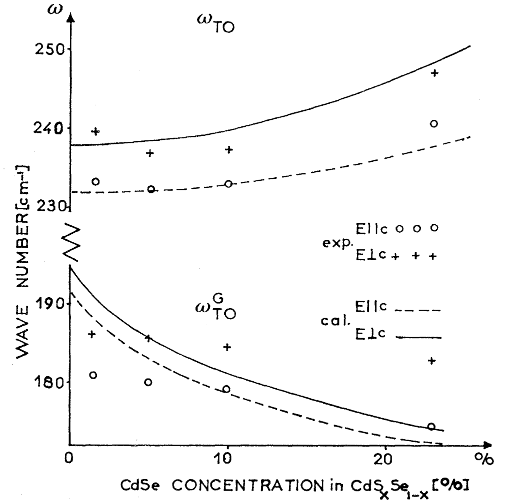

FIG. 8. Comparison between the calculated curves and the data deduced from the experimental reflectivity curves by Kramers-Kronig relations for $\mathbf{E}\perp c$ and $\mathbf{E}\parallel c$.

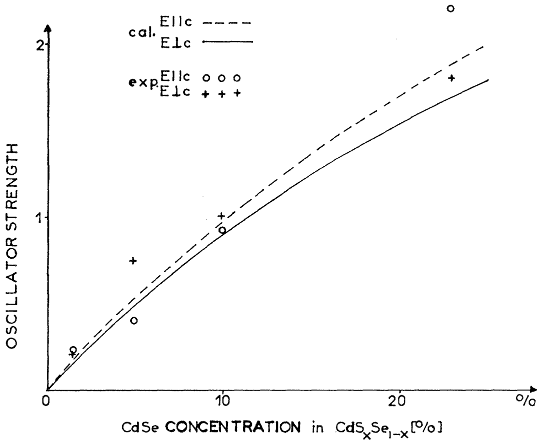

FIG. 9. Comparison between the calculated oscillator strength and the data deduced from the experimental reflectivity curves by Kramers-Kronig relations for $\mathbf{E}\perp c$ and $\mathbf{E}\parallel c$.

The normal-mode frequency of CdS is given by the solution of $\omega^2[1-\Delta(\omega)]=\omega_j{}^2$, where $\Delta(\omega)$ is related to the CdS Green's functions by (13) and (14).

The Se impurity gives a gap mode outside the region of the allowed normal-mode frequencies; the absorption occurs at

$$\omega_G{}^2[1-\Delta(\omega_G)]=\omega_j{}^2.$$

In the limit of low concentration, the gap-mode frequency ω_G is given by

$$\epsilon\omega_G{}^2G'(\omega_G)=1.$$

Figure 8 gives the calculated curves, as well as the values deduced by Kramers-Kronig relations from the reflectivity spectrum of CdS_xSe_{1-x}. The comparison between the calculated curves and the experimental data is fairly good for the ω_{TO} frequencies, but not as

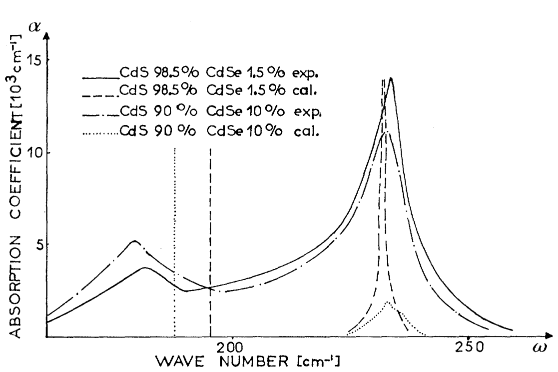

FIG. 10. Comparison between the calculated absorption curves and the curves deduced from the experimental reflectivity by Kramers-Kronig relations for two mixed crystals of CdS_xSe_{1-x}, with $x=0.985$ and 0.9.

good for the ω_G frequencies. This result is not surprising, because the spring constants were fitted to the CdS experimental values of ω_{TO} and ω_{LO} in the center of the Brillouin zone. The CdS density of states is probably more accurate near the experimentally known frequencies than in the gap of the density of states.

