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EPR and Luminescence Studies of Er^{+3} in Acceptor-Doped ZnTe

BILLY L. CROWDER, R. S. TITLE, AND G. D. PETTIT
IBM Watson Research Center, Yorktown Heights, New York 10598

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Er^{+3} can be incorporated in the ZnTe lattice in significant concentrations by co-doping with an acceptor species. From EPR studies at 4°K, the symmetries of the dominant sites in ZnTe(Er,P) are trigonal ($g_{\parallel}=1.254$, $g_{\perp}=9.469$) and cubic ($g=5.93$). For ZnTe(Er,Li) crystals, the same cubic site is observed, but the dominant site has trigonal symmetry ($g_{\parallel}=4.066$, $g_{\perp}=8.068$). Thermal treatments which are known to remove Li from electrically active centers in ZnTe greatly increase the strength of the cubic spectrum and greatly reduce the strength of the trigonal spectrum. The sharp-line emission observed in photoluminescence occurs in the region 663 nm and represents a transition from ${}^4F_{9/2}$ to the ground state of Er^{+3}. This sharp-line emission is weakest in those samples in which the cubic EPR spectrum is the strongest, which indicates that Er^{+3} on a substitutional Zn site with nonlocal charge compensation is not an efficient radiative-recombination center for rare-earth emission. Rare-earth electroluminescence at 77°K is observed from diodes fabricated from ZnTe(Er,Li) and ZnTe(Er,P) substrates.

I. INTRODUCTION

Electron paramagnetic resonance (EPR) studies of rare-earth impurities incorporated into II-VI compounds have revealed that the rare-earth ion is trivalent and can be found in a variety of local environments.[1–4] The trivalent rare-earth ion has been found on two sites: (1) the substitutional cation site or (2) the interstitial site which has four cations for nearest neighbors and six anions as next-nearest neighbors. One of the important factors determining the site preference (substitutional or interstitial) is the mechanism of charge compensation which is required to provide electrical neutrality when the trivalent rare earth is incorporated into the lattice. In a previous study, the site occupied by the rare-earth ions Yb^{+3} or Er^{+3} in CdTe depended upon whether charge compensation was accomplished by the acceptor P (which occupies a Te site) or the acceptor Li (which substitutes for the Cd).[1] In the former case, the rare-earth ion was found on a substitutional site either with nonlocal charge compensation (cubic symmetry) or with the compensating *P* located on a neighboring Te site (trigonal symmetry). The concentrations of rare-earth ions observed on the two sites were comparable. Similar results were also observed for the case of ZnTe(Yb,P)[2]. When Li was used as the compensating species, the trivalent rare-earth ion was located primarily in the interstitial position with one of the neighboring cations replaced by a Li (trigonal symmetry). In this case, some of the rare-earth ions were located on the cation site with nonlocal charge compensation, but the numbers involved on these cubic-symmetry sites were much lower than those on interstitial sites. The rare-earth ion has also been observed in the interstitial site discussed above when group Ib elements (Cu,Ag,Au) are used for charge compensation but the local environment is different. Watts and Holton have observed interstitial Yb^{+3} in CdTe either with three of the neighboring cations replaced by monovalent group Ib ions or with all four replaced.[3] Kingsley and Aven have observed an analogous center in ZnSe doped with Er and with Cu or Ag in which all four cations surrounding the interstitial rare-earth ion are replaced by monovalent group Ib ions.[4] In addition to this interstitial Er^{+3} complex in ZnSe, Kingsley and Aven also studied Er^{+3} in the substitutional cation site with cubic symmetry and reported the existence of six sites of noncubic symmetry, which were not studied in detail.

A major motivation for studying rare-earth ions in a II-VI semiconducting compound is the possibility of achieving narrow-line emission from transitions within the $4f^n$ configuration of the rare-earth ion from a system which can be electrically pumped. The efficiency of the rare-earth ion as a radiative recombination center in a II-VI compound depends markedly upon the local environment. For example. Kinglsey, Prener, and Aven reported on the excitation of rare-earth fluorescence by energy transfer from Cu or Ag in ZnS, CdS, and ZnSe.[5] The presence of the group Ib ion greatly enhanced the rare-earth emission, and, since the emission spectrum of the rare earth was sensitive to the specific group Ib ion, the center responsible for the emission most probably included the rare-earth ion and the group Ib ion in close proximity.

A combination of EPR studies and luminescence studies on the same crystals would therefore be very valuable, but, in general, the EPR studies and the optical emission and absorption studies have been accomplished independently. A notable exception is the above mentioned work of Kingsley and Aven.[4] Their

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[1] R. S. Title, B. L. Crowder, and J. W. Mayo, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, 1967*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1968), p. 1367.

[2] R. S. Title, in *Physics and Chemistry of II-VI Compounds*, edited by J. S. Prener and M. Aven (North-Holland Publishing Co., Amsterdam, 1967), Chap. 6.

