# Evidence for Self-Activated Luminescence in GaAs: The Gallium Vacancy-Donor Center

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Evidence for self-activated luminescence at 1.2 eV at low temperatures in *n*-type GaAs was obtained by a comparison with ZnS luminescence. Both luminescence lines have a Gaussian-like shape, and a similar temperature dependence of half-width, peak energy, and intensity. The half-width temperature variation was predicted by the configurational coordinate model. A vibrational energy of 0.022 eV is calculated for the excited state of the center. The luminescence was observed in GaAs samples doped with a single donor to a carrier concentration of from $1\times10^{18}$ to $5\times10^{18}$/cc. The following donors were studied: C, Si, Ge, Sn, S, Se, and Te. Each donor modified the luminescence to some extent, and the emission peak energy shift of 0.02 eV of group-IV donors from group-VI donors in the same period is similar, though smaller, to the shift observed in the analogous centers in ZnS and ZnSe. This supports the conclusion that the center is a gallium vacancy bound to a donor.

## I. INTRODUCTION

SELF-ACTIVATED (SA) luminescence in ZnS has been extensively studied.[1,2] Prener and Williams[3] suggested that the center responsible for the luminescence was of a complex nature and consisted of a zinc vacancy in association with a group-III (Ga) or group-VI (Cl) substitutional donor which was situated on one of the nearest-neighbor zinc or sulphur lattice sites, respectively. Since the zinc vacancy $(V)_{Zn}$ is an acceptor, there is a Coulombic attraction between it and the donor (say $Cl_S$); and the stable, localized center $(V)_{Zn}$-$Cl_S$ is formed in the lattice. The localized electron transitions from the excited state to the ground state of this molecular-like center produce the characteristic SA luminescence.

Numerous luminescence measurements were carried out on ZnS and ZnSe in an attempt to substantiate this model. The shift in emission peak between donors from different groups in the periodic table could be thought of as due to the different lattice positions of the donors and their consequent different separations from the zinc vacancy in ZnS and ZnSe to which they were bound.[4,5] The temperature dependence of the half-width could be explained in terms of a localized molecular model.[6-8] The one-dimensional configurational coordinate curve[9] was successfully constructed by a combination of temperature, pressure, absorption, and excitation measurements on ZnS doped with chlorine by Koda *et al.*[10] Polarization experiments on single-crystal samples confirmed the symmetry of the center and were in complete agreement with the proposed model.[11]

The symmetry was further confirmed by electron-paramagnetic-resonance experiments on photoexcited ZnS: Al [12-15] and ZnS: Cl.[7,16] The resonance experiments of Schneider *et al.*[14] were the most conclusive and could only be explained in terms of the Prener-Williams model. They observed hyperfine structure which was characteristic of the different donor impurities in ZnS doped with either a group-III impurity (Al or Ga) or a group-VII impurity (Cl, Br, or I).

Since III-V compounds are related both in structure and semiconducting properties to the zinc-blende II–VI compounds, it is possible that self-activated luminescence might occur in them if the excited state were stable. For instance, in GaAs it is possible that complexes such as $(V)_{Ga}$-$Te_{As}$ or $(V)_{Ga}$-$Sn_{Ga}$ could be formed. An indication of the existence of such a center in III-V compounds has so far only been found for GaAs.

* The experimental work on which this paper is based was carried out at Texas Instruments Incorporated, Dallas, Tex.

1 S. Shionoya [in *Luminescence of Inorganic Solids*, edited by P. Goldberg (Academic Press Inc., New York, 1966), pp. 225–286] gives a review of the large number of papers published on self-activated luminescence in ZnS.

2 D. Curie and J. S. Prener [in *Physics and Chemistry of II–VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland Publishing Co., Amsterdam, 1967), pp. 445–452] reviews self-activated luminescence in ZnS and ZnSe.

3 J. S. Prener and F. E. Williams, J. Chem. Phys. **25**, 261 (1956).

4 J. S. Prener, and D. J. Weil, J. Electrochem. Soc. **106**, 409 (1959).

5 W. C. Holton, M. de Wit, and T. L. Estle, in Proceedings of the International Symposium on Luminescence, Munich, 1965, p. 454 (unpublished), and references therein.

6 H. Samelson and A. Lempicki, Phys. Rev. **125**, 901 (1962).

7 S. Shionoya, T. Koda, K. Era, and H. Fujiwara, J. Phys. Soc. Japan **18**, Suppl. 2, 299 (1963).

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

9 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] gives a review of the application of the configurational-coordinate model to luminescence.

