[17]O. Wolman and A. Ron, Phys. Rev. 148, 548 (1966).
[18]L. M. Roth and P. Argyres, in Ref. 15.
[19]The spherical Bessel functions of complex argument and low order n were calculated using a combination upward recursion and series expansion method outlined in F. L. Galeener, Ph.D. thesis (Purdue University, 1970) (unpublished).
[20]For alternative computational methods see G. W. Kattawar and G. N. Plass, Appl. Opt. 6, 1377.
[21]F. L. Galeener, Phys. Rev. Letters 22, 1292 (1969).
[22]Annotated bibliography of Rayleigh's papers on scattering has been given by V. Twersky, Appl. Opt. 3, 1150 (1964).
[23]G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. 98, 368 (1955); 100, 618 (1955).
[24]J. K. Furdyna, Phys. Rev. Letters 14, 635 (1965).
[25]C. Hilsum and A. C. Rose-Innes, *Semiconducting III-V Compounds* (Pergamon, New York, 1961), curves 1 and 4 of Fig. 6.6, as well as Fig. 6.5 with theoretical extension to lower temperatures.
[26]F. L. Galeener, A. A. Saralkar, and J. K. Furdyna, Appl. Phys. Letters 17, 486 (1970).
[27]Hollow glass spheres wetted with a Teflon base adhesive: Eccospheres S1, supplied by Emerson and Cuming, Inc., Canton, Mass. and Adhesive 80, supplied by Fluoro Plastics, Inc., G and Venango Streets, Philadelphia, Penn. 19134.
[28]See, e.g., A. C. Hardy and F. H. Perrin, *The Principles of Optics* (McGraw-Hill, New York, 1932), p. 24.
[29]J. K. Furdyna, Phys. Rev. Letters 16, 646 (1966).
[30]L. E. Gurevich and A. L. Efros, Zh. Eksperim. i Teor. Fiz. 43, 561 (1962); [Sov. Phys. JETP 16, 402 (1963)].
[31]See, e.g., Kh. I. Amirkhanov and R. I. Bashirov, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiya 1, 49 (1965); [Sov. Phys. JETP Letters 1, 49 (1965)].

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Bound-Phonon Quasiparticle in CdS

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Bound optical phonons associated with the phonon-assisted I_1 (4888 Å) transition in CdS have been observed. These states arise from the bonding of an LO phonon to a neutral acceptor, which provides an attractive interaction for the phonon. The interaction is with LO phonons of small wave vector (near $\vec{\kappa}=0$). Both the Γ_1 and Γ_5 LO phonons, which result from a splitting due to anisotropic short-range interatomic forces, are observed in the bound states. The optical transitions described in this paper are similar to those described by Dean *et al.*, which involved optical phonons bound to neutral donors in GaP. The observed bound states were identified as $2S$, $2P$, and $3D$ states with measured binding energies of 26.4, 21.6, and 11.6 cm^{-1}, respectively.

I. INTRODUCTION

Phonon interactions with both free and bound excitons as well as other types of optical transitions in CdS have been reported by a number of investigators[1-5] over a period of more than two decades. Electron-phonon and exciton-phonon interactions are, indeed, quite strong in highly polar crystals, such as CdS, whose Fröhlich[6] polaron coupling constant is $\alpha \cong 0.7$, where

$$\alpha = \frac{e^2}{\sqrt{2}}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\left(\frac{m^*}{\omega_0 \hbar^3}\right)^{1/2} .$$

In CdS, as in other polar materials, phonon interactions with optical transitions are strongest of all for the LO phonons. But, among the many optical transitions observed in this material, it is the I_1 transition which shows the strongest interaction with the LO phonon. The I_1 transition in CdS has been identified as an exciton bound to a neutral acceptor site,[5] and it has been observed to couple to both the Γ_1 and Γ_5 LO phonons.[7]

Optical transitions have been observed in a number of ionic crystals[8-10] in which the energy separating the parent transition and its LO phonon sideband is less than the LO phonon energy $\hbar\omega_0$ by approximately 10%. In absorption spectra of AgBr:I transitions associated with the bound exciton occur at energy separations approximately 30% less than $\hbar\omega_0$. Several theories[11-13] have been produced in terms of which these results can be explained, bearing mostly upon the bound-phonon quasiparticle model.