[3] R. K. Watts and W. C. Holton, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, 1967*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1968), p. 1390. Also, R. K. Watts and W. C. Holton, Phys. Rev. **173**, 417 (1968).

[4] J. D. Kingsley and M. Aven, Phys. Rev. **155**, 235 (1967).

[5] J. D. Kingsley, J. S. Prener, and M. Aven, Phys. Rev. Letters **14**, 136 (1965).

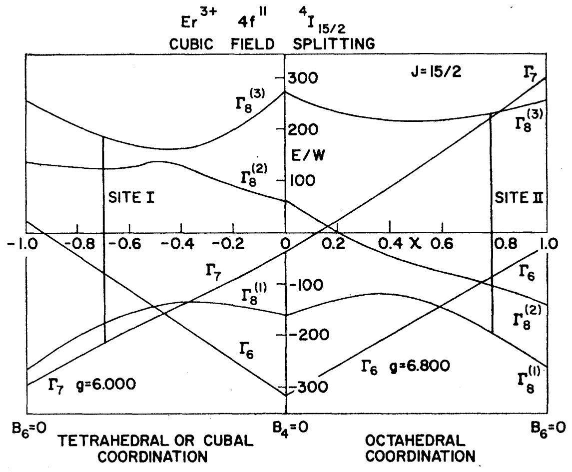

FIG. 1. Splitting in cubic symmetry of the $^4I_{15/2}$ ground state of Er^{+3}. The two cubic sites observed for Er^{+3} in ZnSe by Kingsley and Aven are also shown (Ref. 4).

detailed studies of the system ZnSe(Er,Cu) revealed that the interstitial Er^{+3} surrounded by four Cu^+ ions was an efficient radiative-recombination center. No luminescence was observed which could be attributed to transitions involving Er^{+3} on a Zn site with cubic symmetry, although EPR spectra clearly revealed the existence of this species.[4]

In this paper we report on the luminescence and EPR studies of Er^{+3} in ZnTe. The influence of different charge-compensation mechanisms are examined in ZnTe(Er), ZnTe(Er,Li), and ZnTe(Er,P) single crystals. The intensity and spectral distribution of the narrow-line rare-earth emission is shown to depend upon the environment of the rare-earth ion. In particular, it is shown that an isolated substitutional Er^{+3} (cubic symmetry) is not an efficient radiative-recombination center in ZnTe. Finally, we demonstrate that rare-earth emission can be produced from a ZnTe electroluminescent diode at 77°K.

II. THEORY

The theory of EPR is applied to rare-earth ions in the environments likely to exist in II-VI compounds, has been adequately covered in previous publications.[1–4] The crystalline field splits the ground state of the rare-earth ion into a number of levels. Experimental EPR results for the g tensor of the lowest level can be compared to the g tensor calculated for each of these crystalline field-split levels in order to determine which level lies lowest. Calculations based on a point-charge model of the crystal can then be used to determine at which site(s) this level should lie lowest. These comparisons can be most readily made in those cases involving sites of cubic symmetry. For sites of lower symmetry than cubic, it is still possible to determine the representation of the lowest lying level. In an axial field characterized by $g_{\parallel}$ along a direction parallel to the axis of symmetry and $g_{\perp}$ along a direction perpendicular to this axis, the g tensor can be related to the g value for that level in cubic symmetry by the relationship $3\,g(\text{cubic})=g_{\parallel}+2g_{\perp}$, provided the axial field is small compared with cubic field.[6] This result was quite useful in determining the coordination of the rare-earth ion in an axial field in our previous work[1] and will be utilized in the present study.

The $4f^{11}$ electron configuration of the Er^{+3} ion has a $^4I_{15/2}$ ground state. The splitting of this ground state in a cubic field, as determined by Lea, Leask, and Wolf (LLW),[7] is shown in Fig. 1. The labeling at the states has been changed to conform to convention in T_d symmetry. Also shown on this figure are the locations of the two cubic sites observed in ZnSe(Er,Cu) by Kingsley and Aven.[4] The right-hand side of the diagram is applicable for Er^{+3} in octahedral coordination and the left-hand side for tetrahedral (or cubal) coordination. The abscissa x is a parameter which depends on the ratio of the fourth-order and sixth-order parts of the cubic crystalline field.[7] The Γ_7 level ($g=6.000$) lies lowest only in tetrahedral coordination, and the Γ_8 level lies lowest only in octahedral coordination.[1] The Γ_6 level ($g=6.800$) may lie lowest in either octahedral or tetrahedral coordination.