10 From the luminescence studies as a function of temperature and pressure, and absorption and excitation measurements of the self-activated luminescence in ZnS:Cl, Koda *et al.* were able to construct the one-dimensional configurational-coordinate curves from which they calculated values of half-width and temperature shift of the emission peak which agreed with these measured experimentally. T. Koda, S. Shionoya, M. Ichikawa, and S. Minomura, J. Phys. Chem. Solids **27**, 1577 (1966).

11 T. Koda and S. Shionoya, Phys. Rev. **136**, A541 (1964).

12 J. Schneider, W. C. Holton, T. L. Estle, and A. Rauber, Phys. Letters **5**, 322 (1963).

13 A. Rauber and J. Schneider, Phys. Letters **2**, 230 (1963).

14 J. Schneider, A. Rauber, B. Dischler, T. L. Estle, and W. C. Holton, J. Chem. Phys. **42**, 1839 (1965).

15 R. A. Title, G. Mandel, and F. F. Morehead, Phys. Rev. **136**, A300 (1964).

16 R. A. Title [in *Physics and Chemistry of II–VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland Publishing Co., Amsterdam, 1967), pp. 303–308] gives a review of the electron paramagnetic experiments. A brief review is also given in Ref. 2.

The first indication that a gallium vacancy was responsible for some of the infrared emission in GaAs was deduced from a study of GaAs prepared under different conditions. It was noted that in GaAs:Te for a doping level of $6\times10^{17}$ electrons/cc or greater, there was a broad emission peak at about 1.3 eV at 77°K which was only present in Bridgman-grown and floating-zone-grown crystals but not in single-crystal samples grown from a gallium solution.[17] This luminescence was probably the same as the broad emission lines previously observed in the energy region 1.2–1.3 eV in *n*-type GaAs at 77°K.[18,19] Queisser and Fuller[20] were the first to measure this deep level accurately in GaAs:Te by carefully correcting their spectrum taken at 20°K for the wavelength-dependent filter transmission and photomultiplier response. The level was found to be close to 1.2 eV. On heat treatment, the emission was enhanced and copper diffusion was found to eliminate the emission altogether. These experiments, and the fact that gallium vacancies would be minimized in a crystal grown from a gallium solution, led them to postulate that the center responsible for the luminescence was due to one or more gallium vacancies with a donor bound to them.

This was confirmed by other authors, who not only noted the absence of the emission in solution-grown GaAs but also in all heavily zinc- and cadmium-doped GaAs in which the gallium vacancy concentration should also be reduced since the acceptors are substitutional and on the gallium lattice sites.[21] The latter authors observed the emission in the region of 1.2 eV in all *n*-type GaAs doped to a level of $1\times10^{18}$ donors/cc or greater with either group-IV or group-VI impurities. Heavy *n*-type doping with a group-VI element should reduce the arsenic vacancy concentration and hence increase the gallium vacancy concentration, since the product of the two vacancy concentrations must remain constant at a given temperature. The inverse is true for the group-IV element explaining the observation of emission at much lower doping levels in GaAs:VI than in GaAs:IV.

All of the above is therefore consistent with the emission being attributable to a gallium vacancy in GaAs, but it does not indicate whether the vacancy has donor atoms bound to it as in ZnS. The possibility that this was analogous to SA luminescence in ZnS was first pointed out by this author who observed that the emission-peak shift in energy for the GaAs:Te emission between 20 and 80°K was in the opposite direction to the band gap and other simple acceptor centers in GaAs.[22]

[17] M. B. Pannish, H. J. Queisser, L. Derick, and S. Sumski, Solid State Electron. **9**, 311 (1966).
[18] M. I. Nathan, G. Burns, S. E. Blum, and J. C. Marinace, Phys. Rev. **132**, 1482 (1963).
[19] D. E. Hill, Phys. Rev. **133**, A866 (1964).
[20] H. J. Queisser and C. S. Fuller, J. Appl. Phys. **37**, 4895 (1966).
[21] E. W. Williams and D. M. Blacknall, Trans. AIME **239**, 387 (1967).
[22] E. W. Williams, Brit. J. Appl. Phys. **18**, 253 (1967).

The purpose of the present work was to make a detailed study of this luminescence in GaAs and to compare it with the II–VI compounds. The line shape was studied at a fixed temperature and as a function of temperature, the differences in the emission peak for four group-IV donors (C, Si, Ge, and Sn) and three group-VI donors (S, Se, and Te) were noted; and the change in peak position with temperature and the thermal quenching of the emission were observed for GaAs:C, GaAs:Sn, and GaAs:Te.