In Fig. 9 the calculated oscillator strengths of CdSe are compared with the values deduced by Kramers-Kronig relations from the reflectivity spectrum of CdS_xSe_{1-x}. The agreement between the calculated curves and the experimental values is satisfactory.

The absorption coefficient is proportional to the imaginary part of the inpurity Green's function:

$$\alpha(\omega)=\{2\omega(1-\epsilon)/\pi[1-(1-c)\epsilon]\}\ \mathrm{Im}\bar{G}(0,\omega).$$

In Fig. 10 the calculated and experimental absorption curves of two mixed crystals are compared. The agreement is poor, the discrepancies between calculation and experiment being the following:

(1) The calculated curve has one absorption band, which is maximum at the ω_{TO} frequency of CdS plus a δ function at ω_G, but the experimental curve shows two absorption bands which are maximum at the ω_{TO} and ω_G frequencies.

(2) The width of the calculated absorption coefficient curves is too small compared with the experimental width.

(3) The decrease of the maximum of the calculated magnitude of the absorption coefficient with the concentration of CdSe is too fast compared with the experimental decrease.

Two reasons can be given for the narrowness of the calculated Se absorption relative to the experimentally observed structure.

The expansion of the Green's function only to first order in the impurity concentration may not be sufficient: It results in an imaginary part of the impurity Green's function that is zero in the CdS phonon gap. An expansion to higher powers of the concentration would introduce a nonzero contribution to the Green's function in the gap, due to interactions among impurities.

On the other hand, if the CdS density of modes were not exactly equal to zero in its gap, the perturbed lattice Green's functions would not be zero in this gap, and the absorption coefficient of CdS_xSe_{1-x} would show two absorption bands. The difficulty may therefore also be due to inexactness in the calculated density of modes.

IV. DISCUSSION

The impurity-mode frequencies of S in CdSe have been calculated from the CdS density of states under the assumption that the density of states does not change between CdS and CdSe, provided we perform the appropriate frequency scaling by substituting for the ω_{LO} of CdS the value of the LO-mode frequency of CdSe. The calculated localized-mode frequencies are

$$\omega_{L\ E\parallel c}=266\ \mathrm{cm}^{-1},\quad \omega_{L\ E\perp c}=271\ \mathrm{cm}^{-1}.$$

These values are very close to the experimental frequencies,

$$\omega_{L\ E\parallel c}=266.5\ \mathrm{cm}^{-1},\quad \omega_{L\ E\perp c}=269\ \mathrm{cm}^{-1}.$$

This agreement supports the assumption made concerning the analogy between the densities of states in CdS and CdSe.

The gap-mode frequencies of Se in CdS have been directly calculated from the CdS Green's functions[20]:

$$\omega_{G\ E\parallel c}=191\ \mathrm{cm}^{-1},\quad \omega_{G\ E\perp c}=195\ \mathrm{cm}^{-1}.$$

These results are in good agreement with our experimental data,

$$\omega_{G\ E\parallel c}=182.5\ \mathrm{cm}^{-1},\quad \omega_{G\ E\perp c}=187\ \mathrm{cm}^{-1}.$$

In the case of heavy doping, an increase in the Se concentration creates two new constituents of the ω_G band having, respectively, the character of a LO ($\omega_{LO}{}^G$) and a TO ($\omega_{TO}{}^G$) mode, which depend on the impurity concentration and tend towards the normal-mode frequencies of CdSe in the high-concentration limit.

Experimentally, we have a continuous relation between localized- and normal-mode frequencies depending on concentration. Such behavior has been explained theoretically up to concentrations of 20% impurities in the host lattice.

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