Table I lists energy of excited states relative to the $^4I_{15/2}$ ground state of the $4f^{11}$ electron configuration of Er^{+3} in two different environments: ZnSe(Er,Cu) (Ref. 4) and $LaCl_3$(Er) (Ref. 8). In the case of II-VI compounds in which excitation of fluorescence is accomplished by greater than band-gap radiation, the mechanism(s) by which energy is transferred to the $4f^n$ manifold of the rare-earth ion is not clear. The maximum energy of rare-earth fluorescence which can be observed is limited by the band gap of the host lattice. For ZnTe at 4°K, this is 2.39 eV.[9] If the mechanism by which the rare-earth ion is excited involves trapping of one (or both) of the charge carriers involved in the recombination, the maximum energy which can be observed

TABLE I. Energy levels of Er^{+3} ($4f^{11}$) location of level relative to ground state (in eV).

State	ZnSe-(Er,Cu)[a]	$LaCl_3$-(Er)[b]
$^4I_{15/2}$	0	0
$^4I_{13/2}$	0.80	0.81
$^4I_{11/2}$	···	1.27
$^4I_{9/2}$	1.51	1.54
$^4F_{9/2}$	1.85	1.89
$^4S_{3/2}$	2.23	2.28
$^2H_{11/2}$	···	2.38
$^4F_{7/2}$	···	2.52

[a] Reference 4.
[b] Reference 8.

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[6] H. R. Lewis and E. S. Sabisky, Phys. Rev. **130**, 1370 (1963).

[7] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[8] F. Varsanyi and G. H. Dieke, J. Chem. Phys. **36**, 2951 (1962).

[9] R. E. Halsted, M. Aven, and H. D. Coghill, J. Electrochem. Soc. **112**, 177 (1965).

is further reduced by the binding energies involved in the capture process. For example, if the binding energies involved were 0.2 eV, emission from states of Er^{+3} higher in energy than $^4F_{9/2}$ would not be observed from a ZnTe lattice.

III. EXPERIMENTAL

The single crystals of ZnTe used in these studies were grown by Kucza. They were grown from a melt containing an excess of 25 mole% Te, 0.1 mole% of the desired rare-earth metal, and 0.1 mole% of either Li or P, or with no intentionally added co-dopant. Subsequent heat treatments of portions of these single crystals were conducted in sealed, evacuated (to about 10^{-6} Torr) quartz ampoules. If a known Zn overpressure was desired, a chip of high purity Zn was placed in the sample ampoule in a quartz plug. If liquid extraction was desired, the sample was held under liquid Zn by a quartz finger. Samples which were heat-treated were quenched by immersing the ampoule in a water bath in order to freeze in that atomic disorder more characteristic of the elevated firing temperature. In the following discussion of experimental results, crystals which were fired in Zn vapor at 850°C for 2 to 4 h will be referred to as "zinc fired," crystals given similar treatment in a bath of liquid Zn will be referred to as "zinc extracted," and crystals which were annealed in vacuum at 250°C for several days will be referred to as "vacuum annealed." To minimize the influence of damaged surface regions (as produced, e.g., by lapping and polishing), the samples were cleaved to expose a surface for luminescence studies. Photoluminescence was excited by greater than band-gap radiation from a filtered Hg arc source (primarily 365 nm excitation), and spectra were obtained using a Perkin-Elmer Model 98 monochromator in conjunction with an *S*-20 photomultiplier tube. The samples were totally immersed in the cooling liquid. The photoluminescence studies were made at 2.2 and 77°K.

The same crystals were used for the EPR studies. Since the cleavage is along (110) planes, the orientation of the samples in the EPR cavity was facilitated. The EPR measurements were carried out at 4.2°K.

Electrical properties of several of the samples used for EPR and luminescence studies were obtained using the van der Pauw technique to measure resistivities and Hall coefficients.[10]

ZnTe(Er)

No detectable EPR signals were observed for samples of ZnTe(Er) either as grown or zinc fired. "As grown" refers to crystals which were grown by the modified Bridgman technique mentioned above which utilizes excess Te. These crystals were, therefore, slow-cooled under a Te overpressure.

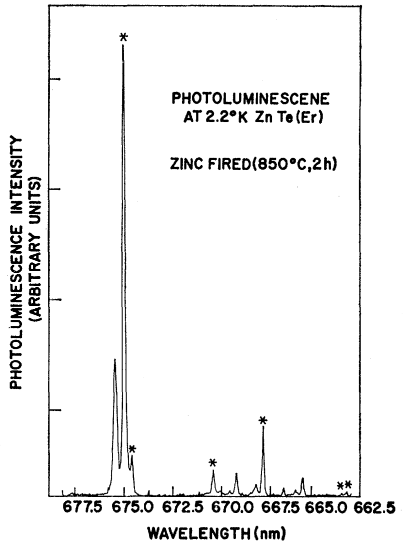

FIG. 2. Red photoluminescence spectrum (2.2°K) of zinc-fired ZnTe(Er). The peaks marked * have increased in intensity relative to the other peaks shown by a factor of 3 over the ratio observed in ZnTe(Er) as grown.

