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Phosphorus and Arsenic Impurity Centers in ZnSe. II. Optical and Electrical Properties*

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ZnSe crystals containing phosphorus or arsenic which are grown under conditions enhancing their incorporation as uncompensated acceptors show broad luminescence bands in the red and infrared portions of the spectrum. Excitation bands are found which are resolved from the band-edge absorption. Infrared quenching of photoluminescence and photoconductivity identify the 1.91-eV luminescence of ZnSe : P as originating from the P_{Se} center identified by EPR. The crystals behave electrically as high-resistivity material showing *p*-type conductivity in the dark at elevated temperatures. Photoconductivity at low temperatures is *n* type and is sensitized by the ionized P'_{Se} acceptor. Configuration coordinate curves for the ground and excited states of the P_{Se} center are derived which are consistent with the distortions from T_d symmetry observed previously by EPR.

I. INTRODUCTION

ZnSe crystals have been prepared with the group-V impurity dopants P and As using crystal-growth conditions such that these dopants are present as uncompensated acceptors. In the preceding paper,[1] hereafter referred to as I, the occurrence of the defect center, phosphorus or arsenic substitutional for selenium P_{Se} or As_{Se},[2] was confirmed by electron paramagnetic resonance, and some details of the atomic structure were deduced from the measured g factors and hyperfine-interaction parameters. The charge state of the center, which is paramagnetic, corresponds to an electron configuration np^5, i.e., an un-ionized acceptor, P_{Se} or As_{Se}. The paramagnetic resonance intensity was found to be photosensitive, being enhanced by near band-gap radiation and quenched by radiation near 1.3 μm (see Fig. 2 of I). Simultaneous with these changes in the P_{Se} charge state, a brilliant red photoluminescence and a dramatic photosensitive behavior is observed. This paper, No. II, describes the electrical and optical behavior of the crystals, relating these properties to the P_{Se} center by correlation with the optically induced changes in the paramagnetic resonance intensity. P_{Se} is found to be the dominant electrically active defect, not entirely compensated by shallow donors of unknown identity. Dark conductivity at elevated temperature is via holes, while photoconductivity at reduced temperatures is via electrons with P'_{Se} serving as the sensitizing defect. The red photoluminescence arises from an internal transition of the P_{Se} defect, best described in terms of a configuration-coordinate model.

Similar photoelectronic properties of Cu-doped ZnSe crystals have been studied by Stringfellow and Bube.[3] The Cu($3d^9$) impurity ion is believed to occur substitutionally for Zn, Cu_{Zn}, and be a deep neutral acceptor. The ionized acceptor Cu_{Zn} is postulated to be the major sensitizing center for *n*-type photoconductivity, and *p*-type dark condutivity is observed at and above room temperature. Red and green photoluminescence bands are also observed. In general, the photoelectronic properties of Cu and P or As are very similar.

The paramagnetic resonance of one of the Stringfellow and Bube Cu-doped ZnSe crystals was examined in our spectrometer. A weak paramagnetic resonance displaying clearly resolved copper hyperfine structure is observed. The identification of copper is made by observing the expected intensity and hyperfine splitting ratios for the naturally occurring abundance and known nuclear moments of the Cu^{63} and Cu^{65} isotopes. The resonance has axial symmetry with a $\langle 111\rangle$ axis [$g_{\parallel} = 2.166$, $g_{\perp} = 2.045$, $A_{\parallel}(Cu^{63}) = 153\times 10^{-4}\ \text{cm}^{-1}$]. No additional hyperfine structure is observed. Although the resonance is photosensitive (sample temperature = 1.3 K), being enhanced with near band-gap radiation and bleached with ~ 1.1-μm radiation, unlike the *p*-doped ZnSe, it is not observed in the dark before exposure to light. Consequently, in this sample, the Cu_{Zn} center is compensated by an unknown donor. The paramagnetic resonance is analogous to those of copper in ZnS.[4] It is not known whether the trigonal distortion arises from a defect association or because of the Jahn-Teller effect. Experiments were not performed to establish a correlation between the paramagnetic center and the photoelectronic properties.

