Evidence for Luminescence Involving Arsenic Vacancy-Acceptor Centers in p-Type GaAs

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The observed similarity in the temperature behavior of peak shift, half-width, and intensity of the 1.37-eV band in p-type GaAs and the self-coactivated luminescence in ZnS substantiate a previously proposed model of recombination at an arsenic vacancy bound to an acceptor (Zn or Cd). The excitation spectra obtained through the use of GaAs laser diodes show a shoulder at 1.46 eV, just on the lower-energy side of the absorption edge. The shoulder is ascribable to absorption at the luminescence center responsible for the 1.37-eV band. Approximate configuration-coordinate curves are constructed for the centers in both Zn- and Cd-doped GaAs crystals from the experimental values of the low-temperature emission and excitation peak energies, the vibration frequency of the center in its excited state, and the activation energy for the temperature dependence of intensity. The non-Gaussian shape of the emission band is explained in terms of a small displacement between the minima of the configuration-coordinate curves. A vibration energy of 0.011 eV is determined for the excited state of the center, and a value between 0.011 and 0.0344 eV for the ground state of the center.

I. INTRODUCTION

THE first indication that an arsenic-vacancy–Zn-acceptor ($V_{As}Zn_{Ga}$) center was responsible for the 1.37-eV emission band at 20°K in Zn-doped GaAs was deduced from a study of melt-grown, Zn-doped GaAs heat treated under different conditions. It was noted that in GaAs:Zn the 1.37-eV band disappeared after heat treatment above 650°C. Saturation of the crystal with Ga at 800°C was found to have the effect of preserving the 1.37-eV band.[1] After the crystal GaAs:Zn was diffused with Cu under extrinsic condition, the band was replaced by a band of similar shape possessing sharp line structure with a zero-phonon line at 1.429-eV. The diffusion kinetics showed that this new sharp line band cannot be due to interstitial Cu nor due to any effect produced by the interstitial Cu on the centers responsible for the 1.37-eV band.[2] From these experiments and other observations in both n-type and undoped GaAs, the present author proposed that the center responsible for the 1.37-eV band are $V_{As}Zn_{Ga}$ pairs and that the effect of copper diffusion is to replace Zn_{Ga} to form a new center, $V_{As}Cu_{Ga}$.[2] These new $V_{As}Cu_{Ga}$ pairs are responsible for the band with sharp line structure.

The above model is consistent with the results of the following recent experiment. The luminescence of GaAs doped with Cd was studied. The GaAs:Cd crystals show a band similar to the 1.37-eV band in GaAs:Zn at a somewhat lower peak energy, 1.3631 eV as compared with a peak energy of 1.3676 eV for GaAs:Zn. This observation indicates that the peak energy for the emission depends on the specific acceptor involved. However, after the crystal GaAs:Cd was diffused with Cu under extrinsic conditions of the crystal, the band with peak energy of 1.3631 eV was replaced by a sharp line band identical to that observed in copper-diffused GaAs:Zn. The results are consistent with the model that the 1.37-eV band in GaAs:Cd is due to $Cd_{Ga}V_{As}$ pairs and that the effect of copper diffusion is to replace the Cd atom from the pair.

In contrast to the present work on the arsenic vacancy-acceptor center in p-type GaAs, Williams[3] recently examined the Ga vacancy-donor complex in n-type crystals. Evidence for luminescence from a Ga vacancy-donor center was presented from a parallel comparison with the self-activated luminescence from an analogous center, the Zn vacancy-donor center in ZnS.[3] The similarity in the observed peak shift, thermal quenching, and the half-width variation with temperature for both GaAs and ZnS indicates that the emission at 1.2 eV in n-type GaAs is due to localized electronic transitions from the excited state to the ground state of the Ga vacancy-donor center and that the configuration coordinate model can be used to explain the temperature behavior of the 1.2-eV band.

