Electronic structure of a neutral Cu-related complex defect with a bound exciton at 2.3296 eV in ZnTe

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A complex defect with a bound exciton (BE) at 2.3296 eV (at 2 K) in Cu-diffused ZnTe is studied in detail with laser spectroscopy, including magneto-optical measurements in fields up to 10 T. The defect is found to be axial and (110)-oriented, suggesting a substitutional pair Cu_{Zn}-D_{Zn} as the identity, where D_{Zn} is a shallow donor on a Zn site. This suggestion is consistent with the fact that the defect is neutral, from the absence of thermalization in Zeeman transmission data. The Zeeman data can be fitted with a spin Hamiltonian dominated by a rather strong tensional local strain field, with a small electron-hole exchange interaction (≈ 0.02 meV). The defect has a moderately strong hole-attractive local potential, presumably due to Cu_{Zn}, and the angular momentum for the bound hole is not quenched. The tensional sign of the local strain field leaves a $|J,M_J\rangle = |\frac{3}{2},\pm\frac{3}{2}\rangle$ doublet as the lowest hole state, with a hole g factor given by $K = 1.25\pm 0.02$, $L = -0.21\pm 0.01$. The electron in this BE is loosely bound as a secondary particle, with an isotropic g value $g_e = -0.38\pm 0.02$, quite similar to the value $g_e = -0.40$ for shallow donors in ZnTe.

I. INTRODUCTION

The electronic structure of complex defects in semiconductors is an important problem, which is not well understood at the moment, in contrast to the case of point defects.[1] This is partly due to lack of detailed experimental data, including identification of the defects. Another problem is on the theoretical side: Very little is done so far when it comes to basic calculations of the electronic structure of complex defects.[2]

Previous experimental studies of complex defects in compound semiconductors are scarce. Some early well-known cases were studied in indirect-band-gap GaP, notably GaP:Zn,O and GaP:Cd,O[3,4] GaP:Li,O,[5] GaP:Cu,[6,7] and GaP:Cu,Li.[8-11] In direct-band-gap materials a few such defects have recently been studied in some detail, including GaAs:Cu (Ref. 12) and CdTe:Ag.[13] ZnTe doped with Cu is an interesting system for fundamental studies of complex defects, since a large number of different such defects are easily prepared.[14] A few detailed studies of the electronic structure of complex defects with a trigonal symmetry in ZnTe, believed to involve substitutional-interstitial pairs, have recently been published.[15-17] In this paper a neutral Cu-related defect in ZnTe is discussed, with a C_{1h} axial $\langle 110\rangle$-oriented symmetry, believed to be a typical example of a neutral defect composed of a substitutional pair on neighboring Zn sites in ZnTe.

The investigations reported in this paper are concentrated to a bound exciton (BE) with an electronic line at 2.3296 eV at 2 K, associated with the complex defect under study. The experimental techniques are photoluminescence (PL) and photoluminescence excitation (PLE) spectra, in both cases including tunable dye-laser excitation. The absorption spectrum of this BE was also studied in plain transmission. In addition, magneto-optical Zeeman data were obtained, in magnetic fields up to 10 T, in both PL emission and absorption.

The experimental data, in particular those from the Zeeman experiments, are fitted to an explicit spin Hamiltonian for a BE bound to a neutral complex defect. It has been possible to evaluate quite accurate numerical values for the parameters in this spin Hamiltonian, which are also consistent with the derived geometrical structure and identity of the defect. We believe these results serve as an important model system for the electronic structure of a neutral complex defect composed of a substitutional pair in ZnTe and similar materials. The spin-orbit splitting is the dominating low-symmetry perturbation, but the local strain field is also rather strong. This means that the angular momentum of the bound hole is retained, and a $|J,M_J\rangle = |\frac{3}{2},\pm\frac{3}{2}\rangle$ doublet is the lowest bound hole state at zero field. The bound electron is shallow donorlike, consistent with the Hopfield-Thomas-Lynch (HTL) model for excitons bound to neutral (isoelectronic) defects.[18]

The paper is organized in the following way. In Sec. II is given a brief account of samples and experimental conditions. In Sec. III the experimental data are exposed, in particular the Zeeman data, together with a detailed evaluation of these data with the aid of a spin Hamiltonian and theoretically computed spectra of the BE in a magnetic field. In Sec. IV the BE electronic structure is discussed in more detail in reference to similar work on other defects. Also, a geometrical model for the defect identity is derived and discussed.