## II. EXPERIMENTAL TECHNIQUE

Front-surface photoluminescence was studied and the apparatus used has been previously described.[23] The exciting radiation was supplied by a 200-W high-pressure mercury arc filtered with a copper sulfate solution. A $\frac{3}{4}$-m SPEX grating spectrometer was used and an *S*1 photomultiplier cooled with nitrogen gas was mounted on its exit slit. The photoluminescence spectra were corrected for the detector cutoff, since this was rather sharp in the region studied, and for any transmission or reflection changes that occurred in the optical components. In order to do this the sample was replaced by a tungsten lamp whose spectral output at a constant temperature was accurately known. All of the other components in the optical setup were unchanged. The spectrum of the lamp was then measured and by combining this with the lamp calibration spectrum the correction to be applied at a given wavelength was calculated.

The samples were mounted on a heat sink in a vacuum in a cryogenic Dewar and were not exposed directly to the coolant liquid. A calibrated iron-constantin thermocouple and a calibrated germanium thermometer were mounted in the heat sink close to the sample. The sample was cooled to approximately 20°K when the Dewar was filled with liquid helium. After expelling the helium the Dewar was allowed to warm up to room temperature. If the vacuum in the Dewar was below $1\times10^{-6}$ Torr, the warmup time from 20–200°K was more than 4 h. This meant that measurements every 3 or 4°K could be made with reasonable accuracy. The temperature was measured during the scan when the emission-peak intensity was a maximum and the total variation in temperature during the scan never exceeded 1 deg.

The GaAs samples were all single crystals and their orientations, dopants, and carrier concentrations are given in Table I. They were all melt grown with the exception of Nos. 3 and 6 which were grown epitaxially by hallide vapor transport. Each sample was doped with only a single impurity to a level in the range $1\text{–}5\times10^{18}$ donors/cc. This reasonably heavy doping level was chosen because the luminescence under study was strongest in this doping region and the number of

[23] E. W. Williams and R. A. Chapman, J. Appl. Phys. **38**, 2547 (1967).

TABLE I. Description of GaAs samples. The peak energy and half-width of the self-activated luminescence are shown.

| Sample No. | Crystal orientation | Type | Carrier concentration[a] | Dopant | Emission peak energy (eV) | Half-width $W$ (eV) | Temperature (°K) |
|---|---|---|---|---|---|---|---|
| 1 | ⟨111⟩ | $n$ | $1.1\times10^{18}$ | Carbon | $1.173\pm0.004$ | 0.158 | 82[b] |
| 2 | 111 | $n$ | $2.3\times10^{18}$ | Silicon | $1.179\pm0.004$ | 0.171 | 74 |
| 3 | 100 | $n$ | $5\times10^{18}$ | Germanium[c] | $1.199\pm0.004$ | 0.185 | 78 |
| 4 | 111 | $n$ | $1\times10^{18}$ | Tin | $1.196\pm0.004$ | 0.205 | 74[b] |
| 5 | 111 | $n$ | $1\times10^{18}$ | Tin | $1.200\pm0.006$ | [d] | 77[b] |
| 6 | 100 | $n$ | $2\times10^{18}$ | Sulphur[c] | $1.197\pm0.004$ | 0.165 | 74 |
| 7 | 111 | $n$ | $5\times10^{18}$ | Selenium | $1.224\pm0.004$ | 0.175 | 74 |
| 8 | 100 | $n$ | $2\times10^{18}$ | Tellurium | $1.216\pm0.004$ | 0.165 | 76[b] |
| 9 | 100 | $n$ | $5\times10^{18}$ | Tellurium | $1.200\pm0.004$ | 0.181 | 74 |

[a] Hall measurements at 77°K.
[b] Temperature runs made on these samples.
[c] Epitaxial samples; the rest were melt-grown.
[d] The emission intensity was so weak that the half-width could not be measured.

other background impurities was two orders of magnitude smaller and would not be expected to mask any properties due to the single donor element.

## III. EXPERIMENTAL OBSERVATIONS

### A. General Characteristics

The spectral distribution of the SA luminescence[24] is shown for six donors in Fig. 1. The emission-peak energy, half-width, and temperature of these spectra are specified in Table I. All of the emission-line peaks lie in the energy range 1.17–1.22 eV and have a similar shape. They are very broad and do not have any fine structure, and their half-widths are all of the same order. The lines appear to be approximately symmetrical about the peak energy. Three pairs of curves have been plotted to compare the donor elements that lie within the same period of the periodic table. For each pair of curves a similar sample doping level and temperature was chosen since these parameters effect the linewidth and peak position to some extent. A comparison of the half-width and peak energy of samples 8 and 9 in Table I show that doping affects the emission. This was not fully investigated but the detailed changes in the spectra with temperature are outlined below.