In addition to these group-I and group-V impurities which are obtained in melt grown ZnSe, acceptor centers are also formed by growing the ZnSe crystal in an atmosphere containing halide ions. A defect associate of the halogen ion substitional for selenium and a zinc vacancy is formed; however, isolated substitutional halide ions behaving as shallow donor centers are also present so that these crystals are usually *n* type. Similar photoconductance and photoluminescence behavior is observed; in particular, the luminescence arises from an internal transition of the $(V_{Zn}-Cl_{Se})'$ center.[5]

II. EXPERIMENTAL DETAILS

Single-crystal ZnSe specimens were cleaved from boules grown by a modified Bridgemann technique. The dopant impurity was added in elemental form prior to crystal growth, using high-density ZnSe powder initially prepared in a gas-phase reactor employing zinc and H_2Se in a stream of hydrogen-carrier gas. The details of these procedures are described elsewhere.[6] Attempts to incorporate the group-V impurities into already grown crystals by diffusion were unsuccessful. Gold electrical contacts for the conductivity and Hall-effect measurements were applied using a modification of the technique described by Aven and Garwicki[7] for p-type ZnSeTe. A heavy indium layer was usually applied over the gold to facilitate bonding of wires to the sample. Samples were not subjected to temperatures in excess of 200 °C to avoid possible contamination from the indium.

Luminescence excitation and emission spectra were obtained primarily with a spectrofluorometer constructed from a single and a double Leiss prism monochrometer. Appropriate detectors and excitation sources were used for the various spectral regions examined. The nonlinear response of the complete system was carefully calibrated using a standard lamp and, except where noted, spectra have been corrected for the system response. Cathodoluminescence spectra were obtained with a 45-kV 20-mA electron gun and analyzed using time-resolved spectrographic techniques. Photoconductivity, dark conductivity, and Hall effect were obtained with a specially constructed high-impedance sample holder. Where possible, samples were immersed in the appropriate cryogenic fluid for both the electrical and optical measurements. Temperature dependence for other ranges were obtained with a "Cryotip" Joule-Thompson cooler or by allowing the cryogenic fluid to boil away in the immersion Dewar, where the subsequent slow warming of the sample was monitored with a copper-constantan thermocouple. A Keithley high-speed picoammeter was the basic electrical measuring instrument.

III. RESULTS

A. Luminescence Spectra

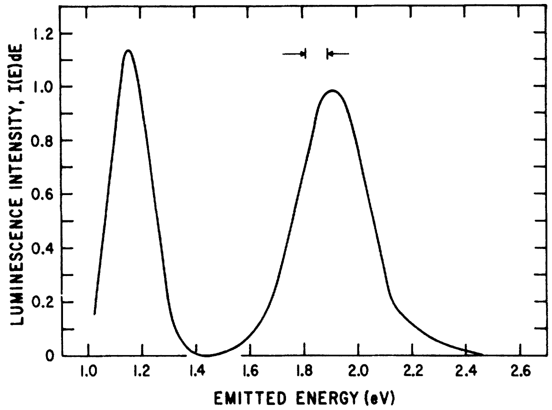

FIG. 1. Photoluminescence of ZnSe : P using 2.8-eV excitation with the sample temperature of 34 K. The resolution of the spectrometer is indicated by the opposing arrows.

If phosphorus- or arsenic-doped ZnSe crystals or powders are excited at room temperature with an intense source, such as an electron beam or an argon ion laser, they luminesce a brilliant red color; with weaker excitation sources, such as an unfocused broad-band Hg lamp, the luminescence is generally not observed at room temperature but increases markedly on cooling the sample to liquid-nitrogen temperature. Figures 1 and 2 are the luminescence spectra at 77 K obtained using the 4340-Å Hg line as the excitation source. For ZnSe : P (see Fig. 1), in addition to the red line which peaks at 1.91 eV, an additional line at 1.15 eV is also usually observed. Both bands are nearly Gaussian in shape. Since they are seen in various intensity ratios in different samples and after various annealing treatments, they are presumed not to arise from the same charge state of a given defect. Annealing in zinc vapor at 900 °C for 4 h diminishes the intensity of the 1.91-eV luminescence and causes the paramagnetic resonance of P_{Se} to become completely photosensitive. Other samples which exhibit only the P_{Se} paramagnetic center do not exhibit the 1.15-eV luminescence. A similar correlation of the As_{Se} center observable by its paramagnetic resonance and a single one of the three luminescence bands (see Fig. 2) could not be established.

