derivation of the EMA in the $\vec{R}$ and $\vec{q}$ coordinates should be stressed. These coordinates are most suitable for the description of the motion of an electron in a perturbed crystal because they lead to a separation of variables. It is because of the simplicity of the method developed in this paper that it becomes possible to calculate higher-order terms in the effective-mass Hamiltonian. Corrections that are connected with the slowness of variation of the impurity potential were never before introduced in the EMA. As was shown here, these corrections can be very significant and lead in general to a better agreement with experiments.

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Role of Oxygen in (Zn, O) Doped GaP

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A study of the temperature dependence of the decay time and luminescent intensity of the infrared emission in (Zn,O) doped GaP has unambiguously identified this emission at room temperature as a radiative transition resulting from the recombination of a bound electron at an oxygen donor with a free hole in the valence band. From the temperature dependence of the decay time and the variation of the decay times as a function of free-hole concentration at room temperature, it is concluded that the recombination of the bound electron at an oxygen donor with the free hole is primarily radiative.

I. INTRODUCTION

The ionization energy of the oxygen donor (E_D) in GaP at 1.6 °K is 0.895 eV.[1,2] GaP doped with oxygen and shallow acceptors has revealed the following radiative recombinations at low temperatures: (i) a bound exciton transition[3,4] at the nearest-neighbor O-Zn or O-Cd complex, responsible for the efficient luminescence in red diodes; (ii) overlapping with this bound exciton emission, a red pair emission[4] due to the recombination of an electron bound at the oxygen site of the complex with a hole at a remote Zn or Cd acceptor; (iii) an electron capture "internal" emission involving a transition from the excited state of the oxygen donor to its ground state[5]; (iv) conventional donor-acceptor (DA) pair recombination involving the oxygen donor and shallow acceptors such as C, Zn, and Cd. An example of (iv) involves an isolated oxygen donor and zinc acceptor ($E_A \sim 0.064$ eV) to yield a DA pair spectrum in the near infrared (peaked at ~1.35 eV) at low temperatures. At 300 °K and at higher temperatures most of the zinc acceptors are ionized,[6,7] which implies that DA spectra should be weak or absent at these temperatures. However, because of the increased availability of the free holes, the bound electrons at O^+ are likely to recombine with free holes. This paper reports on the association of the room-temperature infrared spectrum peaked at ~1.36 eV in (Zn, O) doped GaP with the luminescence caused by the radiative recombination of a bound electron at an oxygen site with a free hole (henceforth referred to as BF transition), as reflected in the decay time and the temperature dependence of the intensity of the infrared emission. In the past it has been difficult to distinguish between conventional DA spectrum involving oxygen and zinc, and BF emission, at room temperature because of the similarity in their spectral characteristics.[8] Speculation exists that this infrared emission is a BF transition rather than a DA transition.[9]

In addition, the recombination at 300 °K of the deeply trapped electron at the oxygen donor is discussed in terms of radiative and nonradiative processes.

In Sec. II the experimental technique and sample preparation are discussed. In Sec. III the temperature dependence of the time decay and the spectral characteristics of the infrared emission in the temperature range between 77 and 440 °K are discussed. In Sec. IV the variation of the lifetime of an electron bound to oxygen is considered as a function of hole concentration; in particular, it is pointed out that the radiative path associated with the deep-donor oxygen may have only a weakly associated nonradiative path. The results are summarized in Sec. V.