We have observed similar temperature behavior of the 1.37-eV band in GaAs:Zn and GaAs:Cd. This observation, when compared with the self-coactivated luminescence from the sulphur vacancy-acceptor center in ZnS,[4,5] appears to substantiate our proposed model for the arsenic vacancy-acceptor center in GaAs. The purpose of this work is to present the above result and, for completeness, to construct the configuration-coordinate (CC) curves for $V_{As}Zn_{Ga}$ and $V_{As}Cd_{Ga}$ in GaAs:Cd. We first compare the 1.37-eV band with the analogous luminescence in ZnS, following Williams' work.[3] We then show the excitation spectra and compute the CC curves. Finally, we explain the non-Gaussian band shape in terms of the computed CC curves.

[1] C. J. Hwang, J. Appl. Phys. **39**, 4307 (1968).

[2] C. J. Hwang, Bull. Am. Phys. Soc. **13**, 404 (1968); J. Appl. Phys. **39**, 4313 (1968).

[3] E. W. Williams, Phys. Rev. **168**, 922 (1968).

[4] S. Schionoya, in *Luminescence of Inorganic Solids*, edited by P. Goldberg (Academic Press Inc., New York, 1966), p. 205, and references therein.

[5] S. Shionoya, K. Urabe, T. Koda, and H. Fujiwara, J. Phys. Chem. Solids **27**, 865 (1966).
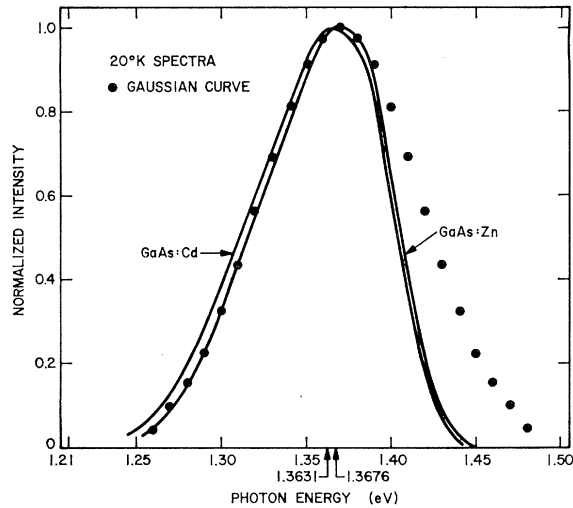
FIG. 1. The 1.37-eV band in GaAs:Zn and GaAs:Cd at 20°K. The solid circles are points of a Gaussian curve computed to get the best fit of the GaAs:Zn curve.

II. EXPERIMENTAL

Front-surface photoluminescence was used in the experimental arrangement previously described.[6] For a temperature variation study of the emission spectra, a He-Ne laser with 1.96-eV photon energy was used as the excitation source. The output power of the laser was about 1 mW and the laser beam was focused to a spot about 100 μ in diam. The excitation spectra were obtained through the use of a GaAs laser diode. The laser diode was operated continuously and the variation of the excitation wavelength was accomplished by changing the temperature and the injection current of the diode. The laser wavelength can be varied within about 100 Å in this way. Sometimes different diodes lasing at different wavelengths were used in wavelength ranges which could not be obtained through the above operation. The peak position of the 1.37-eV band appeared to be independent of the excitation power levels used. The excitation spectra were corrected to equal numbers of incident photons, and the emission spectra were all corrected for the wavelength dependence of the photomultiplier and the filter transmission.

The GaAs crystals were all melt-grown single crystals. The peak position at 20°K of the 1.37-eV band is practically independent of the doping level from 4×10^{16} to 2×10^{19} cm^{-3} for Zn-doped crystals and 1×10^{16} to 2×10^{17} cm^{-3} for Cd-doped crystals. In general, the heavier the doping, the stronger the emission of the 1.37-eV band. However, since the edge emission intensity also increases with the doping and its emission peak shifts to lower energy as the temperature rises, there will be some interferences between the edge emission band and the 1.37-eV band at higher temperatures. Consequently, the crystals chosen in this study

[6] C. J. Hwang, J. Appl. Phys. **38**, 4811 (1967).

are those which exhibit moderately strong 1.37-eV luminescence and the least overlap of the edge emission and the 1.37-eV bands. Several crystals were investigated. The data shown in this paper were taken from crystals whose room-temperature carrier concentrations are 5×10^{17} cm^{-3} for GaAs:Zn and 1×10^{17} cm^{-3} for GaAs:Cd.