In contrast to undoped ZnTe crystals as grown, which are typically of the order of 100 Ω cm resistivity at 300°K, the ZnTe(Er) crystals as grown had resistivities at 300°K greater than 10^7 Ω cm and were photoconducting *p* type. These results are more typical of ZnTe that has been doped with donor-type species. After zinc firing, the room-temperature resistivity of ZnTe(Er) decreased to 3 Ω cm (2×10^{16} holes/cm^3 and a Hall mobility of 100 cm^2/V sec). This behavior is quite similar to that of undoped ZnTe which has been zinc fired.

The photoluminescence spectrum at 2.2°K of ZnTe(Er) revealed a plethora of broad emission peaks from 2.0 to 2.2 eV together with near-band-edge emissions which are observed also in undoped ZnTe. Between these two groups of lines was a series of peaks separated in energy by an LO phonon (0.026 eV). This series began at 2.32_2 eV. Upon zinc firing, this series became the dominant emission in the region 2 eV to the band edge, increasing in intensity by a factor of 40 while the other emission peaks did not change appreciably in intensity. A group of narrow emission lines in the region 1.837 to 1.869 eV was observed in both samples. The relative intensities of one group of lines relative to a second group of lines increased upon firing in Zn vapor. Figure 2 shows the emission peaks observed in this region of the spectrum for ZnTe(Er) Zn-fired in vapor at 850°C for 2 h. The lines indicated by an asterisk increased in intensity by a factor of 3 relative to the other lines shown.

ZnTe(Er,Li)

Several EPR spectra were observed in ZnTe(Er,Li) but two were most prominent. In ZnTe(Er,Li) which

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[10] L. J. van der Pauw, Philips Res. Rept. **13**, 1 (1958).

TABLE II. Green photoluminescence peaks observed in ZnTe(Er,Li).

Treatment	Near-band-edge emission(s)		Emission exhibiting LO phonon[a] replicas	
	Peak (eV)[b]	Relative peak height	Peak (eV)	Relative peak height
As grown	2.37_1(0.007)	0.30	2.33_2(0.015)	1.00
Zinc fired [Zn(v), 850°C, 2 h]	···		2.33_1(0.018)	1.00
Zinc fired [Zn(v), 850°C, 16 h]	2.37_5(<0.001)	0.1	2.33_0(0.013)	1.00
Zinc extracted [Zn(l), 850°C, 2 h]	2.37_5(<0.001) 2.37_1(···)	0.27 0.03	2.32_3(0.016) 2.33_4(···)	1.00 (···)[c]
Vacuum annealed [Vacuum, 250°C, 8 d]	2.37_6(<0.001) 2.37_2(<0.001)	0.01 0.01	2.32_5(0.011)	1.00

[a] LO phonon replicas are clearly observed (0.026-eV spacing between peaks).
[b] The location of the peak of the emission is given. The values in parenthesis are full widths at half-maximum intensity.
[c] This peak appears as a small shoulder on the 2.32_3-eV emission band.

had been zinc fired, the strongest EPR spectrum was due to Er^{+3} at a site of trigonal symmetry with $g_\parallel = 4.066$, $g_\perp = 8.068$, and the average of the g tensor $\frac{1}{3}(g_\parallel + 2g_\perp) = 6.73$. The other spectrum (about $\frac{1}{4}$ the intensity of the trigonal spectrum) was isotropic with a g value of 5.95. Several other spectra of lower intensity were also observed including an isotropic EPR spectrum with $g = 6.83$. When the sample of ZnTe(Er,Li) was subjected to tretaments which are known to remove Li from electrically active sites in ZnTe [annealing at 250°C for 8 d (Ref. 11) or extracting Li with a bath of liquid Zn (Ref. 12)], the only EPR spectra observed for Er^{+3} were the cubic spectrum with $g = 5.95$ and a spectrum due to an excited state of Er^{+3} on this site of cubic symmetry.

ZnTe(Er,Li) as grown exhibited room-temperature hole concentrations of about 1×10^{17} cm^{-3}. The electrical properties of these crystals were quite similar to those observed for ZnTe(Li) crystals prepared with the same amount of Li (0.1 mole%) in the growth melt. In addition, the changes in the electrical properties of ZnTe(Er,Li) due to various thermal treatments were quite similar to those observed for ZnTe(Li) given comparable thermal treatments—vacuum annealing at 250°C for 8 d to remove Li from electrically active sites and brief firings at 850°C in Zn vapor followed by rapid quenching to room temperature to increase the number of Li atoms in electrically active sites.[11]

The green photoluminescence spectra of ZnTe(Er,Li) as grown were quite similar to those observed in ZnTe-(Li).[13] The major green emission peaks observed in ZnTe(Er,Li) subjected to various thermal treatments are compiled in Table II. The series of peaks beginning at 2.33_2 eV can be assigned to transitions involving

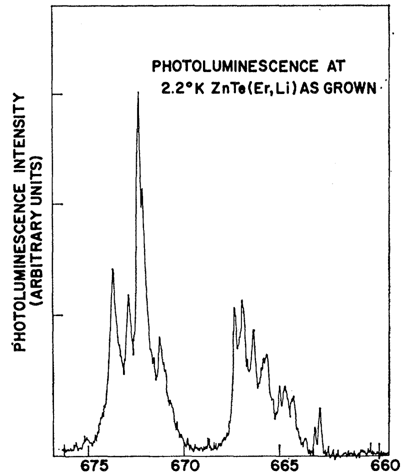

FIG. 3. Red photoluminescence spectrum (2.2°K) of as-grown ZnTe(Er,Li).