Toyozawa and Hermanson[11] have described a quasiparticle consisting of the exciton-phonon bound state. They have calculated binding energies and oscillator strengths for this new quasiparticle which can account for phonon interactions whose energies are less than that of the LO phonon, $\hbar\omega_0$. Recently Dean *et al.*[14] have observed LO phonons bound to neutral donors in both Raman-scattered and luminescence spectra of GaP crystals, which were doped with S, Te, Si, and Sn.

They have interpreted their results as impurity modes associated with dielectric effects of the neutral donors, rather than as local modes associated with mass defects of the substituents.

In this paper we report bound optical phonons associated with the I_1 (4888 Å) transition in CdS. Several bound-state transitions have been observed, to which we have given the spectral assignments $2S$, $2P$, and $3D$. These states arise from the binding of an LO phonon to the neutral acceptor, to which an exciton is also bound, a configuration in which an attractive interaction is provided for the phonon. The interaction may be thought of as one in which the I_1 complex is coupled to LO phonons of small wave vector (near $\vec{\kappa} = 0$). Both the Γ_1 and Γ_5 LO phonon states,[7] which result from a splitting due to anisotropic short-range interatomic forces, are observed in the bound-phonon transitions.

II. EXPERIMENTAL METHOD

The CdS crystals used in this investigation were of the platelet type grown in an argon atmosphere. Since S doping seems to enhance the I_1 transition in CdS, crystals which were grown to a sulfur-rich condition were used in the present experiments. Such crystals are characterized by a strong green photoluminescence and a strong I_1 line. On the other hand, crystals grown to a cadmium-rich condition show a strong blue photoluminescence and the I_1 line is absent. Photoluminescence spectra were used to study the phonon interaction with the I_1 transition. The crystalline photoluminescence was excited by a 500-W high-pressure Hg lamp, equipped with black-light filter, and was photographically recorded using a high-resolution 2-m Bausch and Lomb grating spectrometer. The spectrometer produced a reciprocal dispersion of 2 Å/mm in first order and a spectral resolution of approximately 0.022 Å over the spectral region examined in the present experiments; i.e., the effective spectral slit width was $\sim 1\times10^{-5}$ eV. The samples were placed in the tip of a glass Dewar, immersed in liquid He, and maintained at a temperature of 1.2 °K. Magneto-optical measurements on the specimens were made in a conventional (iron-core) dc electromagnet, whose field strength ranged up to 40 000 G.

III. THEORETICAL BACKGROUND

Although it would appear that the local modes reported in the present paper are similar to the mass-defect modes described by Elliott and Dawber,[12] a closer examination reveals that the mass-defect model does not apply and that the present results can best be explained in terms of the dielectric-mode model developed by Toyozawa and Hermanson[11,13] and later modified and applied to bound-phonon donor states in GaP by Dean, Manchon, and Hopfield.[14] In fact, as Dean *et al.* have pointed out, the mass-defect local-mode theory does not account for the GaP local modes, even when large changes in the short-range spring constant are introduced. A similar argument can be advanced for the local modes observed in CdS. A further justification of the dielectric-mode model over that of the mass-defect mode can be seen from the computed phonon density of states in CdS, calculated according to a previously outlined procedure[7] and given in Fig. 1. The energy region in which the CdS local modes are observed is shown