III. RESULTS AND DISCUSSION

A. Temperature Variation of 1.37-eV Band

The spectral distribution of the 1.37-eV band is shown for GaAs:Zn and GaAs:Cd in Fig. 1. The emission bands have a similar shape. However, the band in GaAs:Cd is broader and occurs at somewhat lower energy. The dependence of the peak energy on the particular acceptors is similar to the self-coactivated luminescence of Cu and Ag in ZnS although the luminescence in ZnS:Ag occurs at higher energy than that in ZnS:Cu.[7] The 1.37-eV band in GaAs appears asymmetrical about the peak energy. In Fig. 1, we also show as solid circles the Gaussian curve calculated to get the best fit of the band in GaAs:Zn. It is seen that the low-energy side of the emission band can be described approximately as a Gaussian curve while the high-energy side of the band shows a rather steep front. This observation is in contrast with the self-coactivated luminescence in ZnS, which shows a Gaussian shape. The deviation of the 1.37-eV band from Gaussian will be discussed later.

Figure 2 shows the temperature dependence of the half-width W. The dependence appears to follow the
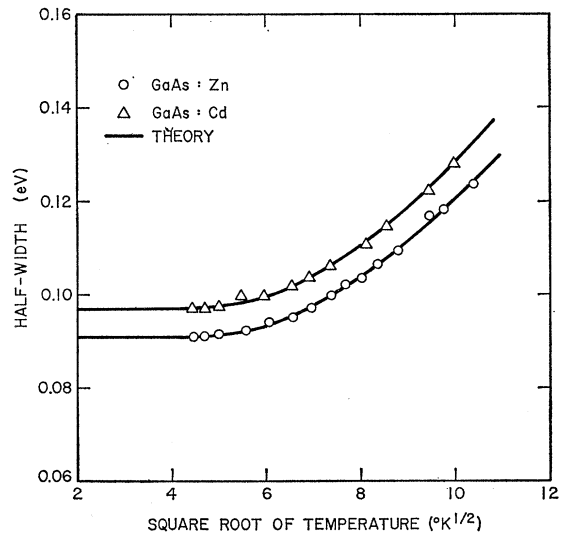

FIG. 2. Variation of the half-width W with the square root of the temperature T for the 1.37-eV band in GaAs:Zn and GaAs:Cd. The theoretical curve is a plot of Eq. (1), with $h\nu_e = 0.011$ eV.

[7] M. A. Aven and R. M. Potter, J. Electrochem. Soc. **105**, 134 (1958).

CC model equation[8]

$$W = A \left(\coth h\nu_e / 2kT \right)^{1/2}, \qquad (1)$$

where A is a constant whose value is equal to W as the temperature approaches $0°K$ and $h\nu_e$ is the energy of the vibration mode of the excited state. The values of 0.011 eV for $h\nu_e$ for both GaAs:Zn and GaAs:Cd were obtained by fitting Eq. (1) to the experimental points in Fig. 1. The value of A so obtained was larger for Cd (0.97 eV) than for Zn (0.91 eV). The measurements of the half-width were not continued above $115°K$ because the intensity decreases rapidly and the interference of the edge emission becomes more pronounced above this temperature. However, the changes in W between 20 and $115°K$ for both GaAs:Zn and GaAs:Cd are large enough to show the functional dependence of Eq. (1). The good fit to Eq. (1) and the fact that both the excited state and ground-state vibration energies, $h\nu_e = 0.011$ eV and $0.011 \leq h\nu_g \leq 0.0344$ eV (see Sec. III B), are smaller than the LO phonon energy of 0.036 eV show the localized nature of the centers and the validity of applying the CC model.[9] The self-coactivated center in ZnS:Cu also has $h\nu$ values for both excited and ground states which were less than the LO phonon energy.[4]