Figure 1 shows that the emission-peak energy at a constant doping level and temperature varies with the element used as the dopant. In every case the group-IV lies below the group-VI element emission peak for each pair. The separation of the lines was very similar for all three pairs and only varied from 0.018 eV for Si and S in Fig. 1(a) to 0.025 eV for Ge and Se in Fig. 1(b) and 0.020 eV for Sn and Te in Fig. 1(c).

The group-IV associate emission half-width is always larger than the group VI one (see Fig. 1 and Table I). The difference varied considerably between pairs and no attempt was made to compare these differences since some of the half-widths could not be as accurately measured as others. This was because the low intensity of the luminescence for some samples produced a scattering of the corrected intensity values on the low-energy side of the emission peak below 1.15 eV.

Quite large differences in intensity were observed from sample to sample at a given temperature. The GaAs:C sample (not shown in Fig. 1 because its pair element O was not studied) and the best tin sample (No. 4) were an order of magnitude more intense than any of the others. This difference was not understood.

The rapid decrease in intensity as the temperature rises above 100°K, combined with the fact that some of the samples only showed a weak emission at lower temperature, meant that only samples doped with carbon, tin, and tellurium could be measured over a wide range of temperature.

### B. Variations with Temperature

The temperature dependence of the half-width, $W$, appears to follow the configurational-coordinate[9] model equation:

$$W=A(\coth h\nu/2kT)^{1/2}. \quad (1)$$

Here $A$ is a constant whose value is equal to $W$ as the temperature approaches 0°K and $h\nu$ is the energy of the vibrational mode of the excited state (see Sec. IV). In Fig. 2, Eq. (1) has been fitted to the experimental values for the GaAs:C and GaAs:Sn samples. The value of $h\nu$ used was 0.022 eV and this appears to fit both curves. The value of the constant $A$ was larger for tin (0.200 eV) than for carbon (0.157 eV). The measurements of the half-width were not continued above 200°K because of the reduced intensity of the emission. From the curves shown in Fig. 3 for the GaAs:C emission at three temperatures, 20, 146, and 195°K, it can be seen that there is already some asymmetry in the emission line at 195°K. It is thought to be due to the inaccuracy of the correction to the photomultiplier cutoff at low energies and low intensities. The symmetry was not so severe for the GaAs:Sn emission because it shifts to higher energies as the temperature increases. This perhaps explains why the high-temperature tin $W$ values are not scattered as

[24] The term SA luminescence will be used for convenience in the rest of the text even though this luminescence line has not been conclusively proved to be self-activated. This was the only deep-level luminescence that was observed down to 1.0 eV. Near-band-gap radiation was also observed for all the samples but this will not be discussed here.

much as the carbon ones since the carbon peak shifts to lower energies, as shown in Figs. 3 and 4.

Preliminary measurements of the shift of the emission peak with temperature were mentioned previously for tellurium-doped GaAs.[22] The tellurium results were confirmed and are compared in Fig. 4 with those of the carbon- and tin-doped samples. Sn(1) is No. 4 in Table I and is the one that is shown in Fig. 2. Sn(2) is a second tin-doped sample that was cut from the same crystal as Sn(1) and is No. 5 in Table I. The value of the peak energy at 0°K was found by extrapolation of a plot of the peak energy against temperature. The peak shift represents the change from this zero value. Both tin and tellurium show an increase in energy as the temperature increases. This is the opposite of the band-gap change which is also shown in Fig. 4.[25] Carbon, on the other hand, although it first appears to be departing a little from the band gap at low temperatures, then changes at the same rate as the band gap from 80–200°K. The experimental error in the peak-energy measurements is indicated by the error bar drawn on some of the carbon points. The error in Sn(2) was larger than for the other curves and this may partly account for its departure from the Sn(1) curve. The variation of Sn(1) and Sn(2) are the same, however, since they both show a rapid change below 90°K and then remain approximately constant above this temperature.