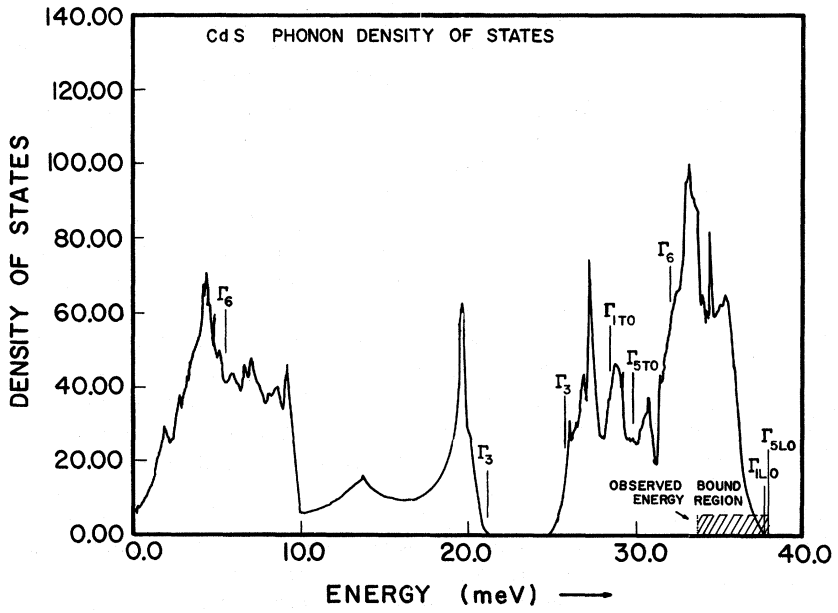

FIG. 1. Calculated phonon density of states for wurtzite CdS, showing the positions of the $\Gamma_{1\,LO}$ and $\Gamma_{5\,LO}$ phonon energies. Note that the region in which the bound-phonon complex states are observed corresponds to a high density of states.

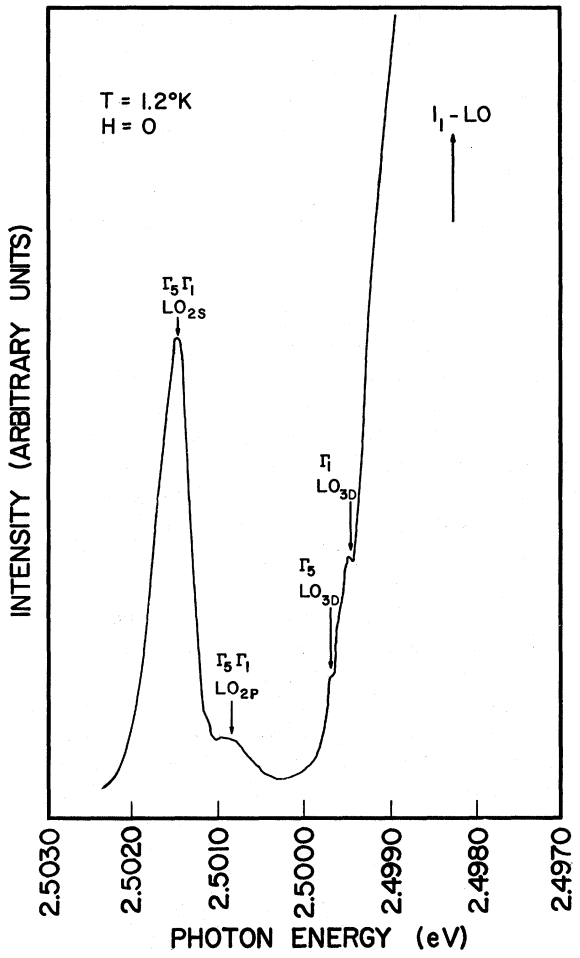

FIG. 2. Densitometer trace of the unpolarized emission spectrum of CdS at 1.2 °K, in the absence of a magnetic field, showing the I_1 LO bound-exciton transition, on whose high-energy side are observed the excited-state transitions of the bound-phonon complex.

in the cross-hatched area. Clearly, the energy spanned by the observed local modes belongs to a region of relatively high state density. Mass-defect modes, on the other hand, belong to regions of low state density, which means that they would lie either above 38 meV or below 26 meV—in either case beyond the range of the observed modes in CdS.