Figure 3 shows the shift of the emission peak as a function of temperature. The shift represents the change from the 0° value obtained by extrapolation of a plot of the peak energy against temperature. Both Zn and Cd show an increase in peak energy as the temperature increases. This is opposite of the band-gap change, which is also shown in Fig. 3. The shifts of the peak energy with temperature appears to be the same for both Zn and Cd. It is interesting to note that the shifts in Fig. 3 were the same as those observed for the self-coactivated luminescence from ZnS:Cu. For both
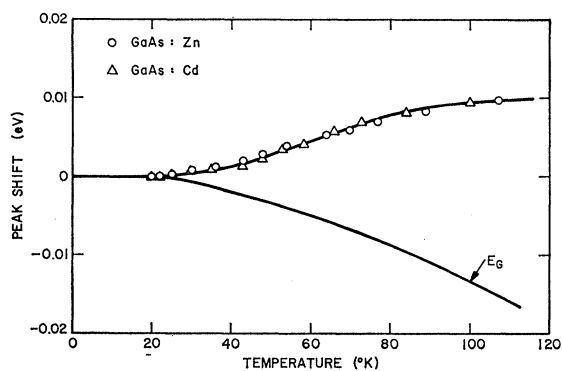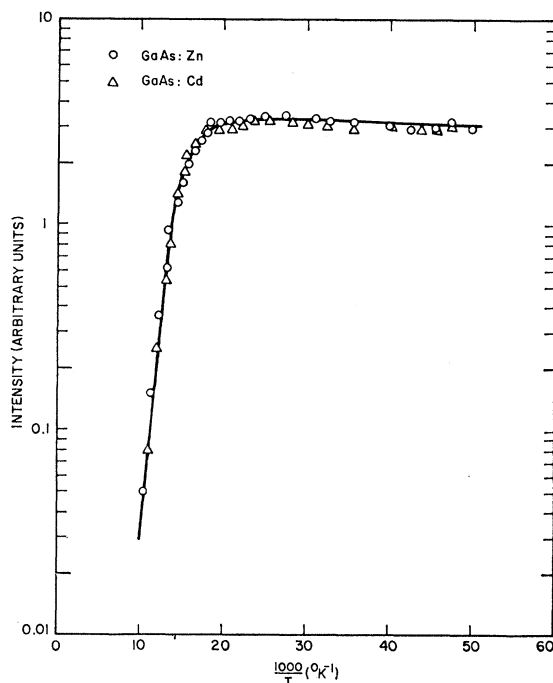

FIG. 4. Variation of the intensity of the 1.37-eV band with the reciprocal temperature in GaAs:Zn and GaAs:Cd. The activation energy E_Q for the thermal quenching is 0.087 eV.

emission bands, the shift changes slowly at first, then more rapidly, and finally levels off above a certain temperature; but for ZnS, this temperature is $190°K$ compared to $100°K$ for GaAs. The magnitude of the shift is about 0.01 eV for GaAs and about 0.03 eV for ZnS.

The intensity variations with temperature, plotted in Fig. 4, were remarkably similar for both Zn- and Cd-doped samples. The intensities at a given temperature were different, but the curves were brought into coincidence by multiplying by a constant. The activation energy E_Q derived from the slope of the straight line is 0.087 eV, which is much smaller than the value of 0.24 eV for the self-coactivated luminescence in ZnS:Cu. There are three mechanisms which can account for the observed luminescence quenching. (a) In terms of the CC model, the quenching is due to the population of an appreciable concentration of excited electrons near the proximity of the ground and excited states which then return to the ground state through nonradiative transitions. This process was used to explain the luminescence quenching in KCl:Tl.[10] (b) Thermal excitation of electrons from the excited state to the conduction band (see Fig. 6) becomes more rapid at higher temperatures than the recombination from the excited state to the ground state of the center. The occurrence of this process should be accompanied by the increase of the emission transitions between the

FIG. 3. Peak shift as a function of temperature for the 1.37-eV band in GaAs:Zn and GaAs:Cd. The change in energy gap E_G derived from Sturge's absorption data [Phys. Rev. **127**, 768 (1962)] is also shown for comparison.