II. SAMPLES AND EXPERIMENTAL TECHNIQUES

The ZnTe material used for these experiments was nominally undoped single crystalline bulk ZnTe, grown at LETI in Grenoble by B. Schaub. The electrically active uncompensated background doping of this material was around 1×10^{15} cm^{-3} (p type). Cu diffusion was done in a single diffusion step, as described in more detail in a

previous paper.[14] Such a doping procedure increased the uncompensated p-type doping, typically to the high 10^{16} cm^{-3} range.

Photoluminescence spectra were obtained at 2 K with an Ar^+ laser or a tunable dye laser (Coumarin 540 dye) as excitation source. The PLE spectra were also obtained with the tunable dye laser as the excitation source, and the detection was obtained via a Spex 1404 0.85-m double monochromator, which was also used in the transmission experiments. The magneto-optical measurements were performed at the Max-Planck-Insitut Hochfeld Magnetlabor in Grenoble, using a split-coil superconducting magnet, together with a Jobin Yvon THR 1500 high-resolution monochromator.

III. EXPERIMENTAL DATA AND COMPARISON WITH THEORETICALLY COMPUTED SPECTRA

In Fig. 1(a) is shown a photoluminescence spectrum of the 2.3296 eV BE [also called Z_2^0 (Refs. 14, 19, and 20)], also with selective excitation below the band gap, so that other overlapping spectra can be eliminated. A single electronic line Z_2^0 occurs at 2.3296 eV at 2 K, with a rather weak coupling to quasilocalized phonon modes in the one-phonon range towards lower photon energies. The LO^Γ replica dominates the phonon coupling in PL emission, with a coupling strength about 0.4. In the PLE spectrum also, only one electronic line is observed below the band gap [Fig. 1(b)], an important observation, to be further discussed below. The phonon coupling in absorption is much larger than in emission, as discussed separately.[21] The details of the phonon spectrum coupling to the BE will not be discussed in this paper. As a comparison to the selective curve in Fig. 1(b) a regular transmission curve for the same sample is shown in Fig. 1(c). Obviously, the overlap between BE spectra associated with different centers in such a transmission spectrum [Fig. 1(c)] would make evaluations of spectral details associated with each BE quite difficult.

Zeeman data were obtained in both PL emission and absorption, in the Voigt configuration, and in fields up to 10 T. In Fig. 2 is shown a typical Zeeman splitting pattern (fan diagram) of the 2.3296-eV line developing for fields up to 10 T, in the (001) crystal direction. From this behavior the quadratic shift rate of the BE line with the field can be evaluated (see below). In addition, the angular dependence of the Zeeman data was measured for a rotation of the sample with **B** in a $\{1\bar{1}0\}$ plane, with a 4° misorientation as shown in Fig. 3. The linewidth of the spectra was quite broad (as indicated in the figures), due to the rather high doping level. This means that even at 10 T all the components of the Zeeman-split spectrum cannot always be resolved, in particular for lines with a low transition probability. In spite of this problem of spectral overlap in some situations, it is possible to follow in detail the angular development of the different peaks of the Zeeman-split spectrum at 10 T.

The data points in Figs. 2 and 3 are fitted with a theoretically calculated splitting pattern (solid lines in Figs. 2 and 3), obtained by fitting an appropriate spin