To estimate the energy region belonging to the dielectric modes in CdS, the procedure applied to GaP is used,[14] the only differences being that in the present paper the hydrogenic states belong to an acceptor rather than a donor, and that the binding energy is four times, rather than twice, the LO phonon energy. One has an interaction between the acceptor and the LO phonons of the form

$$\sum_{\vec{q},\lambda,\lambda'} [iV_q(\rho_{\vec{q}\lambda\lambda'} - \delta_{\lambda\lambda'}\rho_{\vec{q}00})a_\lambda^\dagger a_{\lambda'} b_{\vec{q}} + \text{H. c.}], \quad (1)$$

where λ and λ' denote acceptor energy states and $\vec{q}$ is the wave vector of the LO phonon. V_q is the Fröhlich electron-phonon coupling term

$$V_q = \left[2\pi\omega_0\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\right]^{1/2} q^{-1}, \quad (2)$$

$\rho_{\vec{q}} = e^{i\vec{q}\cdot\vec{r}}$, and the $a_\lambda^\dagger$'s ($b_{\vec{q}}^\dagger$'s) are creation operators for the acceptor (phonon) states. Calculating the effective scattering matrix element and neglecting the curvature of the LO-phonon dispersion curve, one obtains

$$4\pi\omega_0\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\frac{1}{K_q}\sum_{\lambda\neq 0}\frac{(E_\lambda - E_{1S})\rho^*_{\vec{k}\lambda_0}\rho_{\vec{q}\lambda 0}}{(E_\lambda - E_{1S})^2 - \omega_0^2}. \quad (3)$$

The next assumption is to use hydrogenic acceptor states and to truncate the series of expression (3) such that only the lowest excited state of each symmetry is considered in the calculation of its phonon binding energy. This gives for the S, P, and

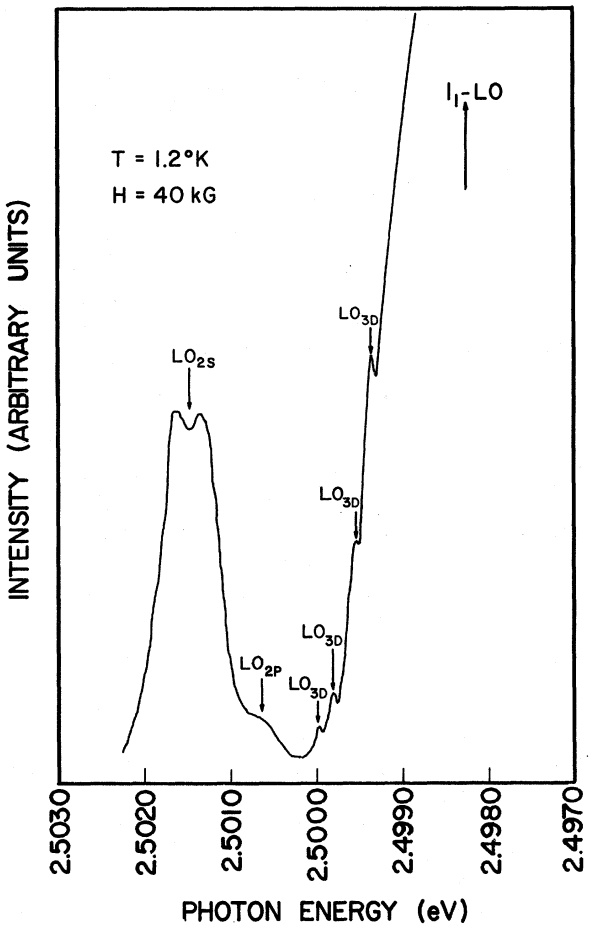

FIG. 3. Densitometer trace of the unpolarized emission spectrum of a CdS specimen at 1.2 °K, held in a magnetic field of 40 kG, in the orientation $C \perp H$, and showing the magnetic splittings of the I_1 phonon complex.

TABLE I. Experimental and calculated binding energies E_S, E_P, and E_D of LO phonons localized at the I_1 neutral acceptor site in CdS. (All units are in cm^{-1}.)