The variation with sample temperature of the peak position of the 1.91-eV luminescence of ZnSe : P is shown in Fig. 3. The shift is towards higher energy with increasing temperature, opposite to the temperature dependence of the bandgap. The half-width, W, of this line as a function of temperature can be fit by the modified configuration-coordinate model equation[8]

$$W = A + B\left[\coth(h\nu/2kT)\right]^{1/2} , \qquad (1)$$

as shown by the solid curve in Fig. 4. A and B are constants, $h\nu$ is the vibrational energy in the excited state of the luminescent center, and kT is the thermal energy at temperature T. The best-fit values to Eq. (1) are $A = 0.052$ eV, $B = 0.236$ eV, and $h\nu = 0.025$ eV. The use of this equation to fit the experimental data is based on the assumption that the phosphorus luminescence is due to a localized excitation and can be described in terms of a configuration-coordinate diagram. The observa-

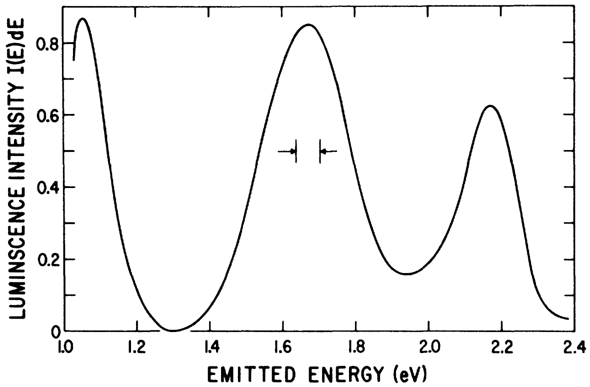

FIG. 2. Photoluminescence of ZnSe : As using 2.8-eV excitation with sample temperature of 2 K.

tion of an excitation peak (see Fig. 5) resolved from the band edge supports this assumption. This peak occurs at lower energy than the peak in the n-type photoconductivity at 77 K sample temperature, shown for comparison in the same figure. The 1.15-eV luminescence has two well-resolved excitation peaks (see Fig. 6) at 2.20 and 2.52 eV, regions which show essentially no photoconductivity. A weak absorption band that nearly coincides with the 2.20-eV excitation peak can be produced in the crystal as a result of strong band-gap irradiation. This band is shown as the dotted line in Fig. 6. The absorption was stable after removal of the exciting radiation but could be bleached with infrared. Except for temperature effects, the photoluminescence and low-energy cathodoluminescence spectral distribution is independent of the means of excitation. However, when crystals of ZnSe : P are excited by a 45-kV electron beam with a current density of the order of 10–20 A/cm^2 in pulses of 50-nsec duration, the spectral dependence is quite different from that obtained by photoexcitation. During the pulse, the 1.91-eV peak appears to shift considerably to higher energies and move towards lower energy after the pulse terminates with a time constant of approximately 2.5 μsec. It finally approaches the position of the steady-state photoluminescent peak. It could not be determined if this was actually a single-band shifting in time or if several different bands were involved. This time-resolved cathodoluminescent spectrum is shown in

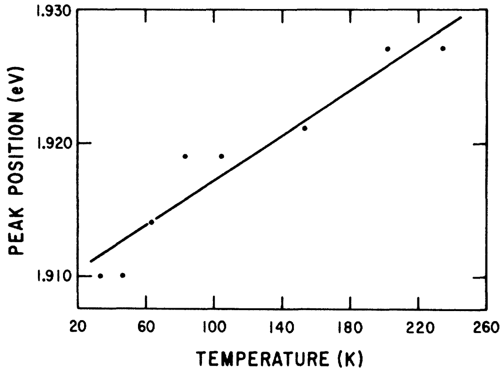

FIG. 3. Variation of the 1.91-eV luminescence peak of ZnSe : P as a function of sample temperature.