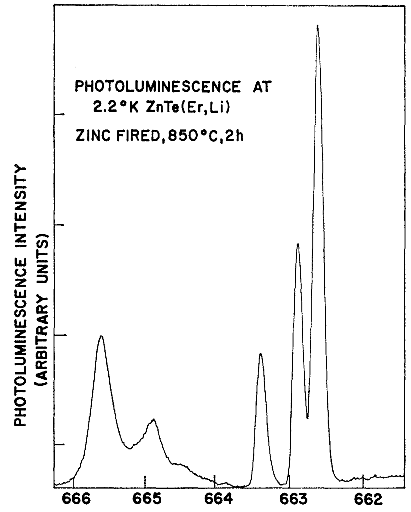

FIG. 4. Red photoluminescence spectrum (2.2°K) of ZnTe-(Er,Li) which has been Zn fired. Similar spectra are observed in ZnTe(Er,Li) which has been Zn extracted or vacuum annealed and in ZnTe(Er,P) samples.

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[11] B. L. Crowder and W. N. Hammer, Phys. Rev. **150**, 541 (1966).
[12] M. Aven and B. Segal, Phys. Rev. **130**, 81 (1963).

TABLE III. Resonance parameters determined from EPR studies for Yb^{3+} and Er^{+3} for the dominant sites observed in acceptor-doped ZnTe and CdTe.

	Trigonal symmetry				Cubic symmetry		
Crystal	$g_{\parallel}$	$g_{\perp}$	$\frac{1}{3}(g_{\parallel}+2g_{\perp})$	Representation[a]	g	Representation[a]	Reference
ZnTe(Er,P)	1.254	9.469	6.73	Γ_6[b]	5.95	Γ_7[c]	d
ZnTe(Yb,P)	1.133	4.404	3.31	Γ_7[c]	3.182	Γ_7[c]	e
CdTe(Yb,P)	0.87	4.323	3.17	Γ_7[c]	3.115	Γ_7[c]	f
ZnTe(Er,Li)	4.066	8.068	6.73	Γ_6[b]	5.95	Γ_7[c]	d
CdTe(Er,Li)	4.301	7.919	6.72	Γ_6[b]	5.94	Γ_7[c]	f
CdTe(Yb,Li)	1.834	2.832	2.499	Γ_6[g]	3.115	Γ_7[c]	f

[a] The representation of the ground-state level is determined by comparing the experimental g value (or average of the g tensor) with those calculated from the data given by LLW (Ref. 7). For Er^{+3} these values are $g(\Gamma_6)=6.800$ and $g(\Gamma_7)=6.000$. For Yb^{+3}, the values are $g(\Gamma_6)=8/3$ and $g(\Gamma_7)=24/7$.

[b] This representation may be the lowest level in either tetrahedral or octahedral coordination.

[c] This representation corresponds to the rare-earth ion in tetrhaderal coordination—a substitutional cation postiion.

[d] This study.

[e] Reference 2.

[f] Reference 1.

[g] This representation corresponds to the rare-earth ion in octahedral coordination—the interstitial position with four cations as nearest neighbors and six cations as next-nearest neighbors.

acceptor levels introduced by Li.[13] The intensity of this series did decrease markedly upon subjecting the crystals to treatments which remove Li from electrically active sites, and another emission series of 0.01 eV lower energy and exhibiting LO phonon structure appeared.

Rare-earth emission was also observed in ZnTe(Er,Li) in the region of 1.86 eV. The emission spectra of ZnTe(Er,Li) as grown contained a large number of emission lines as shown in Fig. 3. For all the other samples of ZnTe(Er,Li) listed in Table II, the rare-earth emission spectra were much simpler and identical (Fig. 4). The widths of the sharper lines were determined by the instrumental resolution, which was about 1.5 Å. In these samples, the strength of the rare-earth emission was appreciably reduced in those samples in which the 2.33_2 eV green emission was weak. The reduction in intensity of the rare-earth emission was two orders of magnitude for ZnTe(Er,Li) vacuum annealed relative to ZnTe(Er,Li) fired in Zn vapor for 2 h at 850°C.