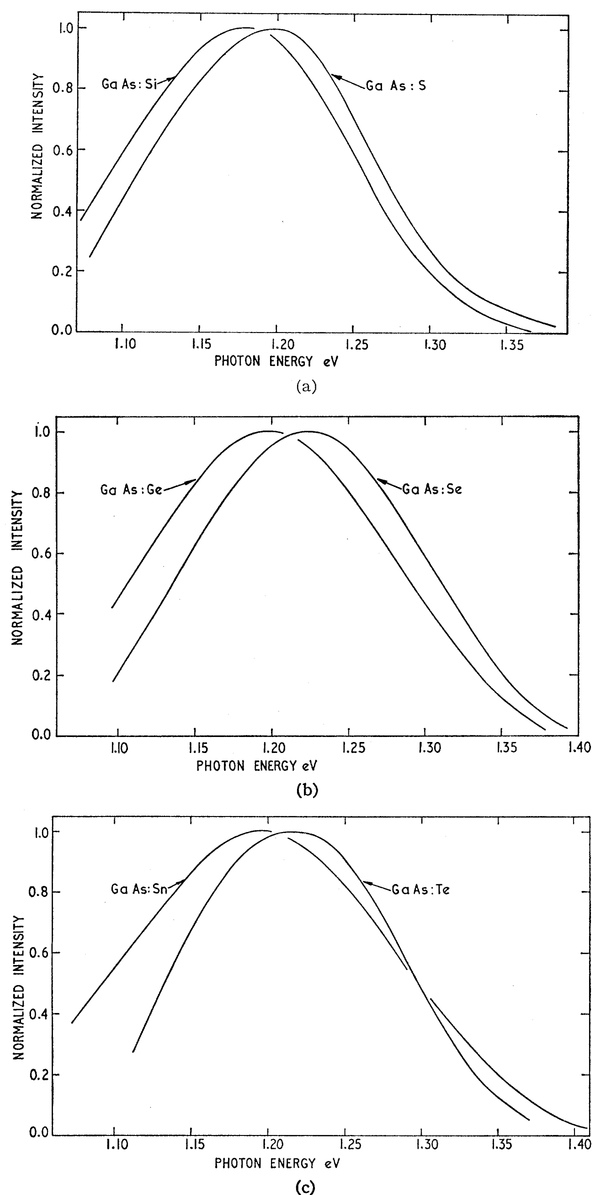


FIG. 1. (a) Self-activated (SA) luminescence in GaAs:Si at 74°K and GaAs:S at 74°K. The peak energies and half-widths are given in Table I. The separation between the peaks is 0.018 eV. (b) SA luminescence in GaAs:Ge at 78°K and GaAs:Se at 74°K. The peak energies and half-widths are given in Table I. The separation between the peaks is 0.025 eV. (c) SA luminescence in GaAs:Sn (sample 4) at 74°K and GaAs:Te at 76°K (sample 8). The peak energies and half-widths are given in Table I. The separation between the peaks is 0.020 eV.

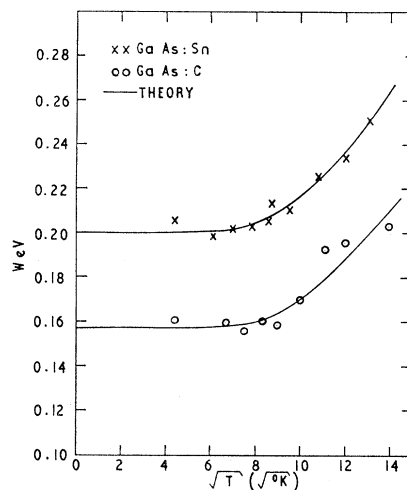


FIG. 2. Variation of the half-width $W$ with the square root of the temperature $T$ for SA in luminescence in GaAs:Sn and GaAs:C. The theoretical curve is a plot of Eq. (1) with $h\nu=0.022$ eV.

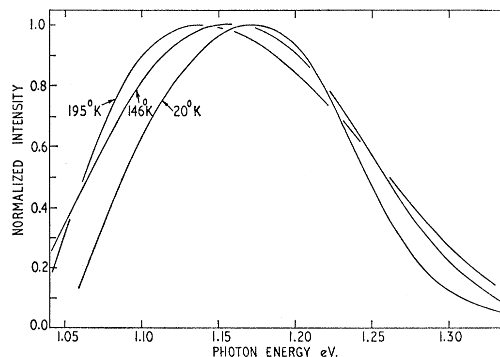


FIG. 3. SA Luminescence in GaAs:C at 20°, 146°, and 195°K.

[25] The band-gap variation was taken from Sturge's absorption measurements as a function of temperature. M. D. Sturge, Phys. Rev. **127**, 768 (1962).