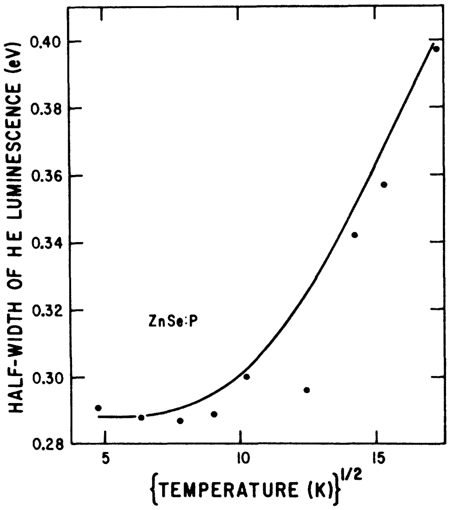

FIG. 4. Variation of the half-width of the 1.91-eV ZnSe : P luminescence as a function of (temperature)$^{1/2}$. Theoretical dependence (see text) is shown by the solid curve.

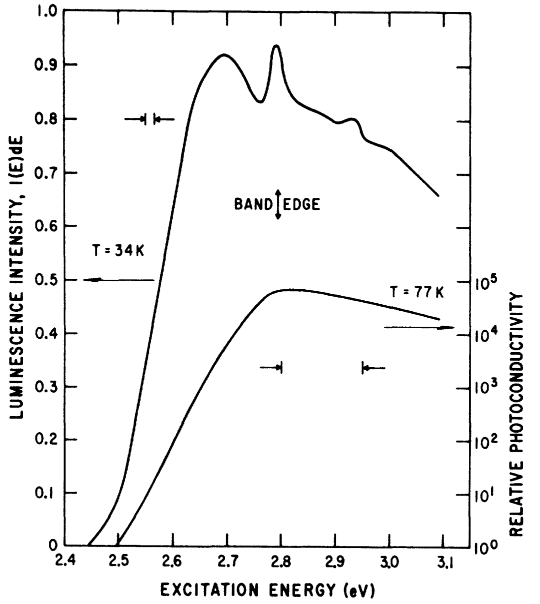

FIG. 5. Excitation spectrum for the 1.91-eV photoluminescence and the photoconductive response of ZnSe : P.

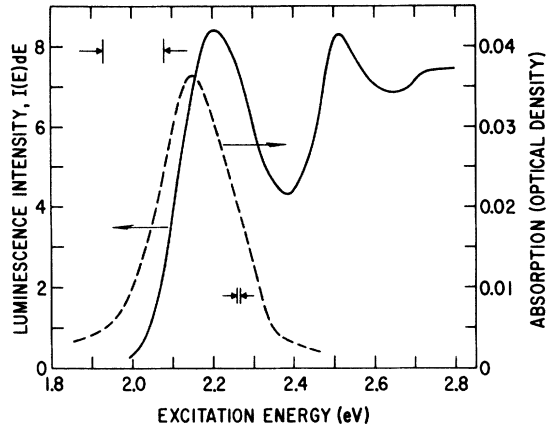

FIG. 6. Excitation spectrum for the 1.15-eV photoluminescence of ZnSe : P with sample temperature of 33 K (solid curve); and corresponding induced absorption spectrum (dashed curve).

Fig. 7. Using a pulsed argon ion laser at 4880 Å, no shifts in the luminescence peak of the 1.91-eV line were observed over a three-order-of-magnitude change in intensity of the excitation source, although there was a small nonlinearity in the intensity dependence. Due to difficulties in detection, these effects were only observed for the 1.91-eV line. Within experimental uncertainty, the lines showed no polarized photoluminescence effects at 2 K.

The luminescence intensity of both the 1.91- and the 1.15-eV bands is a strong function of temperature as shown in Fig. 8. Two activation energies are discernible for the 1.91-eV band, 0.016 and 0.30 eV, whereas only a single activation energy of 0.040 eV describes the 1.15-eV band. The *n*-type photoconductivity excited by band-gap radiation also increases markedly in cooling the crystal from 300 to 77 K.