ZnTe(Er,P)

Two EPR spectra were observed for Er^{+3} in ZnTe(Er,P) as grown. The weaker spectrum was isotropic with a g value of 5.75. The stronger spectrum was due to Er^{+3} in a site of trigonal symmetry with $g_{\parallel}=1.254$, $g_{\perp}=9.469$, and the average of the g tensor ($\frac{1}{3}(g_{\parallel}+2g_{\perp})$) equal to 6.93. The trigonal spectrum was 4 to 5 times as strong as the cubic spectrum. The results for ZnTe(Er,P) vacuum annealed were identical. ZnTe(Er,P) zinc fired exhibited both the trigonal and cubic spectra with approximately equal intensities but, due to cavity loading, the ratio could not be accurately determined.

The electrical properties of ZnTe(Er,P) as grown were also quite similar to the reported results for ZnTe(P) with 0.1 mole% P in the growth melt.[11]

The green photoluminescence observed from ZnTe(Er,P) as grown was quite similar to that observed for ZnTe(P).[13] The dominant emission at 2.2°K was a series of peaks separated by an LO phonon and beginning at 2.32_9 eV. Aside from changes in the weak band-edge emission peaks, the green photoluminescence of ZnTe(Er,P) vacuum annealed was the same as that for as grown samples. High-temperature firings in Zn vapor for 2 h or more produced marked changes in the green photoluminescence of ZnTe(Er,P) and introduced strong red photoluminescence. Similar behavior was observed for ZnTe(P) (Ref. 13) and in both materials the green and red photoluminescence peaks varied in position from sample to sample as the duration of Zn firing was changed.

The rare-earth emission observed in all samples of ZnTe(Er,P) was identical to that observed in most of the samples of ZnTe(Er,Li) as shown in Fig. 4. The intensity of this emission series in ZnTe(Er,P) as grown or vacuum annealed was reduced by a factor of 30 below that observed for zinc-fired ZnTe(Er,Li). The strength of rare-earth emission in ZnTe(Er,P) was further reduced by an order of magnitude for samples which were zinc fired.

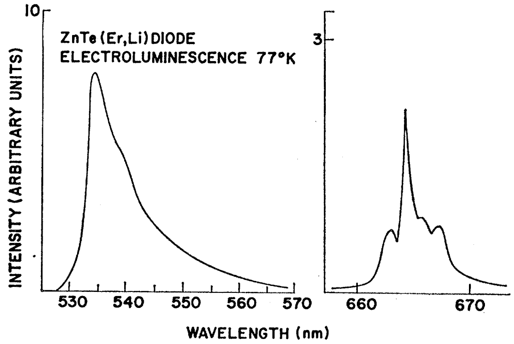

FIG. 5. Electroluminescence spectrum of a ZnTe(Er,Li) diode (77°K).

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[13] B. L. Crowder and G. D. Pettit, Phys. Rev. (to be published).

Electroluminescent Diodes

Diodes which are efficient light sources at 77°K can be prepared in acceptor-doped ZnTe.[14,15] The same techniques, involving the diffusion of Al into ZnTe, when applied to substrates of ZnTe(Er,Li) and ZnTe(Er,P) also yielded electroluminescent diodes. The diodes prepared from ZnTe(Er,Li), in addition to recombination radiation involving the Li acceptors, exhibited rare-earth emission in the 660 to 670 nm region at 77°K. The electroluminescence spectrum at 77°K from such a diode is shown in Fig. 5. The spectrum in the region 660 to 670 nm was identical to the photoluminescence spectra at 77°K for those samples which, at 2.2°K, exhibited the Er^{+3} photoluminescence shown in Fig. 4. Rare-earth emission from diodes prepared from ZnTe(Er,P) was either much weaker relative to the green luminescence than that shown in Fig. 5 for ZnTe(Er,Li) diodes or not even detectable.

IV. DISCUSSION OF EXPERIMENTAL RESULTS AND SUMMARY

The representation of the lowest lying level of the $^4I_{15/2}$ ground state of Er^{+3} in the various environments found in ZnTe crystals can be determined by comparing the experimental g values calculated from the eigenfunctions given by Lea, Leask, and Wolf,[7] namely, 6.800 for the Γ_6 doublet and 6.000 for the Γ_7 doublet. Table III is a compilation of the EPR results obtained in the present study for the dominant sites of cubic and trigonal symmetry in ZnTe(Er,P) and ZnTe(Er,Li) together with the corresponding results obtained in earlier investigations on ZnTe(Yb,P),[2] CdTe(Yb,P), CdTe(Yb,Li), and CdTe(Er,Li).[1] The information on the latter materials will prove to be useful in determining the most probable site for Er^{+3} in the ZnTe samples.