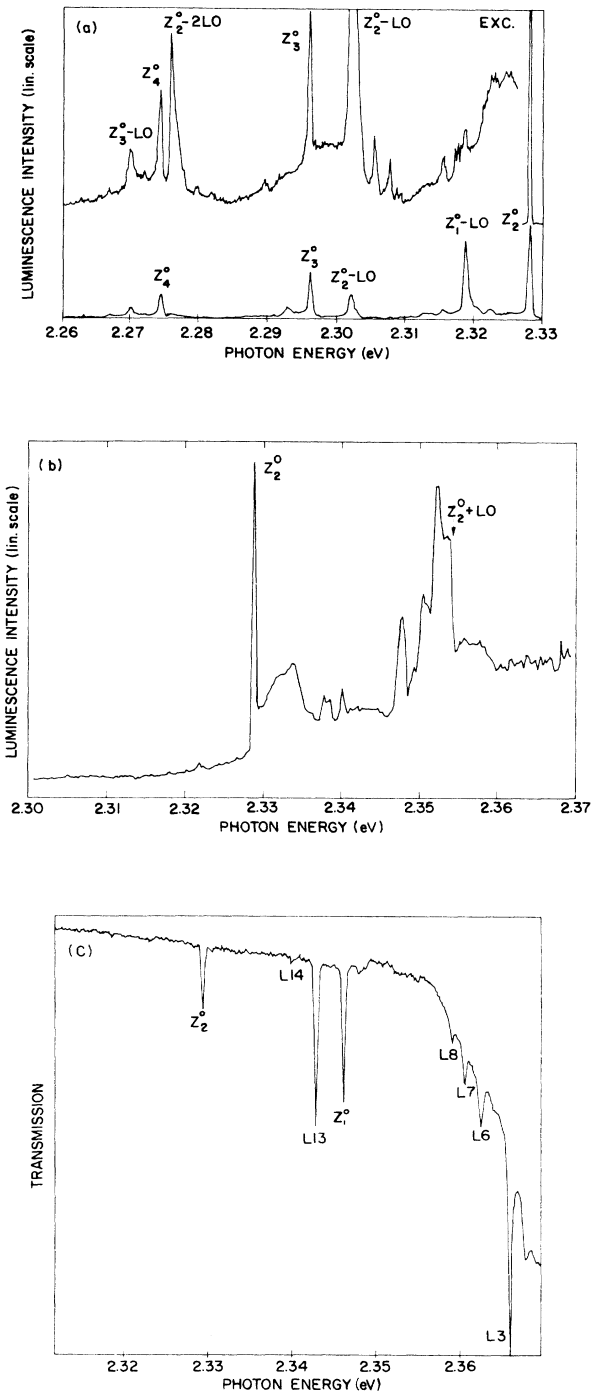

FIG. 1. (a) Photoluminescence spectrum of the Z_2 bound exciton in Cu-doped ZnTe, both with above band-gap excitation (5145 Å) (lower curve) and with selective excitation (SPL spectrum) in the Z_2^0 no-phonon line (upper curve). Both spectra are measured at 2 K. (b) Photoluminescence excitation spectrum for the Z_2 emission, measured with dye-laser excitation on the same sample as in (a). The detection is at the LO^Γ replica of Z_2^0. The phonon spectrum looks quite different than the corresponding PL spectrum [(a)]. Transmission spectrum of the Z_2 bound exciton at 2 K without magnetic field. Other lines beside Z_2^0 were found to be related to other defects.

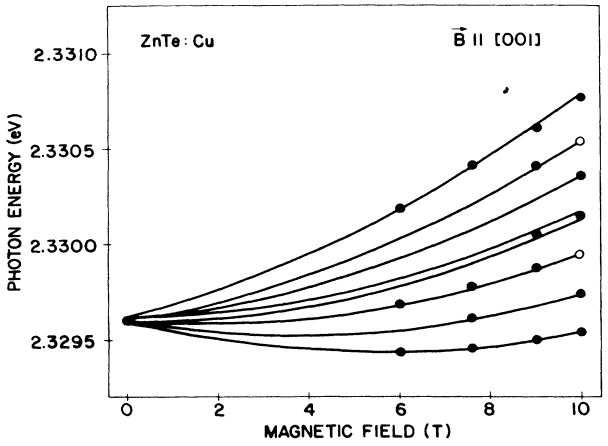

FIG. 2. Fan diagram for the splitting on the Z_2^0 bound exciton line with magnetic field from 0 T up to 10 T in the (001) direction. The solid lines are computer simulated from the spin Hamiltonian given in the text. Solid circles correspond to the strongest experimental lines, while open circles correspond to the weaker lines.