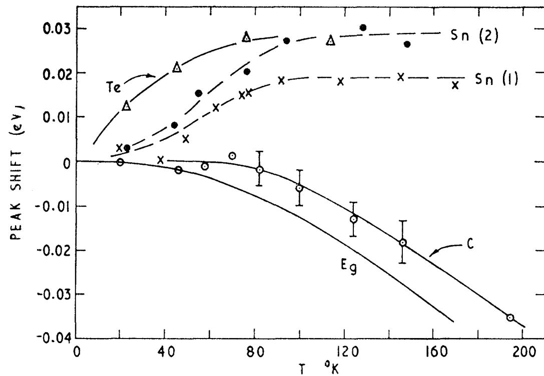


FIG. 4. Peak shift from 0°K as a function of temperature for SA luminescence in GaAs:Sn (1) (sample 4), GaAs:Sn (2) (sample 5), GaAs:Te (sample 8), and GaAs:C (sample 1). The change in energy gap derived from Sturge's (Ref. 25) absorption data is shown for comparison.

The intensity variations with temperature, plotted in Fig. 5, were remarkably similar for all of the above samples. The intensities at a given temperature were different but the curves were brought into coincidence by multiplying by a constant. In the range 20–70°K the intensity changes very little. The values below 40°K are not shown but they differed very little. For example, for GaAs:Sn at 20°K the intensity was 69.7 compared to 64.7 at 43°K. Above 70°K the intensity decreases at a larger rate until it is dominated by a quenching process above 200°K. The activation energy $\Delta E$ for this thermal quenching process is 0.18 eV. This is derived from the equation

$$I=K\exp(\Delta E/kT), \quad (2)$$

where $I$ is the intensity and $K$ is a constant.

The quenching was so efficient that the luminescence was only detected in one sample at room temperature. For this, the tin sample, the intensity was more than ten times smaller at 300°K then the lowest value shown in Fig. 5 (260°K).

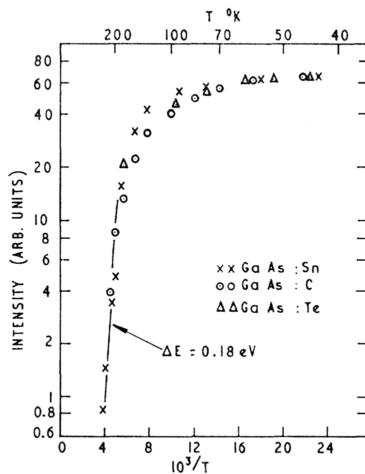


FIG. 5. Variation of intensity with the reciprocal temperature for SA luminescence in GaAs:Sn, GaAs:C, and GaAs:Te. $\Delta E$ =0.18 eV is the activation energy for the thermal quenching as derived from Eq. (2).

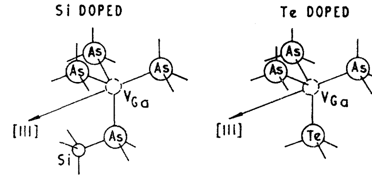


FIG. 6. The Prener-Williams model for SA luminescence in GaAs showing the two different types of center for a group-IV atom and a group-VI atom bound to a gallium vacancy in the zinc-blende lattice.

## IV. DISCUSSION

### A. General Characteristics

The possibility of SA luminescence in $n$-type GaAs is strongly supported by a comparison of the experimental observations given above with those of ZnS. The center predicted by Prener and Williams for SA luminescence in ZnS has been strongly established. The analogous center in GaAs is shown in Fig. 6. It is assumed that the gallium vacancy is an ionized acceptor and that one silicon or tellurium donor atom is bound to the vacancy by a Coulombic force to form the $(V)_{Ga}Si_{Ga}$ and $(V)_{Ga}Te_{As}$ centers, respectively, where (V) means a group-V element.

Since the configurational-coordinate (CC) model was so successful in explaining the behavior of the luminescence associated with such a localized center in ZnS,[10] it was also applied here. Figure 7 shows the model. Following the ZnS work let us assume that the ground state of the localized center is derived from the gallium vacancy-acceptor level, and that the excited state originates from the donor $D$ and that the zero point of both states lies within the band gap.[1] The separation of $A$ and $D$ from the bands will be different from the isolated donor and acceptor because the Coulombic attraction between them modifies the separation slightly.