II. EXPERIMENTAL TECHNIQUE

Luminescence decay times of the infrared emission from (Zn, O) doped GaP have been measured by exciting the samples with a pulsed He-Ne or Ar^+ laser and have been described elsewhere.[10] Care was taken to keep the instrumentation time much shorter than the measured decay time. Using He-Ne laser excitation, it is possible to separate the spectra of the excitonic (red) emission and BF and DA emissions [Fig. 1(b)]. The contribution of the excitonic emission (red) to the total integrated intensity can then be eliminated by the use of a sharp cut filter with a transmission pass band above 8500 Å. The spectra were measured with a f/6.8, $\frac{3}{4}$ SPEX spectrometer, and an S-1 response (RCA 7102) photomultiplier was used as a detector. The cutoff on the lower-energy side of the spectrum [Figs. 1(a) and 1(b)] is modulated strongly by the response of the photomultiplier and shall not be discussed. However, the high-energy tail has significant importance in the identification of the nature of the origin of the spectra and shall be discussed in Sec. III. In the main region of interest (7000-9100 Å) the combined response of the spectrometer and photomultiplier did not vary more than 10%. Consequently, no effort was made to make the above correction. The samples were solution-grown p-type GaP doped with 0.07 mole% of Zn and 0.02 mole% of Ga_2O_3.

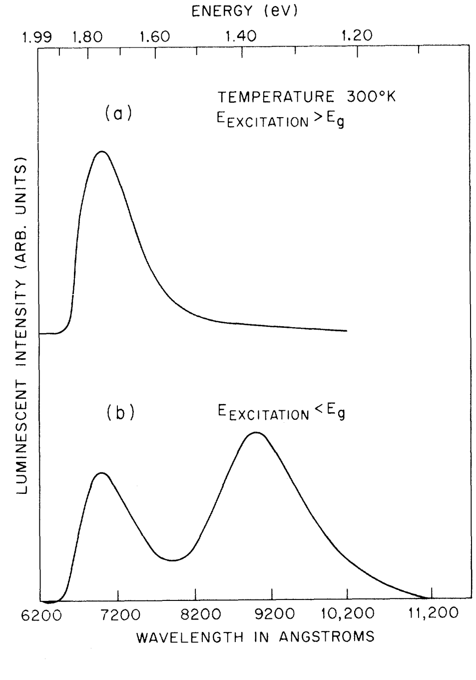

FIG. 1. Comparison of photoluminescence spectra of (Zn, O) doped GaP under two modes of excitation: (a) with above band-gap excitation using 4880 Å line of Ar^+ laser, (b) with below-gap excitation using 6328 Å line of the He-Ne laser. The below-gap excitation enables us to separate the contributions of the red and the infrared emissions at room temperature.

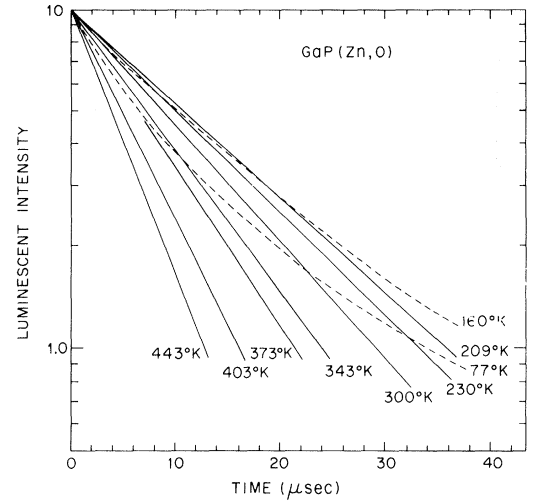

FIG. 2. Time decay of the infrared luminescence at various temperatures after the pulsed excitation with a He-Ne laser.

III. TEMPERATURE DEPENDENCE OF SPECTRA AND TIME DECAY

This section will first discuss the experimental results of the temperature dependence of the decay time and the spectra of the infrared emission measured between 77 and 443 °K. The discussion and interpretation of these experimental results will follow.