I_1 binding energy	Γ_5 LO phonon	Γ_1 LO phonon	2S binding energy Expt	2S binding energy Calc	2P binding energy Expt	2P binding energy Calc	3D binding energy Expt	3D binding energy Calc
1250	304.6	302.2	26.4	19.5	20.9	15.1	Γ_5: 11.8 Γ_1: 11.2	0.27

D binding energies and wave functions,

$$E_S = \frac{2^5}{3^6}\left(\frac{\epsilon_0}{\epsilon_\infty} - 1\right)\frac{1}{2a\epsilon_0}\,\frac{(E_{2S}-E_{1S})\omega_0}{(E_{2S}-E_{1S})^2-\omega_0^2}\,, \tag{4}$$

$$\Psi_S(k) \propto \frac{k\,P_0(\theta)}{[(3/2a)^2+k^2]^3}\,, \tag{5}$$

$$E_P = \frac{2^5\times 7}{3^8}\left(\frac{\epsilon_0}{\epsilon_\infty} - 1\right)\frac{1}{2a\epsilon_0}\,\frac{(E_{2P}-E_{1S})\omega_0}{(E_{2P}-E_{1S})^2-\omega_0^2}\,, \tag{6}$$

$$\Psi(k) \propto \frac{P_1(\theta)}{[(3/2a)^2+k^2]^3}\,, \tag{7}$$

$$E_D = \frac{3^4}{5\times 2^{15}}\left(\frac{\epsilon_0}{\epsilon_\infty} - 1\right)\frac{1}{2a\epsilon_0}\,\frac{(E_{3D}-E_{1S})\omega_0}{(E_{3D}-E_{1S})^2-\omega_0^2}\,, \tag{8}$$

$$\Psi_D(k) \propto \frac{k^2\,P_2(\theta)}{[(4/3a)^2+k^2]^4}\,, \tag{9}$$

where $P_l(\theta)$ are the Legendre polynomials. As we shall see in the following section, binding energies calculated from the above formulas are in satisfactory agreement with the experimental values which are deduced directly from the spectra.

IV. EXPERIMENTAL RESULTS

Within the validity of the effective-mass approximation, the expressions for the binding energies of the bound-phonon states (given in Sec. III) show that one would not expect to observe phonons bound to neutral donors in CdS, since the binding energy of the donor is less than the LO phonon energy. The situation is reversed for neutral acceptors, where 0.155 eV is the smallest binding energy reported for a neutral acceptor, as determined from the convergence limit of donor-acceptor pair spectra.[15] The LO phonon energy in CdS has been determined by several investigators,[16] and is approximately 0.038 eV (306 cm^{-1}). Henry *et al.*[17] report the acceptor binding energy for the I_1 line to be 0.168 ± 0.01 eV.

A densitometer trace of the observed emission spectra near the I_1 LO-phonon-assisted transition at zero magnetic field is shown in Fig. 2. The 2S, 2P, and 3D states are all resolved. The calculated and the observed binding energies are given in Table I. As shown in Fig. 2, the Γ_1-Γ_5 LO-LO splitting is clearly resolved in the 3D state and is measured to be 1.9 cm^{-1}. This splitting is 0.5 cm^{-1} less than that of the Γ_1-Γ_5 LO-LO free lattice phonon which has been measured[7] to be 2.4 cm^{-1}. The splitting that one calculates from Eq. (6) for the 2P state is 0.8 cm^{-1} less than that of the free lattice phonon, which probably accounts for the fact that this splitting was not resolved. One would expect the bound-phonon splitting to approach the free-phonon splitting for the higher excited states, as is observed.