Hamiltonian for the particular BE under study. The following Hamiltonian was used:

$$H_Z = H_{ex} + H_{LCF} + H_{LZ} + H_{QZ} \ , \tag{1}$$

where

$$H_{ex} = -a\mathbf{J}\cdot\mathbf{S}_e \tag{2}$$

denotes the exchange interaction between the bound electron-hole pair, while

$$H_{LCF} = -D[J_\zeta^2 - \tfrac{1}{3}J(J+1)] \tag{3}$$

is the main local-crystal-field term, where D is a scalar denoting the influence of the axial local strain field on the splitting of the BE lines[22] (in a symmetry lower than axial, D is a tensor). The linear Zeeman interaction term is written in the conventional way[23]

$$H_{LZ} = \mu_B[g_e\mathbf{S}_e\cdot\mathbf{H} + K\mathbf{J}\cdot\mathbf{H} + L(J_x^3H_x + J_y^3H_y + J_z^3H_z)] \tag{4}$$

while the quadratic Zeeman term is taken simply as

$$H_{QZ} = C_1H^2 + C_3[\tfrac{1}{2}H_xH_y(J_xJ_y + J_yJ_x) + \text{c.p.}] \ , \tag{5}$$

where c.p. denotes cyclic permutation. Here $\mathbf{J}$ is the total angular momentum of the bound hole, while $\mathbf{S}_e$ is the corresponding quantity for the bound electron. The axes x,y,z are the conventional main cubic axes for the defect system, while ζ is the axis of the axial local crystal field at the defect, which becomes the quantization axis in cases where the crystal-field term dominates the Zeeman term.

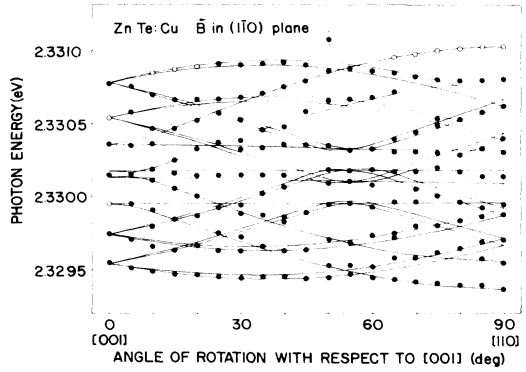

FIG. 3. Angular dependence of the Zeeman splitting of the Z_2^0 bound exciton line in Voigt configuration at 2 K. The sample was rotated with the magnetic field $\mathbf{B}$ in a (1$\bar{1}$0) plane with a 4° misorientation. Solid lines are computer simulated from the spin Hamiltonian given in the text. Weak experimental lines are shown by open circles. The linewidth of the experimental lines is also indicated (I).

TABLE I. A synopsis of the parameters in the perturbation Hamiltonian describing the Zeeman splitting of the Cu-related 2.3296-eV bound exciton.

Parameters	Z_2^0 line
a	0.02±0.005 meV
D	≥120 meV
g_e	−0.38±0.02
K	1.25±0.02
L	−0.21±0.01 meV
C_1	$(0.55\pm0.02)\times10^{-2}$ meV/T^2
C_3	$(0.06\pm0.01)\times10^{-2}$ meV/T^2

In order to make a suitable choice of basis functions to diagonalize the above total perturbation Hamiltonian, it is noted that the Zeeman spectrum is quite anisotropic so the angular momentum of the bound hole is retained, due to the strong spin-orbit splitting in ZnTe.[24] This means that the $J=\frac{3}{2}$ basis set for the hole is relevant. Furthermore, the bound electron behaves like a spinlike $s=\frac{1}{2}$ particle. The proper basis is therefore $s=\frac{1}{2}$ for the electron and $J=\frac{3}{2}$ for the hole. With this basis the spin Hamiltonian was diagonalized numerically (all terms simultaneously) on a computer, to obtain energy eigenvalues and wave functions, corresponding to each value of magnetic field and rotation angle versus the magnetic field direction. A least-squares-fit program of parameters was built in to obtain optimum parameters for best fit to the data. The values obtained for best fit (as shown in Figs. 2 and 3) are given in Table I.