[8] C. C. Klick and J. H. Schulman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 100.

[9] G. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956).

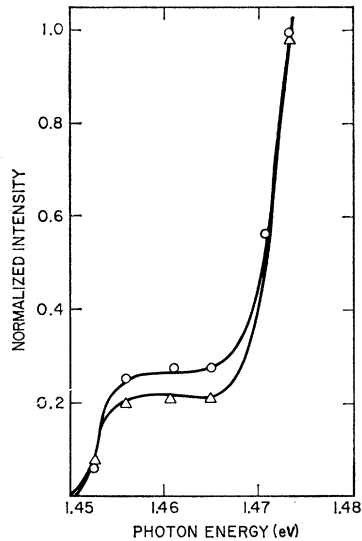[10] F. E. Williams, J. Chem. Phys. **19**, 457 (1951); Phys. Rev. **82**, 381 (1951).

FIG. 5. Excitation spectra at 20°K for centers responsible for the 1.37-eV bands in GaAs:Zn and GaAs:Cd. The spectra were corrected to equal number of incident photons.

conduction band and the Zn acceptor levels (the edge emission). Since this latter emission also decreases as the temperature increases, the above explanation seems unlikely. (c) Other centers may be involved. These centers would have to have an ionization energy such that the emitted photon energy is less than 1 eV, the spectral range measured here. The only other luminescence observed was the 1.485-eV band near edge emission,[1] which appears not related to the 1.37-eV band, as was pointed out above.

B. Excitation Spectra

The normalized excitation spectra of the 1.37-eV band are shown in Fig. 5. The measurements were done at 20°K and the intensities were taken as the peak intensities. The normalization was made with respect to the luminescence intensity when excited with 1.473-eV light. The intensity starts to rise as the excitation light energy passes 1.45 eV. There is a shoulder at about 1.46 eV which is considered ascribable to the absorption of the centers responsible for the 1.37-eV band. As the excitation energy increases beyond 1.47 eV, the intensity increases rapidly. Since this photon energy is near the absorption edge in the p-type GaAs doped with Zn or Cd to a level of about 6×10^{16} to 4×10^{17} cm^{-3},[11,12] the rapid increase may be considered to be due to the excitation of the electrons from the filled Zn or Cd acceptor band to the conduction band. Some of the conduction electrons are subsequently trapped by the excited states of the center and return to the ground state by emission of the 1.37-eV luminescence (see Fig. 6). Such an abrupt rise in excitation spectra has

been seen for self-activated centers in ZnS in which the excitation spectrum is close to the fundamental absorption edge of the crystal.[4]

The value of 1.46 eV will be taken as the peak energy of the absorption band at 20°K, which is equivalent to assuming that the absorption constant is a step function of the photon energy from 1.45 to 1.465 eV. In this case, the absorption lengths of the incident photons should be the same, and correction for the emission intensities resulting from different absorption constants are identical in the same wavelength range. The above assumption can be relaxed when the sample thickness is small compared to the absorption lengths between 1.45 and 1.465 eV. An attempt to obtain the absorption constants of the centers in this energy range was not successful because the effect was largely masked by the edge and the free carrier absorptions. However, we can conclude from this observation that the absorption constant between 1.45 and 1.465 eV must be at least one order of magnitude less than that due to the edge and the free carrier absorptions in the same energy range (about 22 cm^{-1} for GaAs:Cd with $p = 1 \times 10^{17}$ cm^{-3} and about 25 cm^{-1} for GaAs:Zn with $p = 5 \times 10^{17}$ cm^{-3}). For a typical sample thickness of about 375 μ, the condition that the sample thickness is small compared to the absorption length between 1.45 and 1.465 eV is satisfied.

C. Computation of Configuration Coordinate Curves

In this section, we shall construct the CC curves and explain the non-Gaussian emission bands in terms of the CC model.