There is a considerable overlap of spectra in the near-infrared region caused by the O-Zn complex (red exciton and red pair) emission and the isolated oxygen (BF and DA emissions) emission when the 4880 Å line of an Ar$^+$ laser is used for excitation [Fig. 1(a)]. The low-energy tail of the emission spectra caused by the O-Zn complex contributes significantly in the vicinity of 1.35 eV (~9100 Å) when compared to the intensity of the oxygen spectra since the emission due to the complex is much more efficient than the isolated oxygen emission. To avoid this problem the 6328 Å line of a He-Ne laser was used to excite the crystal, and the spectrum so obtained is depicted in Fig. 1(b) where the infrared peak of the oxygen emission is well separated from the peak of emission of the complex. Subsequently, the temperature dependence of the decay time of the total luminescent intensity of BF and DA emissions was measured using a pulsed He-Ne laser and an appropriate filter (long wavelength pass beyond 8500 Å). In Fig. 2 we plot the decay of the total luminescent intensity beyond 8500 Å at various temperatures as a function of time elapsed after the cessation of excitation. The 1/*e* decay times obtained from Fig. 2 are plotted as a function of temperature in Fig. 3. The broad features of the kinetics of the recombination of deeply trapped electrons are reflected from Figs. 2 and 3, where one observes that the lifetime increases from 77 to ~160 °K and is nonexponential and beyond 160 °K decreases rapidly and is exponential. The discussion of this effect is postponed until later.

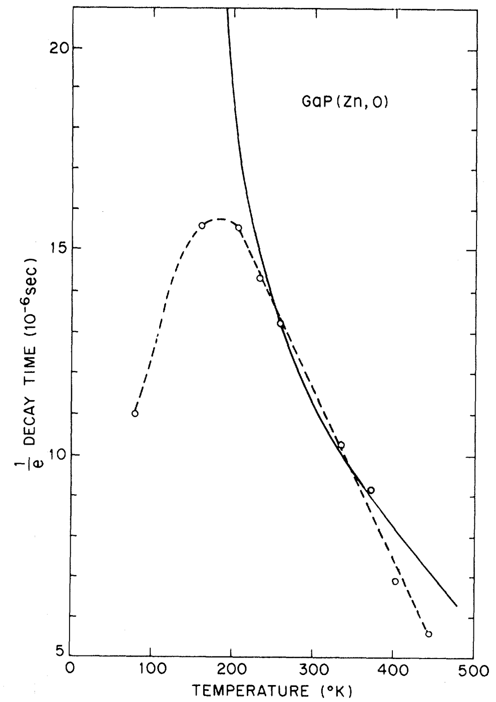

FIG. 3. Plot of 1/*e* decay time taken from Fig. 2. The solid curve represents the variation of the radiative lifetime τ_R^0 as a function of temperature computed on the basis that $(\tau_R^0)^{-1} = Bp$, where B is a constant and p is the free-hole concentration. The lifetime increases because the holes are being depleted from the valence band as the temperature is lowered (see Ref. 6).

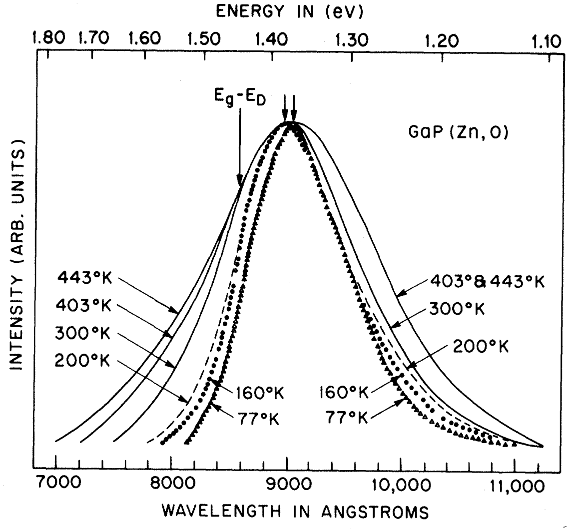

FIG. 4. Temperature variation of spectral characteristics of the infrared spectra. The two arrows on the top of the peak signify a shift of peak opposite to that of the band gap when the temperature is increased. The third arrow points to the energy where the no-phonon line for BF transition should occur.