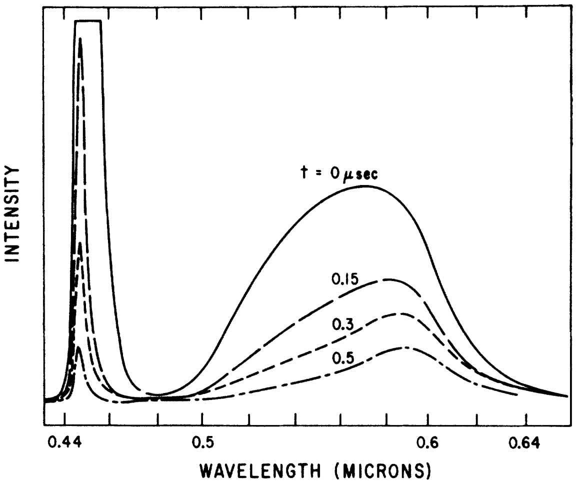

FIG. 7. Time-resolved cathodoluminescence spectrum. Sample temperature is 77 K, beam voltage 25 kV, current density 5 A/cm^2, and pulse length 100 nsec. Uncorrected for system response.

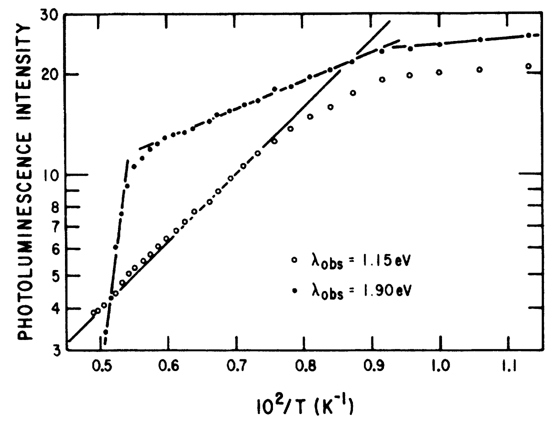

FIG. 8. Thermal quenching of the 1.91 and 1.15-eV photoluminescence of ZnSe : P. Excitation energy is 2.8 eV.

The photoluminescence excitation spectrum for the 1.67-eV emission band in ZnSe : As (see Fig. 9) is similar to those for the ZnSe : P emission bands. An excitation peak well resolved from the band edge is prominent. However, additional photoelectronic measurements were not sample independent, indicating that arsenic may incorporate in ZnSe in a greater number of ways.

B. Infrared Quenching

Although electron paramagnetic resonance (EPR) experiments can give very detailed information about the microscopic structure of a defect (see

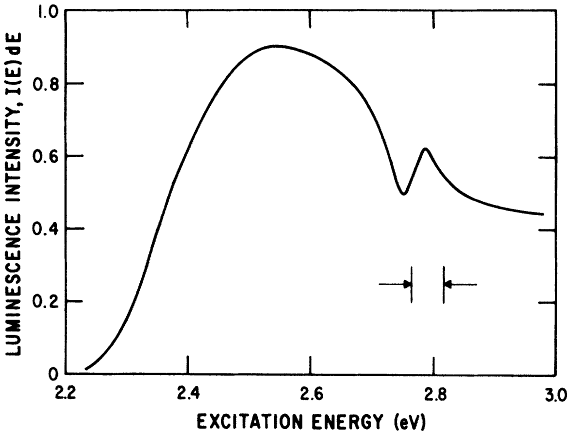

FIG. 9. Excitation spectrum for the 1.67-eV photoluminescence of ZnSe : As with sample temperature of 32 K.