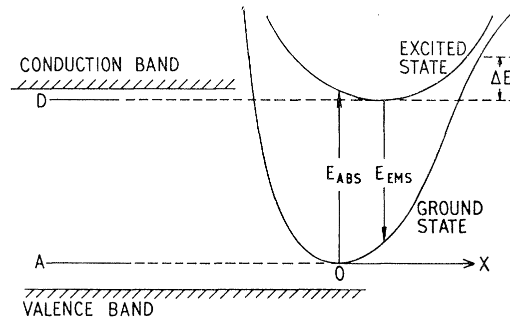


FIG. 7. The configurational coordinate model for SA luminescence in GaAs (Ref. 9). Also shown are the band gap, and donorlike ($D$) and acceptorlike ($A$) levels of the zero-point energies of the ground state and excited states, respectively, which lie within the band gap. $E_{abs}$, the absorption energy, is greater than $E_{ems}$, the emission energy, and the difference is the Stokes shift. The transitions are vertical because of the Franck-Condon principle.

The fact that the bonding between atoms in GaAs is more covalent than ionic means that the displacement $X$ of the minima is small so there would only be a small difference (or Stokes's shift) between the energy of absorption transitions $E_{abs}$ and the energy of emission $E_{ems}$. The electron transitions between the ground state and excited state are vertical because the Franck-Condon principle holds.

It is to be expected that there should be a difference in the CC curves for the $(V)_{Ga}Si_{Ga}$- and $(V)_{Ga}Te_{As}$-type centers shown in Fig. 6. The binding energy of a hole to the center will be less the closer the donor impurity is to the gallium vacancy. The ground state of the $(V)_{Ga}Te_{As}$-type center should be nearer to the valence band than the $(V)_{Ga}Si_{Ga}$-type center. Therefore, the emission-peak energy should be greater for the former center. The CC curves have not been calculated for GaAs since the transition $E_{abs}$ which can be measured from absorption or excitation spectra has not been observed. An unsuccessful excitation experiment with GaAs:C and GaAs:Te using a 500-$W$ tungsten source lamp implies that the probability of the $E_{abs}$ transitions is so small that they will be difficult to observe.

The expected difference in the CC curves for the two types of center is implied by the emission-peak shift of approximately 0.02 eV between all group-IV and group-VI pairs in Fig. 1. A comparison with ZnS and ZnSe shows that in both cases for the analogous center, there is a similar, though somewhat larger, energy shift. Just as in GaAs, when $(V)_{Ga}(IV)_{Ga}$ lies below the $(V)_{Ga}(VI)_{As}$ emission line, in ZnS (or ZnSe) the $(V)_{Zn}(III)_{Zn}$ lies below the $(V)_{Zn}(VII)_S$ (or $V_{Zn}(VII)_{Se}$) line. The shift was 0.04 eV for ZnS:Al and ZnS:Cl,[4] 0.04 eV for ZnS:Ga and ZnS:Br,[4] and 0.05 eV for ZnSe:Al and ZnSe:Cl.[5]

It can be assumed in the classical CC model that the electron density in the vibrational-state continuum of both ground and excited states is given by a Boltzmann distribution. This means that the shape of the emission on absorption spectra will be Gaussian provided that the displacement between the minima is sufficiently large. The emission lines observed for GaAs did have a shape which was close to Gaussian. This is shown for GaAs:C at 58°K in Fig. 8. The scatter in the experimental points on the low-energy side of the peak was not due to fine structure but to errors obtained in correcting the spectra.

### B. Temperature Variations

The quantum-mechanical modification of the configurational-coordinate model predicts that the half-width $W$ is given by Eq. (1), where $\nu$ for emission is the frequency of the excited-state quantized vibrational levels.[9] The good fit to this equation that was found for GaAs:C and GaAs:Sn shows the validity of applying the CC model here. The vibrational energy $h\nu$ of 0.022 eV is somewhat smaller than the longitudinal-optical-

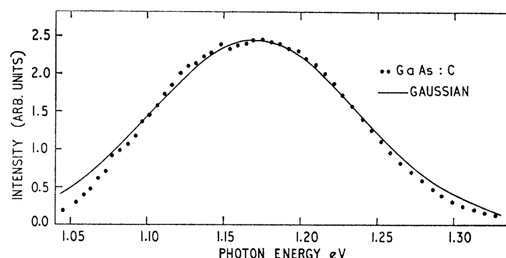


FIG. 8. SA Luminescence in GaAs:C at 58°K compared to a Gaussian distribution.

phonon energy of 0.036 eV.[22] This is reasonable, since it can be assumed that an electron trapped on the center will interact with both optical and acoustic phonons and that the value of 0.022 eV should be less than the maximum value of 0.036 eV for these phonons. That many phonons were involved is shown both by the width and the lack of fine structure on the curves. The curves (see Figs. 1 and 8) were always at least nine or ten longitudinal optical phonons wide.