The implications of a rather large D value of positive sign is a dominating action of a *tensional* crystal field, splitting the $J=\frac{3}{2}$ manifold for the bound hole into two Kramer's doublets $|\frac{3}{2},\pm\frac{3}{2}\rangle$ and $|\frac{3}{2},\pm\frac{1}{2}\rangle$, respectively, of which the lowest energy state is $|\frac{3}{2},\pm\frac{3}{2}\rangle$, while the $|\frac{3}{2},\pm\frac{1}{2}\rangle$ state is degenerate with the valence band. This is consistent with the experimental observation of only one electronic state in the band gap, as discussed above in connection with Fig. 1. Furthermore, the *e-h* exchange interaction is found to be small, so the basis set used with individual wave functions for the electron and hole appears adequate.

In addition to the data in Table I, an important con-

clusion drawn directly from the symmetry pattern in Fig. 3 is a (110)-axial symmetry. This justifies the use of the simplified Hamiltonian for the local strain field [Eq. (3)], and is also very helpful in the modeling of the defect identity (see below).

IV. DISCUSSION

A. The electronic structure of the Z_2 bound exciton

The main perturbations on the bound hole states have already been discussed, but are clarified again with reference to Fig. 4. It is evident from the data in Table I that the defect is hole attractive, since the bound electron is found to have shallow donorlike properties. The localized potential is thus hole attractive, i.e., a hole is bound as the first particle to the defect. Since the potential is of low C_{1h} symmetry, a bound hole state is expected to have a quenched angular momentum, unless the spin-orbit interaction is strong.[24] In ZnTe we have exactly this case, the spin-orbit interaction in the host material is strong [($\approx$0.92 eV (Ref. 25)]. Therefore, the case of a quenched angular momentum for bound hole states rarely occurs in ZnTe, although an example of this case has recently been investigated.[17] The conclusion of a $J=\frac{3}{2}$ bound hole state in the present case is therefore not very surprising, although the localized potential might be rather strong. We believe the hole-attractive part of the potential is caused by Cu_{Zn}, an only moderately deep acceptor in ZnTe, though ($E_a=148$ meV).[26]

The occurrence of a $|\frac{3}{2},\pm\frac{3}{2}\rangle$ Kramer's doublet at lowest energy for the bound hole state is natural in the case of $D>0$, i.e., a tensional local strain field.[27] The same situation has previously been encountered for the Cd-O pair in GaP,[1,27] although in that case the hole was bound as a secondary particle in an effective-mass-like state. In the present case it is difficult to compare with the effective-mass-like situation, since no shallow acceptor with the same low symmetry seems to have been studied in detail in ZnTe. Certainly the values determined for the parameters K and L are different from the values for shallow acceptors in tetrahedral symmetry in ZnTe ($K\approx0.7$, L small).[26,28]

The bound electron state is found to be very close to a shallow donorlike state, as judged from the g_e value $g_e=-0.38$ (Table I). The value deduced for the quadratic shift rate C_1 is somewhat smaller than what is typically found for shallow donors in ZnTe.[28] This is similar to the case of the 2.261-eV BE in ZnTe, however.[16] The very delocalized bound electron state is consistent with a very small electron-hole overlap, i.e., a small value of the e-h exchange parameter a, as noted in Table I and Fig. 4. The small value of a cannot be spectrally resolved at zero field, it is slightly smaller than what was found for the 2.345-eV trigonal BE system in ZnTe.[15]

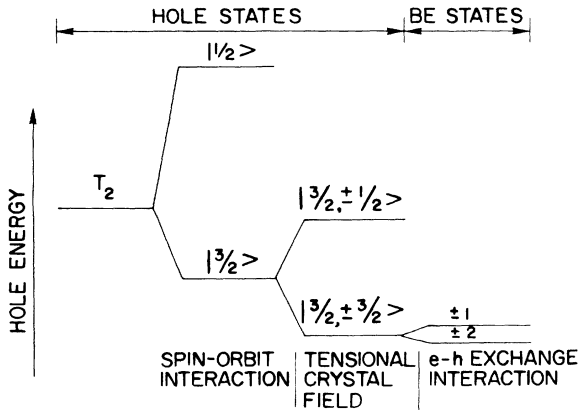

FIG. 4. Schematic picture of the electronic structure for the Z_2 bound exciton at 2.3296 eV in ZnTe. The spin-orbit interaction is the dominating perturbation on the bound hole state, but the effect of the local strain field is also large in this hole-attractive potential. The electron-hole exchange interaction, on the other hand, is rather small and cannot be resolved at zero magnetic field.