I), it is usually extremely difficult to correlate the defect observed in EPR with other properties of the crystal, in this case with the luminescence. The best evidence that has been obtained for the ZnSe : P system has been through the similarity in behavior of the EPR, photoluminescence, and electrical response to infrared radiation in "quenching" experiments. Figure 10 is a composite of the quenching response of these three observations. The luminescence and photoconductivity measurements were made with the sample at 77 K and are steady-state measurements in the sense that they were taken under conditions where the excitation and quenching radiations were simultaneously incident on the crystal. The EPR quenching data (see I) were obtained at 2 K under pulsed conditions where the quenching effects of equal numbers of infrared photons of various wavelengths were recorded after a steady-state intensity of the EPR signal was obtained with band-gap radiation. The quenching spectra for the luminescence and photoconductivity are quite similar, while the EPR data are at least qualitatively similar. Considering the differences in the experimental conditions, the agreement is reasonably satisfactory and strongly suggests that one process is responsible for the quenching of all three phenomena. The luminescence and photoconductivity quenching exhibit a low-energy threshold at 0.6 eV. As discussed below, radiation near 1.0 μm liberates holes so that we may interpret the quenching phenomena in terms of an acceptor center associated with the presence of phosphorus. The results suggest that the luminescence arises from the paramagnetic charge state of the center and that this is also the sensitizing center for the n-type photoconductivity.

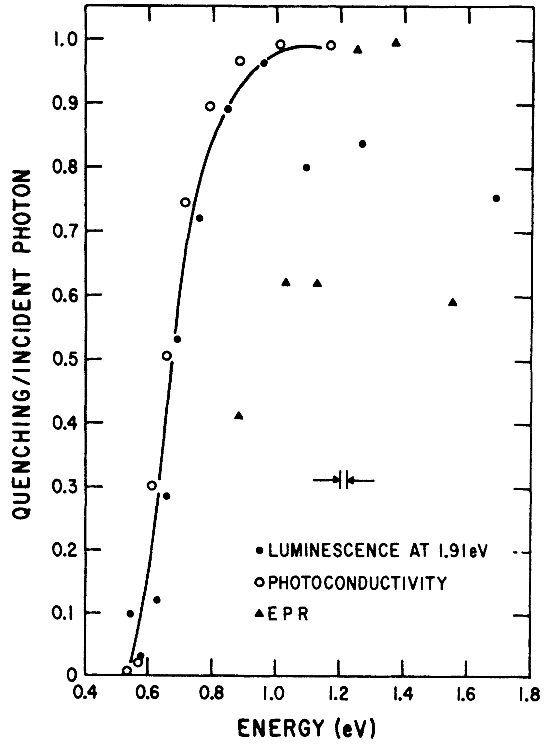

FIG. 10. Fractional quenching per incident photon of (i) 1.91-eV photoluminescence (shown by solid circles), (ii) photoconductivity (shown by open circles), and (iii) EPR of P_{Se} (shown by solid triangles) as a function of the energy of the quenching photon for ZnSe : P at a sample temperature of 77 K.

C. Electrical Measurements

The spectral response of photoconductivity and its infrared quenching have been described. In many ways the photoconductive response is very similar to what is observed for ZnSe : Cu and for other sensitized photoconductors. The photoconductivity is very small at room temperature and increases markedly on cooling. High photoconductive sensitivity results when holes which are produced by band-gap radiation are captured by centers that subsequently have a small-capture cross section for electrons. This results in an increased lifetime for free electrons and, consequently, high photosensitivity.

Thermal activation of the dark conductivity is shown in Fig. 11. The conductivity as determined by Hall-effect measurements in the dark at 500 K reveals that it is p type with a mobility of 24 ± 10 cm^2/V sec and a hole concentration of 4×10^9/cm^3 at 500 °K. An activation energy of 0.685 eV is determined from the temperature dependence of the conductivity. Photoconductivity which results from band-gap radiation is n type as shown by photo–Hall-effect measurements at 77 K. On the other hand, 1-μ radiation which is near the peak in the infrared quenching band liberates holes, as is verified by a reversal of the Hall sign when the band-gap radiation is replaced by infrared.