It is interesting to note that the SA center in ZnS:Cl also had an $h\nu$ value which was below the longitudinal-optical-phonon energy and that the comparative width, shape, and lack of fine structure were all similar when the larger phonon energy was taken into account.[1,7,8]

The peak shift with temperature that was observed for GaAs was similar to that observed for ZnS. The GaAs:Sn and GaAs:Te curves shown in Fig. 4 were the same as those observed for the SA luminescence from a ZnS:Cl powder phosphor.[8] For both emission lines the shift changed rapidly at first and then became constant above a certain temperature. But for ZnS this temperature is 200°K compared to 100°K for GaAs. This flattening off of the curve is not understood and for some reason it was not observed for a single-crystal sample of ZnS:Cl which showed a linear increase as a function of temperature.[8,10] The direction of the linear tempeature variation and the magnitude has been calculated with the CC model for ZnS and the agreement between theory and experiment was very good.[10] The shift is opposite to the band gap when the excited-state vibrational energy is larger than or equal to the ground-state vibrational energy and when the CC curves do not change shape with temperature. The magnitude of the shift from 0–200°K of about 0.02–0.03 eV was the same for both GaAs and ZnS.

The GaAs:C curve in Fig. 4 is anomalous. The peak shift is like the $G$-Cu and $B$-Cu centers in ZnS in that it changes negatively and follows the band-gap change.[8] Shionoya[1] uses the difference in temperature shift to classify luminescence centers in ZnS. Those which shift positively like the SA center are the $B$ group and they are centers of the Prener-Williams type to which the CC model can be applied. The $A$ group consists of centers with a negative shift and these appear to follow the Schon-Klasans model. (This model is just conduction-band–to–impurity-level recombination.) Different po-

larization properties were observed for $A$ and $B$ and it was found that $A$ centers did not change in half-width as much as the $B$ group and did not appear to follow the CC model.[1]

For GaAs this distinction cannot be made since the GaAs:C and GaAs:Sn half-width change in the same manner with temperature and fit the CC model variation. Also, there is no significant difference in the peak energy and line shape at low temperatures, implying that the centers are similar. The fact that they are also both group-IV elements and can be used to make $n$-type GaAs with similar electrical properties also implies little difference between Sn and C in GaAs.

An alternative explanation to this anomaly is that the Prener-Williams model fits for both Sn and C, the difference in temperature dependence being caused by a difference in the CC curves. This difference would have to be in the ground state because the excited-state vibrational energies are the same. The negative shift would occur if the excited-state frequency is smaller than the ground-state vibrational frequency. The verification of this will have to await calculation of the configurational-coordinate model for SA luminescence in GaAs.

The change in intensity with temperature that was observed for the three centers in GaAs is similar to the ZnS:Cl center.[11] The activation energy for the quenching shown in Fig. 5 is much smaller, being 0.18 eV for GaAs compared to 0.64 eV for ZnS, and the onset of the quenching occurs at a lower temperature for GaAs. A similar behavior which was observed for a KCl:Tl $F$ center was explained in terms of the CC model.[26] When the temperature was such that some electrons were $\Delta E$ above the minimum of the excited state (see Fig. 7), then because of the proximity of the ground and excited states at this energy electrons can go directly into the ground state without the emission of light. An equation similar to Eq. (2) was used to determine the activative energy for the nonradiative recombination.

There are two other explanations. The first is that electron recombination from the ground state into the valence band becomes more rapid at higher temperatures then recombination from the excited to the ground state of the center. This could be verified by luminescence and lifetime measurements in the 6-$\mu$ wavelength region where the ground-state–to–valence-band transitions will be observed. The second explanation is that other centers may be involved. These centers would have to be beyond the spectral range measured here and be less than 1.0 eV. The only other luminescence that was observed was near the band edge of GaAs but this also decreased as the temperature increased. It was not rapidly quenched and appeared to be unrelated to the SA luminescence.

Finally, it must be stressed that the work described here only gives some evidence for the existence of SA luminescence in GaAs. As with ZnS and ZnSe, many more experiments will be required before the presence of a molecularlike complex such as $(V)_{Ga}$-$Te_{As}$ can be established. In particular, electron-paramagnetic-resonance experiments would be desirable. It is unlikely that hyperfine structure will be observed in the resonance lines because of their broad width in GaAs. This broadening is thought to be due to hyperfine interaction between nearest-neighbor gallium and arsenic atoms which both have nuclear spins of $\frac{3}{2}$.[27]

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