Before the spectral characteristics are discussed as a function of temperature, it is useful to recall some of the broad features of the conventional DA pair spectrum between O and Zn.[1] At 1.6 °K, it consists of many sharp lines on the high-energy side of the pair band. The sharp lines are due to electron-hole recombinations between isolated oxygen and zinc atoms positioned at particular sites. The pair band is a broad band because of the strong phonon-assisted transitions which arise from the tight binding of the electron at the oxygen donor (unlike the shallow donor-pair spectra in the green[11]). The peak of the O-Zn pair spectrum occurs at ~1.35 eV and is due to the phonon replicas of the "no-phonon pair band" involving phonons of energy 19.5 and 47.0 meV.[1] As the temperature is increased from 77 to 100 °K the peak position and shape of the spectrum do not change because (i) the deep-donor oxygen energy level does not follow the conduction-band minima[10] and (ii) the phonon cooperation is not expected to change. However, above 100 °K the following changes in the spectral characteristics are observed: (i) Between 100 and 160 °K there is a peak shift of approximately 15 meV towards higher energy (see Fig. 4); (ii) the width of the spectrum increases with increasing temperature and the high-energy tail has penetrated considerably into the red. Figure 4 shows the temperature dependence of the infrared spectrum from 77 to 443 °K and confirms the abovementioned variations in peak position and in the shape of the high-energy side of the spectra.

The two observations above can be interpreted as taking into account the change of the emission from a DA pair transition to a BF transition as the temperature is raised from 77 °K.

The emission energies of the DA and BF transitions are given by

$$E_{h\nu}^{\mathrm{DA}} = E_g - (E_A + E_D) + e^2/KR, \qquad (1)$$

$$E_{h\nu}^{\mathrm{BF}} = E_g - E_D, \qquad (2)$$

where E_g, E_A, E_D, and e^2/KR are, respectively, the band gap, acceptor, donor, and Coulombic energies. It is evident from the above equations that the "no-phonon line" position of the above two spectra should differ in energy by $(-E_A + e^2/KR)$. This difference should also be the same for the peak positions of BF and DA spectra, since in both the cases the peak positions are determined by the same phonon cooperation due to the tightly bound electron at O^+. In the O-Zn system $E_A = 64$ meV and $e^2/KR \sim 40$ meV, which shows that the difference in the peak position of the DA pair and the BF transitions should be approximately 24 meV. The observed shift (Fig. 4) in the peak position from 77 to 160 °K of approximately 15 meV is then consistent with a change from the DA pair to the BF transition. It is interesting to note that the shift in the peak position as a function of temperature is in a direction opposite to the variation in the band gap, which is additional evidence of a probable change in the nature of the radiative transition, as the temperature is increased. At temperatures above 160 °K there is a variation in the spectral shape of the emission at energies above $E_g - E_D$ (no-phonon line for the BF transition is indicated in Fig. 4). Since the emission above 160 °K is primarily due to the BF transition (which is also consistent with the time-decay measurements, see below), the two factors which need to be considered to determine the temperature dependence of the spectral distribution at energies above $E_g - E_D$ are (i) the distribution of the free holes in the valence band, (ii) the phonon cooperation from both the Stokes and the anti-Stokes contributions. The effect due to (i) can be estimated from the distribution of free holes $p(E)$ in the valence band and can be expressed as $p(E) \equiv g(E) f(E)$, where $g(E)$ is the density of states per unit energy at energy E and $f(E)$ is the probability of finding a hole at E. For our case, since $E_F > kT$, we have

$$p(E) \sim |E|^{1/2} e^{-(E_F + |E|)/kT}, \qquad (3)$$

where E is the energy measured from top of the valence band. Because of the modulation of the intensity by the phonon cooperation, it is difficult to compute the intensity of the emission at energies greater than $E_g - E_D$. However, the qualitative energy dependence of the emission intensity at energies greater than $E_g - E_D$ is similar to Eq. (3) considering only a "no-phonon line" and its contribution from Eq. (3).