IV. DISCUSSION

We wish to examine the possibility that the electrical and optical properties described above can be ascribed in the case of ZnSe doped with phosphorus to the simple substitutional phosphorus center described in I, i.e., the spontaneous trigonally distorted isolated P_{Se} center observed in EPR. Two pieces of information suggest that this is the same center that is responsible for the 1.91-eV luminescence and for the dominant electrical behavior of the crystals, at least at low temperature. First is the similarity in the infrared quenching behavior, and second the observation that infrared radiation releases holes. These observations establish the presence of an ionized acceptor level P'_{Se} approximately 0.6 eV above the valence band. Since the neutral P_{Se} is the paramagnetic center seen in EPR, we identify it as the charge state of the lumines-

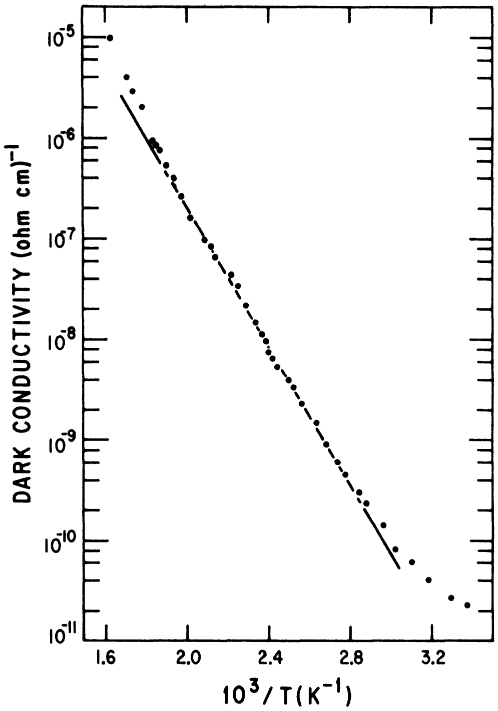

FIG. 11. Dark conductivity of ZnSe : P as a function of (temperature)$^{-1}$.

cence ground state. It is clear that the P'_{Se} center can also act as the sensitizing center for the *n*-type photoconductivity observed at low temperature. The neutral P_{Se} will have a relatively small cross section for electrons, as is required for high photoconductive sensitivity. It is not certain whether the P'_{Se} center is the dominant electrically active species at high temperatures. The uncertainty comes about from the fact that the 1.91-eV luminescence thermally quenches at about 200 K with a thermal activation energy of 0.3 eV, while the high-temperature conductivity is governed by a 0.68-eV level. We expect that the thermal activation energy of the P_{Se} center will be less than the optical activation energy of 0.6 eV measured from the infrared quenching experiments. Since, however, the P_{Se} represents only a small fraction of the phosphorus in the crystals, the possibility of other deep, possibly compensated acceptors, cannot be completely ruled out.

In spite of these uncertainties we can develop a model for the 1.91-eV luminescence of ZnSe : P which is reasonably consistent with the observed electrical and optical properties and with the microscopic structure as determined by EPR. The temperature dependence of the linewidth and the presence of a resolved excitation peak at an energy less than the band gap lead us to believe that the transition involved in the luminescence process may be described in terms of a configuration-coordinate model and that the excited state is a localized level of P_{Se}. The shift in the peak of the luminescence from the excitation band is a normal Stokes shift. From EPR we know that the ground state of the P_{Se} center is highly distorted and that its symmetry is far removed from the T_d symmetry of the undistorted lattice. The electronic structure of this level has been shown to be almost entirely *p*-like with very little *s* electron contribution. We are unable to locate the position of the ground state of the P_{Se} center with respect to the valence band. The 0.6-eV optical activation energy observed in quenching is actually the energy to be associated with the P'_{Se} center, since it includes the effects of an additional electronic charge. We can, however, conclude that the ground state of the P_{Se} center must be closer to the valence band edge than 0.6 eV. The excitation to the excited electronic state may then be well contained within or near the band-gap energy of 2.7 eV.