In all samples containing Er^{+3}, an isotropic spectrum was observed with a g value close to $g(\Gamma_7)=6.00$, indicating that Er^{+3} has substituted for a metal ion with nonlocal charge compensation since the Γ_7 doublet lies lowest only in tetrahedral coordination (Fig. 1). In those samples in which this cubic isotropic spectrum is strongest, one also finds an EPR spectrum due to the Γ_8 (Ref. 1) quartet which, as shown in Fig. 1, is an excited state which lies close in energy to Γ_7 whenever the Γ_7 doublet is the lowest-lying level.

The site of trigonal symmetry observed in ZnTe(Er,P) has an average g value $\frac{1}{3}(g_{\parallel}+2g_{\perp})=6.73$ close to that expected for $g(\Gamma_6)$, 6.800. This representation may lie lowest in either tetrahedral or in octahedral coordination. To decide on the coordination of the Er^{+3}, one can compare the results obtained for ZnTe co-doped with P and a rare earth for which the coordination is more easily determined such as Yb^{+3}. For ZnTe(Yb,P) the EPR results[2] (Table III) indicate that the site of trigonal symmetry has a g tensor consistent with a Γ_7 doublet that lies lowest in tetrahedral coordination.[1,7] Yb^{+3} is, therefore, on a substitutional Zn site. The trigonal symmetry of this site arises from a nearest-neighbor Te being replaced by a P atom ($g_{\parallel}<g_{\perp}$ indicates such a trigonal field). An analogous axial center is also observed in CdTe(Yb,P) as indicated in Table II. Since the behavior of Yb^{+3} and Er^{+3} are likely to be similar as far as site preference is concerned, the axial center observed in ZnTe(Er,P) is most likely an Er^{+3} on a Zn site with a P atom on a nearest-neighbor Te site.

A different axial center with trigonal symmetry was observed in ZnTe(Er,Li), but again the average of the g tensor (6.73) is close to $g(\Gamma_6)$. A center with trigonal symmetry and comparable g values (Table III) has also been observed in CdTe(Er,Li). In the less ambiguous case of Yb^{+3}, the trigonal center observed in CdTe(Yb,Li) has an average g value of 2.499, which is most likely due to Yb^{+3} in an interstitial positon with octahedral coordination $[g(\Gamma_6)=8/3$ for $Yb^{+3}]$. A trigonal field at an Yb^{+3} ion in this site would result if either one or three of the four nearest-neighbor metal ions were replaced with Li, but since $g_{\parallel}<g_{\perp}$ the trigonal field is due to only one Li on a nearest-neighbor cation site.[16] By analogy, the axial centers in ZnTe(Er,Li) and CdTe(Er,Li) listed in Table III consist of Er^{+3} in an interstitial position with a substitutional Li atom as a nearest neighbor. Additional evidence for this interpretation is provided by the fact that treatments which remove Li from electrically active centers in both ZnTe and in CdTe (Ref. 11) greatly enhance the isotropic EPR spectrum due to substitutional Er^{+3} and greatly diminish the strength of the EPR signal due to the axial centers under discussion. This behavior would be expected for the above model of an axial center, since the Li, after its removal, leaves a cation vacancy into which the interstitial rare-earth ion could readily move.

The weak cubic spectrum observed in zinc-fired ZnTe(Er,Li) with a g value equal to 6.833 has a Γ_6 ground state. Since the isolated substitutional Er^{+3} has been identified as having a Γ_7 ground state, the Er^{+3} in this isotropic center is most probably in an interstitial position which has cubic symmetry, i.e., either isolated or with all four nearest-neighbor cations replaced, presumably by Li.

To summarize the EPR results, the predominant sites at which Er^{+3} is found in ZnTe are as follows: site I (observed in ZnTe doped with either Li or P), an isolated Er^{+3} on a substitutional Zn site; site II (observed in P-doped ZnTe), a substitutional Er^{+3} with a P atom on one of the four nearest-neighbor Te sites; and site III (observed in Li-doped ZnTe), an Er^{+3} in an interstitial site surrounded by six next-nearest-neighbor Te, three nearest-neighbor Zn, and one nearest-neighbor Li on a Zn site.

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[15] B. L. Crowder and F. F. Morehead, IEEE Trans. Electron Devices, **13**, 676 (1966).

[16] U. Ranon and W. Low, Phys. Rev. **132**, 1609 (1963).