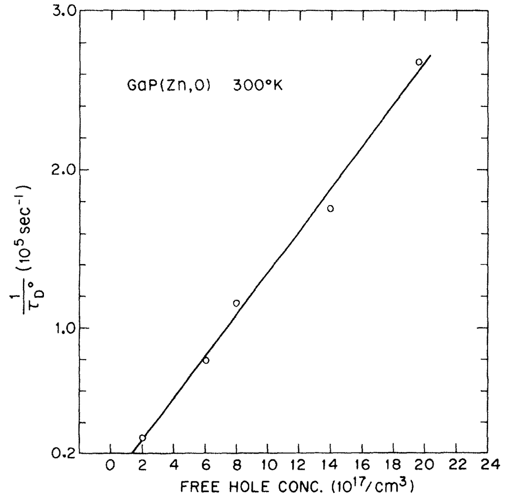

FIG. 5. Plot of $1/\tau_D^0$ versus free-hole concentration where τ_D^0 is the $1/e$ decay time of the infrared emission at 300 °K.

The time decay of the total emission in the infrared (above 8500 Å) has been measured. Figure 2 shows this emission intensity versus the time elapsed after the pulse was switched off. The decay is exponential above 160 °K and is nonexponential at 77 °K. In temperature range between 77 and 160 °K one can observe the slow transition from a nonexponential to an exponential decay. The observation of a nonexponential decay at 77 °K is consistent with a DA pair emission.[12] The existence of a DA pair emission has been demonstrated by the observation of discrete pair lines at 1.6 °K[1] in similar GaP crystals. A similar change from a nonexponential to an exponential decay time is observed with the change of emission from pair to excitonic in the O-Zn complex spectra.[13] The change from nonexponential decay to an exponential decay observed above is therefore attributed to the change of emission from a DA pair emission to a BF transition. This is consistent with the change in the spectral characteristics observed above.

In Fig. 3 the $1/e$ decay times obtained from Fig. 2 are plotted as a function of temperature. The decrease of the $1/e$ decay time above 160 °K is consistent with the conclusion that the emission in this range of temperature is a BF transition. The decay time τ_R^0 for the radiative BF transition should be inversely proportional to the free-hole concentration. Using the data of Casey *et al.*[6] for the variation of the free-hole concentration as a function of temperature, the variation of τ_R^0 as a function of temperature is plotted in Fig. 3. Since the measured decay time τ_D^0 follows closely the variation of τ_R^0 in the temperature range of 160 to 443 °K, it is reasonable to conclude that the lifetime of the bound electron at the oxygen site is primarily radiative transition and may not have an associated nonradiative part. This is consistent with the data reported below on the decay time of BF transitions as a function of free-hole concentration p for various samples doped with different amounts of zinc.

IV. DEPENDENCE OF TIME DECAY ON HOLE CONCENTRATION

The decay time of the infrared emission at room temperature in various p-type solution-grown GaP samples with varying amounts of Zn concentration have been measured. Phenomenologically we can represent the decay time τ_D^0 of the electron at the oxygen site as

$$(\tau_D^0)^{-1} = (\tau_R^0)^{-1} + (\tau_{NR}^0)^{-1}, \qquad (4)$$

where τ_R^0 and τ_{NR}^0 are the radiative and nonradiative lifetimes. For the BF emission the radiative decay rate $(\tau_R^0)^{-1}$ should be proportional to the free-hole concentration p. It is observed that τ_D^0 varies inversely as p (see Fig. 5) from which the following conclusions can be made about the contributions from the nonradiative path: (i) If it is assumed that the nonradiative process is the Auger process involving a free hole as the third particle, then one can set $(\tau_{NR}^0)^{-1} = Cp^2$, where C is a constant of proportionality. Since our data show $(\tau_D^0)^{-1}$ is proportional to p, we believe that such an Auger process is negligible. An upper limit $C \simeq 2 \times 10^{-32}$ cm^6/sec could be set which agrees approximately with a recent estimate.[14] (ii) Consistent with the measurement that the measured τ_D^0 is inversely proportional to p, there can be a nonradiative Auger process which involves one free hole and two electrons. Such an Auger process can exist if the existence of excitons bound to neutral oxygen is assumed similar to excitons bound to neutral donor sulphur in GaP. Such a system had been postulated to explain the relative variation of internal electron capture and O-Zn pair emission as a function of excitation intensity at 1.6 °K.[5] Comparing τ_{NR}^0 with the lifetime of bound excitons to the neutral donor sulphur[15] (which is ≃ 21 nsec), the lifetime τ_{NR}^0 is expected to be comparably short. (The bound-exciton transition involving deep-donor oxygen could be even faster because of the greater overlap of the two tightly bound electron wave functions. Since the observed decay time for an electron captured directly onto the ground state of the oxygen donor (below band-gap excitation) is $\tau_D^0 \simeq 10$ μsec, an Auger process due to excitons bound to neutral oxygen is believed to be absent at room temperature. Thus, it is concluded that the contributions from the Auger processes discussed above are negligible, and the BF emission is primarily radiative.