If we assume that an arsenic vacancy (V_{As}) is a donor,[13] then the arsenic vacancy will be ionized in p-type GaAs. Thus, our proposed center in p-type GaAs will be considered as an acceptor (Zn, Cd) bound to a nearest-neighbor arsenic vacancy by a Coulomb force to form a $V_{As}Zn_{Ga}$ or $V_{As}Cd_{Ga}$ center. Following ZnS work,[4] let us assume that the ground state of the localized center is derived from the Zn(Cd) acceptor level A, and that the excited state originates from the arsenic vacancy donor level D and that the zero-point of both states lies within the band gap.[4] Figure 6 shows
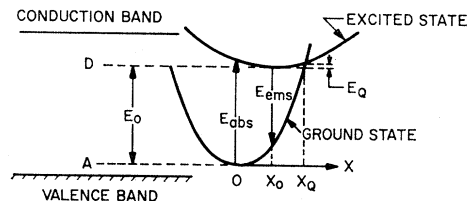

FIG. 6. CC model for the 1.37-eV luminescence in GaAs (Ref. 4). Also shown are the band gap, and donorlike (D) and acceptorlike (A) levels of zero-point energies of the ground and excited states, respectively, which lie within the band gap. E_{abs} and E_{ems} are the absorption and emission energies.

[11] D. E. Hill, Phys. Rev. 133, A866 (1964).
[12] J. I. Pankove, Phys. Rev. 140, A2059 (1965).

[13] F. A. Kröger, The Chemistry of Imperfect Crystals (John Wiley & Sons, Inc., New York, 1964), p. 703.

such a model. The actual separation of D and A from the bands will be different from the isolated donor and acceptor because the Coulomb attraction between them modifies the separation slightly. The CC curves will be constructed based on the following assumptions: (a) A single set of potential-energy curves describing the ground and excited states of the system, (b) these curves are parabolic in shape, and (c) the curves are displaced with respect to each other so that the optical transitions are made from the minimum of one curve to a portion of the side of the second curve. The transition is vertical because the Frank-Condon principle holds. The above assumptions are generally made when experimental data are used to obtain the CC curves.[8]

From Fig. 6, a set of equations relating the experiment with the constants of the CC curves may be written. Taking the zero-point vibrational energy into account, we have

$$E_{abs}(0°K) = E_0 + \tfrac{1}{2}K_e X_0{}^2 - \tfrac{1}{2}h\nu_g \qquad (2)$$

and

$$E_{ems}(0°K) = E_0 - \tfrac{1}{2}K_g X_0{}^2 + \tfrac{1}{2}h\nu_e, \qquad (3)$$

where $E_{abs}(0°K)$ and $E_{ems}(°K)$ are the peak energies of the absorption and emission bands, K is the force constant, ν is the vibration frequency of the system, and the subscripts e and g denote, respectively, the excited and ground states. The excited and ground states are displaced by an amount E_0 in the energy and X_0 in the coordinate. ν_e (ν_g) is simply related to K_e (K_g) by

$$K_e = 4\pi^2\nu_e{}^2 M_e, \quad K_g = 4\pi\nu_g{}^2 M_g, \qquad (4)$$

where M is the mass assigned to the center. E_Q is related to the constants of the curves by[8]

$$E_Q = \frac{K_g K_e X_0[K_e X_0 + K_g X_0 - 2(K_g K_e X_0{}^2 + 2K_g E_0 - 2K_e E_0)^{1/2}] + 2K_e E_0(K_g - K_e)}{2(K_g - K_e)^2}. \qquad (5)$$

However, the accuracy of this last expression should be poor since it assumes that the ground state is accurately parabolic up to the point of intersection. For large amplitudes of oscillation the repulsive forces would cause the curve to rise more rapidly than parabolic.[8] As a result the value of E_Q obtained from Eq. (5) using the constants of the curves should be larger than that obtained from experiment. In other words, if the experimental value of E_Q is used to de-termine K_g from Eq. (5), K_g so obtained will be larger than the actual experimental value.