B. Defect identity

The Z_2 defect is one of the most prominant defects in Cu diffused ZnTe,[14] and should consequently be a simple defect. The (110) orientation, together with the fact that the defect is neutral (isoelectronic), strongly suggests a substitutional pair as the identity. It is natural to suggest that the hole-attractive potential of the defect is due to Cu_{Zn}, a moderately deep acceptor in ZnTe. The donorlike part of the complex would then be a shallow donor on Zn site, such as Al or Ga (see Fig. 5). The original ZnTe material had very low background doping, but it is known that impurities can be stored in Te-rich inclusions in the material, and released from those inclusions during a heat treatment such as Cu diffusion.[29,30] Therefore such impurities may be abundant during the diffusion procedure, to create neutral donor-acceptor nearest-neighbor pairs. Although Al has been found to be a common impurity in the ZnTe starting material, we do not claim the identity of the donorlike part in the complex is known. Nevertheless, it is important to have established the properties of such a neutral substitutional pair in ZnTe for the first time.

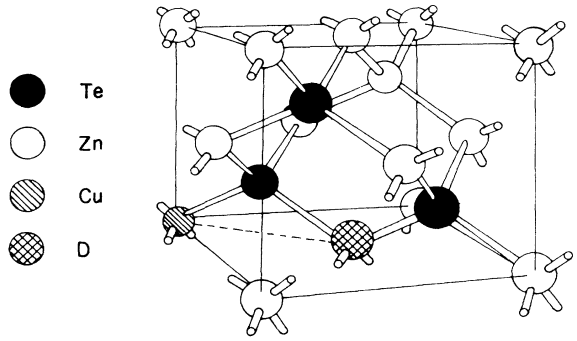

FIG. 5. Model of the suggested defect identity as a Cu_{Zn}-D_{Zn} substitutional pair.

V. SUMMARY AND CONCLUSION

The general significance of this work may be stated in the following two main points.

(1) The electronic structure of a hole-attractive neutral complex in a *tensional* axial strain field has been studied in detail for the case of strong spin-orbit interaction for the bound hole. It is found that the primary bound hole can be adequately described in a rather simple way as a $|J,M_J\rangle = |\frac{3}{2},\pm\frac{3}{2}\rangle$ Kramer's doublet.

(2) The specific defect studied is concluded to be a typical example of a simple *substitutional pair* on Zn site, Cu_{Zn}-D_{Zn}. This is an example of a specific class of simple complex defects, and to our knowledge it is the first example of hole-attractive defects of this class studied in detail in any semiconductor.

In most studies of Zeeman spectroscopy for defects in semiconductors in the past, a very simplified approach has been used, including only one or two leading terms in the spin Hamiltonian. In this work a detailed computer calculation of Zeeman spectra was performed for the BE state, employing a realistic Hamiltonian, where only the spin-orbit interaction is included in the unperturbed Hamiltonian, while the local strain field, the magnetic field, and the *e-h* exchange interaction is included in the spin Hamiltonian. A realistic basis set for the diagonalization is then the $J=\frac{3}{2}$ manifold for the hole, and a spinlike $s=\frac{1}{2}$ state for the electron. It is found that the strain field is by far the dominating perturbation, while the *e-h* exchange interaction is quite small, even compared to the Zeeman terms. The emerging physical picture of the bound exciton is a rather localized bound hole state, and an effective-mass-like electron bound as a secondary particle, in accordance with the classical Hopfield-Thomas-Lynch model.[18] The evaluated constants in the spin Hamiltonian support this model in detail.

The suggested identity of the defect as a substitutional pair of Cu_{Zn} and D_{Zn} is the only alternative readily consistent with the defect symmetry, the involvement of Cu, and a tensional local strain field. The prediction of a tensional sign of the strain field is not unnatural for a substitutional pair, although there is no simple way to back up such a statement without basic calculations.[31] Certainly a substitutional-interstitial pair would be expected to have a compressive local strain field in agreement with recent data.[15]

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[1]For a recent experimental description of point defects in semiconductors, see, e.g., J. Bourgoin and M. Lannoo, *Point Defects in Semiconductors, Parts I and II,* Vol. 35 of *Springer Series in Solid State Sciences* (Springer-Verlag, Berlin, 1983).