Since the center consists of an unassociated phosphorus atom, the excited electronic state lies closer to the conduction band edge than the ground state and its character is more bandlike. The unpolarized luminescence emission that occurs upon excitation with polarized light in the resolved excitation band indicates that the sublevels of the excited

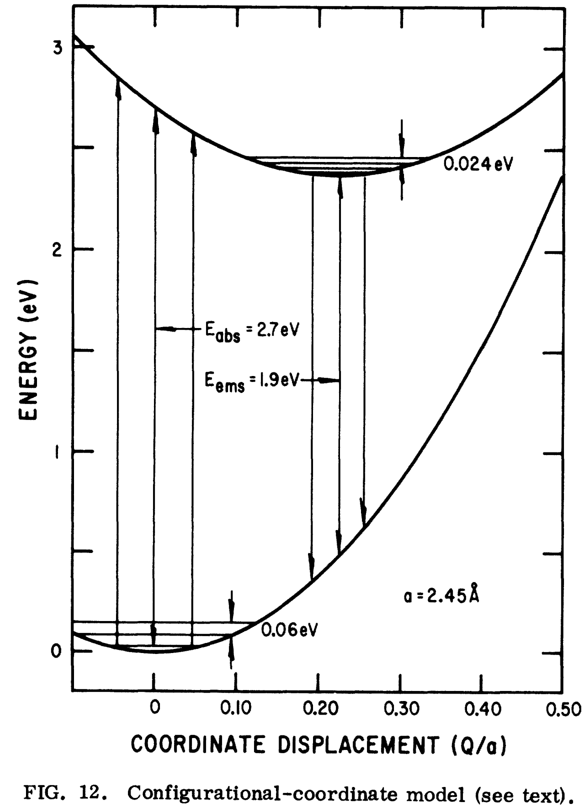

FIG. 12. Configurational-coordinate model (see text).

state get mixed before emission. Such a mixing process may be explained by the assumption that the equilibrium position of the excited state occurs at the T_d site symmetry point of the crystal.

Using these ideas and the data obtained from the luminescence width, we have constructed parabolic configuration-coordinate curves for the ground and localized excited state of the center. These are shown in Fig. 12. In determining these curves we have assumed an excited-state vibrational mass corresponding to the symmetric breathing-mode vibration. The emission peak shift with temperature and the displacement of the two minima from one another are then predictable. The predicted emission peak shift is 1.2×10^{-4} eV/K, while the measured shift is 0.86×10^{-4} eV/K. If we assume that the particular configuration coordinate is the distortion of the tetrahedron from T_d to C_{3v} as observed in EPR, a comparison can be made of this distortion as deduced by EPR and by the configuration-coordinate description. Both values are approximately 0.5 Å. The configuration-coordinate model also explains, at least qualitatively, the difference between the optical and the thermal activation energies for quenching the 1.9-eV luminescence since the model should apply equally well to excited-hole states of the P_{Se} center. These excited states are expected to lie very close to the valence band edge, as evidenced by the fact that infrared radiation produces free holes leading to *p*-type conductivity. The excited-hole states are expected to be more nearly cubic than the ground state, leading to a displacement in the equilibrium positions and a difference between the thermal and optical activation energies.

The nature of the center responsible for the 1.15-eV luminescence remains obscure. An interesting possibility is that it arises from an electronic transition of the ionized P_{Se} center, i.e., P'_{Se}. The variable intensity of this luminescence with post-growth annealing and the absorption band which is produced by band-gap radiation are qualitatively in agreement with this supposition, but substantiating evidence is not available.

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Hot-Electron Transfer in Gallium Antimonide from Infrared Faraday Effect*

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Measurements of the infrared Faraday effect at 3.39 μm have been performed to obtain information about the carrier transfer between the Γ_1 and L_1 conduction-band minima at high electric fields in GaSb. For high-mobility semiconductors in the near infrared, the Faraday effect is practically independent of the momentum relaxation time, and its decrease with electric field can be related to carrier transfer between minima. An analyzer has been built with a minimum resolution of 3×10^{-3} deg. A decrease of 14% has been observed in the electron population of the Γ_1 valley at 1.1 kV/cm, which is in good agreement with calculated values. Influences of nonparabolic conduction-band and carrier heating on the Faraday effect are considered.

I. INTRODUCTION

Carrier transfer by high electric fields in many-valley semiconductors with nonequivalent conduction-band minima has been investigated several times in the past. Most of this work has been directed towards a better understanding of the conduction mechanism in GaAs, because of its practical