Though the electron captured at the oxygen donor primarily recombines radiatively with a hole, the quantum efficiency for the above band-gap excitation at room temperature of the BF transition is low when compared to excitonic (red) emission. This low quantum efficiency is related to the long electron capture time for the ground state of the O^+, when compared to the electron capture for time the O-Zn complex. This is consistent with the recent observation that the lifetime of internal electron capture luminescence is approximately 10 μsec.[16]

V. CONCLUSIONS

The temperature dependence of the luminescent intensity and the decay time of the infrared emission at room temperature in (Zn, O) doped GaP is identified as a radiative recombination of a bound electron at an oxygen donor with a free hole. It is also shown that the O-Zn DA pair emission dominates the emission below 100 °K and the bound-to-free emission begins to dominate above 160 °K. From the temperature dependence of the decay time of the infrared emission and the variation of the decay time as a function of free-hole concentration, it is concluded that the BF emission is primarily radiative.

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Pseudopotential Calculation of the Band Structure of $CdIn_2S_4$

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The band structure of the spinel-type semiconductor $CdIn_2S_4$ has been calculated by the empirical-pseudopotential method. The form factors have been determined to agree with the values previously chosen by Cohen and Bergstresser for semiconductors with diamond and zinc-blende structures. Because of the large number of atoms per unit cell, a simplified model of the actual crystal structure has been developed, thus obtaining a feasible way to get meaningful results and to make direct comparisons with the band structures of many well-known elementary and binary semiconductors. The band structure obtained with the use of our model, and the results of the full calculations made for symmetry points, are discussed and compared with the available experimental information.

1. INTRODUCTION

During the last decade pseudopotential theory[1] proved to be a very useful basis for the study of the optical properties of a large class of solids. In fact, there are now several methods[2-5] to determine the pseudopotential to be used in actual calculations, depending on whether one wants to make a kind of *a priori* calculation or to obtain, by comparison with optical data, very accurate band structures. A notable point is that there are no great differences[6,7] between the pseudopotentials computed from first principles and the ones empirically determined, so that the gross features of a band structure can now be predicted with sufficient reliability; furthermore, as shown by very recent calculations[7-11] based on the empirical-pseudopotential method (EPM), quite good results can be obtained by associating a pseudopotential with each ion, independent of its chemical state, so that it is now possible to build good pseudopotentials even for complex structures like, e.g., ternary compounds. For these reasons we have chosen to investigate the band structure of spinel-type semiconductors by using the EPM. We expect these calculations to give reliable results, even in absence of detailed experimental information, of course, apart from possible "sensitive"[12] energy levels.

In this paper we report on a theoretical study of the band structure of the spinel-type semiconductor $CdIn_2S_4$; the form factors of our pseudopotential are those empirically determined by Cohen and Bergstresser[7] (CB) and modified to take into account the variation of the lattice constant, as explained in Sec. 2. This choice has been made essentially for two reasons: There is no other way to get a reliable approximation to the sulphur form factors, which are not given in the tables by Animalu and Heine,[5] and we regard the use of empirical form factors as more likely to get good results, because of taking into account crystalline effects such as charge redistribution and of a more realistic screening of the ionic potentials.

A preliminary analysis of the band structure of spinel-type semiconductors has been made recently