A plot of emission peak energy as a function of temperature shows the extrapolated values of $E_{ems}(0°K)$ = 1.3676 eV for GaAs:Zn and $E_{ems}(0°K) = 1.3631$ eV for GaAs:Cd. Since these values show no deviation from the 20°K values, we shall assume $E_{abs}(0°K)$ = $E_{abs}(20°K) \simeq 1.46$ eV for both GaAs:Zn and GaAs: Cd. As the temperature increases, more electrons in the excited state will populate near the point X_Q in Fig. 6 and can return to the ground state through the radia-tionless transitions. If the quenching process observed in Fig. 4 corresponds to the above mechanism, we have $E_Q = 0.087$ eV. In addition, it is assumed, as was done in the case of KCl:Tl,[10,14] that the vibration mode of importance is one in which the ions immediately surrounding the luminescence center move in a radial direction from it, and the coordinate X is the varia-tion from an equilibrium position of the distance be-tween the center and its nearest neighbors. In this case, the mass M is taken to be that of three As atoms surrounding the Zn (Cd) acceptor and three Ga atoms surrounding the As vacancy so that $M_e = M_g = 7.2 \times 10^{-22}$ g. This value might be a reasonable one be-cause, as we have seen from Fig. 2, the excited state vibration frequency does not depend on the specific acceptor Zn or Cd involved. In fact, the assignment of the mass M to a specific value is unimportant as far as the relative position of the two curves are concerned. Different values of M will correspond to different scales used for the horizontal axis X of the CC diagram, as is evidenced from Eqs. (2)-(5).
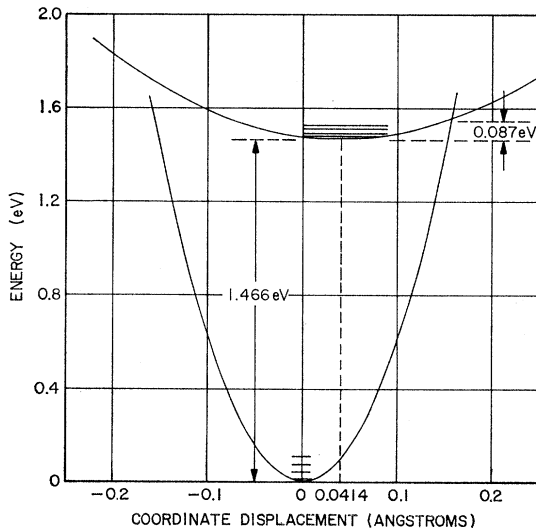

FIG. 7. Approximate CC curves for the 1.37-eV band in GaAs:Zn and GaAs:Cd. Constants for curves are $K_e = 2 \times 10^5$ dyn/cm, $K_g = 20 \times 10^5$ dyn/cm, $X_0 = 3.95 \times 10^{-10}$ cm, $E_0 = 1.466$ eV, $E_Q = 0.087$ eV, and $M_e = M_g = 7.2 \times 10^{-22}$ g. The energy levels are drawn corresponding to a vibrational energy in the ground state of 0.011 eV and for an energy of 0.0344 eV in the excited state.
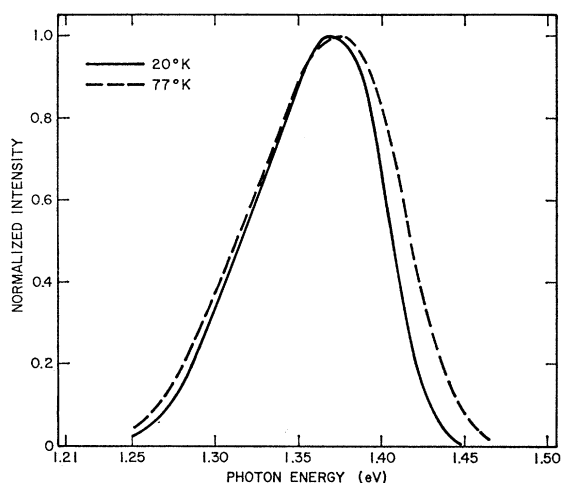
[14] C. C. Klick, Phys. Rev. 85, 154 (1952).