Several crystal specimens were placed in a magnetic field of 40 000 G, in the orientation $C \perp H$, and their photoluminescence spectra were photographed. A densitometer trace of a typical spectrum near the I_1 LO-phonon-assisted transition is shown in Fig. 3. The magnetic field splitting of the 2S and 3D states is readily resolved. Since the I_1 complex (exciton bound to a neutral acceptor)

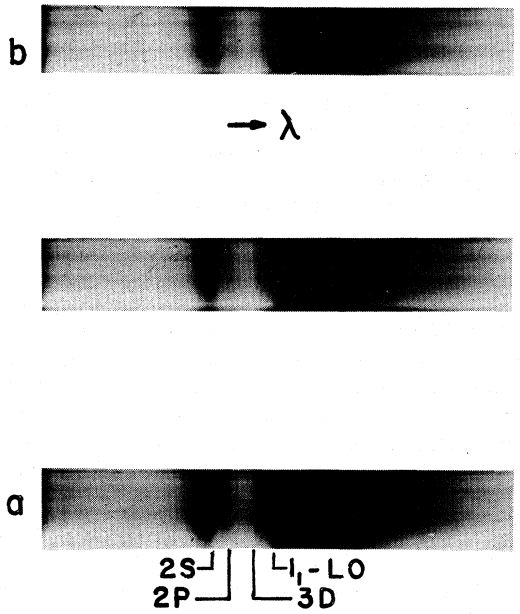

FIG. 4. (a) Photograph of the CdS emission spectrum in zero magnetic field, showing the bound-phonon structure near the I_1 LO parent line. (b) Photograph of the same spectral region as in (a) but in a field of 40 000 G. Note that the LO_{2S} and LO_{3D} bound-phonon peaks are split and clearly resolved. The middle spectrum represents an intermediate field strength.

splits into a doublet in this orientation,[5] the 2*S* and 3*D* peaks reflect the splitting of the neutral acceptor to which the LO phonon is bound. The splitting of the 2*P* state is not observed because this peak is of such low intensity and is merged into the wing of the much stronger 2*S* peak.

Photoluminescence spectra of a specimen in the same spectral region as described above are shown tor beyond the $n = 3$ state were not considered, but the inclusion of the higher excited states in the calculation would doubtless increase the binding energy. The calculated energies of the bound states (through $n = 2$) are approximately 30% lower than the observed values, as indicated in Table I. This is comparable with the GaP results of Dean *et al.*,[14] in which they report approximately the same difference between measured and calculated values for the bound states of donors. The experimental value which we observe for the binding energy of the 3*D* state is much larger than that calculated from the above model. However, the observed binding energy of the 3*D* state in CdS is comparable to that reported for the tentatively assigned 3*D* state in GaP. Although many simplifying assumptions are made in order to make the problem mathematically tractable, the general features of the dielectric-mode model, in which the LO phonon is localized at the neutral acceptor, provide a satisfactory explanation of the experimental results. in the photograph of Fig. 4. Shown in Fig. 4(a) is a spectrum at zero magnetic field, while Fig. 4(b) shows the same spectrum in a field of 40 000 G. The I_1 LO line is highly overexposed, as is the much more intense I_1 line which is merged with the acoustic phonon wing such that it appears uncharacteristically broad, but the magnetic splitting of the bound states is easily observed.

V. CONCLUSIONS

In the above formulation of the model, contributions involving excited configurations of the acceptor beyond the $n = 3$ state were not considered, but the inclusion of the higher excited states in the calculation would doubtless increase the binding energy. The calculated energies of the bound states (through $n = 2$) are approximately 30% lower than the observed values, as indicated in Table I. This is comparable with the GaP results of Dean *et al.*,[14] in which they report approximately the same difference between measured and calculated values for the bound states of donors. The experimental value which we observe for the binding energy of the 3*D* state in much larger than that calculated from the above model. However, the observed binding energy of the 3*D* state in CdS is comparable to that reported for the tentatively assigned 3*D* state in GaP. Although many simplifying assumptions are made in order to make the problem mathematically tractable, the general features of the dielectric-mode model, in which the LO phonon is localized at the neutral acceptor, provide a satisfactory explanation of the experimental results.

[1] F. A. Kroger, Physica 7, 1 (1940).