[2]G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 1327 (1985).

[3]T. N. Morgan, B. Welber, and R. N. Bhargava, Phys. Rev. **166**, 751 (1986).

[4]C. H. Henry, P. J. Dean, and J. D. Cuthbert, Phys. Rev. **166**, 754 (1968).

[5]P. J. Dean, Phys. Rev. B **4**, 2596 (1971).

[6]B. Monemar, H. P. Gislason, P. J. Dean, and D. C. Herbert, Phys. Rev. B **25**, 7719 (1982).

[7]H. P. Gislason, B. Monemar, P. J. Dean, D. C. Herbert, S. Depinna, B. C. Cavenett, and N. Killoran, Phys. Rev. B **26**, 827 (1982).

[8]H. P. Gislason, B. Monemar, M. E. Pistol, P. J. Dean, D. C. Herbert, A. Kanaàh, and B. C. Cavenett, Phys. Rev. B **31**, 3774 (1985).

[9]H. P. Gislason, B. Monemar, M. E. Pistol, P. J. Dean, D. C. Herbert, S. Depinna, A. Kanaàh, and B. C. Cavenett, Phys. Rev. B **32**, 3958 (1985).

[10]H. P. Gislason, B. Monemar, M. E. Pistol, A. Kanaàh, and B. C. Cavenett, Phys. Rev. B **33**, 1233 (1986).

[11]W. M. Chen and B. Monemar (unpublished).

[12]H. P. Gislason, B. Monemar, Z. G. Wang, Ch. Uihlein, and P. L. Liu, Phys. Rev. B **32**, 3723 (1985).

[13]B. Monemar, E. Molva, and L. S. Dang, Phys. Rev. B **33**, 1134 (1986).

[14]P. O. Holtz, B. Monemar, H. P. Gislason, and N. Magnea, J. Lumin. **34**, 245 (1986).

[15]W. M. Chen, Q. X. Zhao, B. Monemar, H. P. Gislason, and P. O. Holtz, Phys. Rev. B **35**, 5722 (1987).

[16]B. Monemar, P. O. Holtz, W. M. Chen, H. P. Gislason, U. Lindefelt, and M. E. Pistol, Phys. Rev. B **34**, 8656 (1986).

[17]W. M. Chen, B. Monemar, P. O. Holtz, Q. X. Zhao, and H. P. Gislason, Phys. Rev. B **35**, 5714 (1987).

[18]J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. **17**, 312 (1966).

[19]B. Monemar, P. O. Holtz, H. P. Gislason, N. Magnea, Ch. Uihlein, and P. L. Liu, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors, San Francisco, 1984,* edited by J. D. Chadi and W. A. Harrison (Springer-Verlag, New York, 1985), p. 675.

[20]P. O. Holtz, B. Monemar, H. P. Gislason, Ch. Uihlein, and P. L. Liu, Phys. Rev. B **32**, 3730 (1985).

[21]P. O. Holtz and B. Monemar, Phys. Rev. B **33**, 1233 (1986).

[22]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[23]J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).

[24]B. Monemar, U. Lindefelt, and M. E. Pistol, J. Lumin. **36**, 149 (1986).

[25]M. Cardona and D. L. Greenaway, Phys. Rev. **131**, 98 (1963).

[26]H. Venghaus and P. J. Dean, Phys. Rev. B **21**, 1596 (1980).

[27]J. W. Morgan and T. N. Morgan, Phys. Rev. B **1**, 739 (1970).

[28]P. J. Dean, H. Venghaus, J. C. Pfister, B. Schaub, and J. C. Marine, J. Lumin. **16**, 363 (1978).

[29]J. L. Pautrat, N. Magnea, and J. P. Faurie, J. Appl. Phys. **53**, 8668 (1982).

[30]D. Bensahel, N. Magnea, and M. Dupuy, Solid State Commun. **30**, 467 (1979).

[31]For a recent discussion on atomic sizes and relaxation effects at impurities, see, e.g., M. Scheffler, Proceedings of the Second International Conference on Shallow Impurities Trieste, 1986 (unpublished).