The absence of detectable resonances due to Er^{+3} in ZnTe(Er) samples implies that the Er^{+3} concentration which is soluble in the ZnTe lattice is considerably lower than that present in either ZnTe(Er,P) or ZnTe(Er,Li). The trivalent rare-earth ion, most likely to be found either on a substitutional cation site or in an interstitial position, should act as a donor species in II-VI compounds (by analogy with the behavior of group IIIb atoms). Increased solubility in acceptor-doped ZnTe is, therefore, not surprising. The electrical properties of ZnTe(Er) as grown indicate that Er is indeed acting as a donor species, since these samples are semi-insulating. The *net* acceptor concentration in as-grown undoped ZnTe is of the order of 10^{15} cm^{-3}, and concentrations of rare-earth ions of this order of magnitude could produce high resistivity as-grown material, as observed. Upon zinc firing and rapid quenching, the behavior of ZnTe(Er) is quite similar to that of undoped ZnTe, with net acceptor concentrations of the order of 3 to 5×10^{16} cm^{-3} being observed. The amount of Er^{+3} soluble in ZnTe(Er) crystals is therefore most likely between 10^{15} and 10^{16} cm^{-3}. From the strength of the EPR signal, the concentration of Er^{+3} in ZnTe(Er,Li) and in ZnTe(Er,P) samples is of the order of 10^{17} cm^{-3}. If the trivalent rare-earth ion indeed exhibits donor activity, the fact that for either ZnTe(Er,P) or ZnTe(Er,Li) the electrical properties (hole concentration and Hall mobility between 77 and 300°K) are quite similar to comparably doped ZnTe(P) or ZnTe(Li), respectively, implies that the concentration of Er^{+3} is of the order of 5×10^{17} cm^{-3} *or less* in these materials [the total donor concentrations in ZnTe(P) or ZnTe(Li) are of the order of 5×10^{17} cm^{-3} for 0.1 mole% acceptor concentrations in the growth melt].[11]

The narrow-line emissions observed only in samples of ZnTe containing Er, all lie in the region 1.84 to 1.86 eV. The transition involved is, therefore, almost certainly from the $^4F_{9/2}$ manifold of the $4f^{11}$ configuration of Er^{+3} to the $^4I_{15/2}$ ground state (see Table I).

The experimental evidence presented in Sec. III for ZnTe(Er) samples indicates that at least two environments for Er^{+3} ions active in luminescence are present (Fig. 2). The multiplicity of lines observed in ZnTe(Er,Li) as grown (Fig. 3) also indicates a variety of different sites active in luminescence. The simplicity of the Er^{+3} spectra observed in all other samples of ZnTe(Er,Li) and all samples of ZnTe(Er,P) implies that only one Er^{+3} environment is involved in the luminescence, and the fact that identical spectra are obtained for all these samples indicates that the same center involving Er^{+3} is responsible for the red narrow-line emission. The strength of this particular rare-earth emission series (as given in Fig. 4) in the various ZnTe crystals studied can be related to the EPR data on the same crystals in order to gain an insight into the local environment of the Er^{+3} ions involved in the luminescence transition. Actually, as will be shown, the results are negative in the sense that certain environments can be shown not to be responsible for the observed luminescence. The intensity of this emission series is the strongest for zinc-fired ZnTe(Er,Li) and decreases as Li is removed from the crystal (as deduced from both the electrical properties of the crystal and from the strength of the green emission series beginning at 2.33_2 eV associated with the Li acceptors). The EPR signal due to Er^{+3} in the substitutional site I becomes quite strong as Li is removed while that due to the interstitial site III decreases. An isolated Er^{+3} on a substitutional Zn site (site I) is therefore not an efficient radiative recombination center which involves the $^4F_{9/2}$ to $^4I_{15/2}$ transition of the $4f^{11}$ configuration. Furthermore, the intensity of the EPR signal due to Er^{+3} in site III decreases much more rapidly than the intensity of the observed red photo-luminescence as Li is removed from the sample, and the same red photoluminescence is observed in ZnTe(Er,P), although with over an order-of-magnitude decrease in intensity relative to zinc-fired ZnTe(Er,Li). These observations tend to rule out Er^{+3} on either the substitution site II (Er-P) or the interstitial site III (Er-Li) as an efficient luminescence center for the transition under discussion, and the environment of Er^{+3} involved in this red luminescence is not known. The EPR studies of the crystal in which the intensity of this red luminescence transition is the strongest, zinc-fired ZnTe(Er,Li), revealed other sites in addition to sites I and III, including one in which the Er was interstitial, which may have four Li ions as nearest neighbors. Such a center would be analogous to the cubic center in ZnSe(Er,Cu), referred to as site II by Kingsley and Aven and shown in Fig. 1,[4] which was an efficient luminescence center in that material. Although the nature of the Er^{+3} luminescence center in ZnTe(Er,Li) and ZnTe(Er,P) is not known, it is obvious that most of the Er^{+3} incorporated into the crystal is not part of a center which is efficient in producing the observed red photoluminescence shown in Fig. 4. If the concentration of such centers could be greatly increased, the efficiency of these recombination centers relative to the green emission centers characteristic of the acceptor-doped ZnTe would be quite good.

The results obtained from electroluminescent diodes prepared from ZnTe(Er,Li) indicate that rare-earth emission can be obtained from recombination of injected minority carriers at a center involving the rare-earth ion. These radiative-recombination centers involving the trivalent rare earth can compete effectively with the radiative-recombination centers due to the acceptor species Li, even though only a fraction of the trivalent rare-earth ions appear to be located on sites which serve as efficient recombination centers.

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