FIG. 8. The 1.37-eV bands in GaAs:Zn at 20 and 77°K.

A series of values for ν_g are chosen, and Eqs. (2)–(4) solved for K_e, K_g, X_0, and E_0. These values are substituted in Eq. (5) until a value of ν_g is found giving a value of E_Q which checks the experimentally determined one. For GaAs:Zn, the value of ν_g found in this way corresponds to an energy $h\nu_g$ of 0.0344 eV. The constants describing the CC curves are $K_e = 2\times10^5$ dyn/cm, $K_g = 20\times10^5$ dyn/cm, $X_0 = 4.14\times10^{-10}$ cm, and $E_0 = 1.466$ eV. For GaAs:Cd, the small difference in $E_{ems}(0°K)$ yields essentially the same constants for the CC curves. The CC curves computed from these constants are plotted in Fig. 7. Four vibrational levels are also shown for both excited and ground states. We note that the two curves are only slightly displaced due to the small value of X_0, and that the emission transitions are to the lowest levels of the ground state. This observation means that the emission band will deviate from Gaussian on the high-energy side as we have observed. The CC model predicts a Gaussian emission band only when X_0 is large enough such that the ground-state-energy curve can be approximated by a straight line.[15] Since K_g computed in this way should be larger than the actual value, as we have pointed out before, the actual ground-state-energy curve will have a slower variation of energy with X for smaller X. In this case, more transitions to lowest levels of the ground state are allowed. At low temperatures, such as 20°K, only the lowest levels of the excited state are occupied. A transition from the lowest level of the excited state to the lowest level of the ground state limits the high-energy extent of the emission. There should be no

such abrupt termination on the low-energy side of the emission, and the spectrum should be approximately Gaussian on the low-energy side. This conclusion is in qualitative agreement with the spectra shown in Fig. 1. A similar spectrum was observed in Zn_2SiO_4:Mn, in which the computed X_0 was also small.[16] As the temperature increases, more high-energy levels are occupied, and the high-energy side should be less abrupt. This is indeed seen in Fig. 8, which shows the comparison between the spectra taken at 20 and 77°K, respectively.

The CC model shows that the shift of the peak energy should be opposite to the band gap when $h\nu_g \geq h\nu_e$.[17] Thus, $h\nu_g$ in our luminescent systems must lie between 0.011 and 0.0344 eV.

IV. CONCLUSION

This work appears to have shown that the emission band around 1.37 eV in p-type GaAs exhibits properties which are characteristic of self-coactivated luminescence in ZnS crystals. This observation substantiates our model proposed earlier that the center is an As vacancy bound to an acceptor. The variation of emission half-width can be described by an equation derived from the CC model. The excitation spectra have been obtained through the use of GaAs laser diodes. The approximate CC curves have been computed both for GaAs:Zn and GaAs:Cd from the low-temperature emission peak energy, peak energy for the excitation spectra, the vibrational frequency for the excited state of the center, and the activation energy for the thermal quenching. The deviation of the band shape from Gaussian was successfully explained in terms of a small coordinate displacement of the CC curves thus computed.

As it is in the case of a Ga vacancy-donor complex, the CC model can be applied to describe an As vacancy-acceptor center. The Gaussian band shape of the 1.2-eV band in n-type GaAs will therefore imply a larger coordinate shift of the excited- and ground-state-energy curves for the Ga vacancy-donor center.

ACKNOWLEDGMENTS

[15] D. Curie, *Luminescence in Crystals* (John Wiley & Sons, Inc., New York, 1963), p. 50.

[16] C. C. Klick and J. H. Schulman, J. Opt. Soc. Am. **42**, 910 (1952).

[17] S. Shionoya, T. Koda, K. Era, and H. Fujiwara, J. Phys. Soc. Japan **19**, 1157 (1964).