[2] L. R. Furlong and C. F. Ravilious, Phys. Rev. 98, 954 (1955).

[3] C. C. Klick, J. Opt. Soc. Am. 41, 816 (1951).

[4] L. S. Pedrotti and D. C. Reynolds, Phys. Rev. 119, 1897 (1960).

[5] D. G. Thomas and J. J. Hopfield, Phys. Rev. 128, 2135 (1962).

[6] H. Fröhlich, H. Pelzer, and S. Zienau, Phil. Mag. 41, 221 (1950).

[7] D. C. Reynolds, C. W. Litton, T. C. Collins, and E. N. Frank, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge*, 1970 (U.S. AEC Press, Washington, D. C., 1970), p. 519.

[8] W. Y. Liang and A. D. Yoffe, Phys. Rev. 20, 59 (1968).

[9] W. C. Walker, D. M. Roessler, and E. Loh, Phys. Rev. Letters 20, 847 (1968).

[10] R. Z. Bachrach and F. C. Brown, Phys. Rev. Letters 21, 685 (1968).

[11] Y. Toyozawa and J. C. Hermanson, Phys. Rev. Letters 21, 1637 (1968).

[12] R. J. Elliott and P. G. Dawber, Proc. Phys. Soc. (London) 81, 521 (1963).

[13] J. C. Hermanson, Phys. Rev. B 2, 5043 (1970).

[14] P. J. Dean, D. D. Manchon, and J. J. Hopfield, Phys. Rev. Letters 25, 1027 (1970).

[15] D. C. Reynolds and T. C. Collins, Phys. Rev. 188, 1267 (1969).

[16] M. Balkanski and J. Besson, J. Appl. Phys. 32, 2292 (1961); T. Deutsch, *ibid.* 33, 751 (1962); S. S. Mitra, Phys. Letters 6, 249 (1963); R. E. Halsted, M. R. Lorentz, and B. Segall, J. Phys. Chem. Solids 22, 109 (1961). The Γ_1 and Γ_5 components of the CdS LO phonon have been measured by the present authors (see Ref. 7): $\bar{\nu}_0\Gamma_1 = 302.2$ cm^{-1}; $\bar{\nu}_0\Gamma_5 = 304.6$ cm^{-1}. The Γ_1 and Γ_5 components have also been calculated by M. A. Nusimovici, M. Balkanski, and J. L. Birman [Phys. Rev. B 1, 595 (1970)], who put their values at 298 and 308 cm^{-1}, respectively.

[17] C. H. Henry, R. A. Faulkner, and K. Nassau, Phys. Rev. 183, 798 (1969).

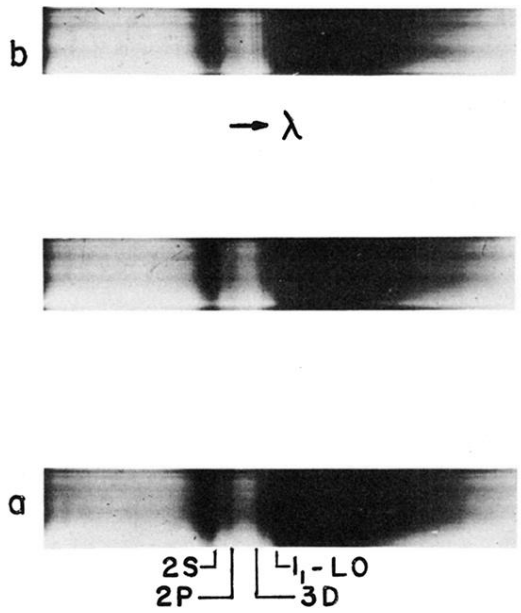

FIG. 4. (a) Photograph of the CdS emission spectrum in zero magnetic field, showing the bound-phonon structure near the I_1 LO parent line. (b) Photograph of the same spectral region as in (a) but in a field of 40 000 G. Note that the LO_{2S} and LO_{3D} bound-phonon peaks are split and clearly resolved. The middle spectrum represents an intermediate field strength.