The positions of the energy levels of Mn^{2+} in ZnS_xSe_{1-x} crystals

The positions of the energy levels of Mn^{2+} in ZnS_xSe_{1-x} crystals

Hai Ying, Yu Jiaqi and Yang Baojun

Changchun Institute of Physics, Academia Sinica, People's Republic of China

Abstract. The photoconductivity bands corresponding to the transitions from $^6A_1$ to $^4T_1$, $^4T_2$ and ^4E of Mn^{2+} in ZnS_xSe_{1-x} ($x = 0, 0.01, 0.02, 0.05, 0.10, 0.14$) are found. The intensities of these bands relative to that of the intrinsic photoconductivity band are found to vary with x. The configuration model of the manganese centre in ZnS_xSe_{1-x} is proposed to explain the experimental results. The positions of the energy levels of Mn^{2+} in ZnS_xSe_{1-x} ($x = 0$–0.10) relative to the conduction band are deduced systematically. The minimum of the configuration curve for $^6A_1$ of Mn^{2+} is deduced to be 0.44 eV above that of the valence band of ZnSe. The threshold energy for optical excitation from the valence band to ZnSe to the $^6A_1$ state of Mn^{2+} is found to be 0.69 eV.

1. Introduction

Mn^{2+} ions are efficient luminescence centres for II–VI compounds. The investigation of the positions of the energy levels of Mn^{2+} in ZnS_xSe_{1-x} is important not only for understanding luminescence properties of Mn^{2+} ions in II–VI compounds, but also for the investigation of deep centres in semiconductors. There are a few papers concerning the positions of Mn^{2+} ions in ZnSe. Grimmeiss, Allen and co-workers placed the ground state of Mn^{2+} in ZnSe at 0.68 eV above the valence band; this positioning was based on photocapacitance and photocurrent measurements (Braun *et al* 1972, Grimmeiss *et al* 1976). Woods and co-workers suggested that the ground state of Mn^{2+} was 0.3 eV above the valence band in ZnSe (Jones and Woods 1973, Ozsan and Woods 1975).

The authors investigated the positioning of the energy levels of Mn^{2+} in ZnSe through photoconductivity (Jiang Xueyin *et al* 1983). In this work the positions of the energy levels of Mn^{2+} ions in ZnS_xSe_{1-x} ($x = 0$–0.14) have been investigated by the same method. The photoconductivity of $ZnS_xSe_{1-x}:Mn^{2+}$ has been measured, configuration models have been put forward to explain the experimental results, the parameters of the configuration curves have been calculated and the positions of Mn^{2+} levels relative to the conduction band of ZnS_xSe_{1-x} ($x = 0$–0.10) have been deduced.

2. Experimental details

The samples of $ZnS_xSe_{1-x}:Mn^{2+}$ were grown by the vapour-transfer method at our Institute. Mn^{2+} ions were introduced during growth. Two ohmic electrodes were placed on a polished surface of each crystal sample.

The $ZnS_xSe_{1-x}:Mn^{2+}$ sample was put in a cryostat and excited with light from a 1 kW tungsten bromide lamp after it had been passed through a D330 grating monochromator. The photoconductivity signal was detected using a CGZ-17B high-resistance meter and recorded on a chart recorder. The excitation spectra of the photoconductivity were decomposed into gaussian bands using a PDP-11/03 microcomputer.

3. Experimental results

The excitation spectra of the photoconductivity of $ZnS_xSe_{1-x}:Mn^{2+}$ and ZnS_xSe_{1-x} samples are quite different (figure 1). The pure samples have only one intrinsic peak, corresponding to the transition between the valence band and the conduction band. At room temperature, the samples doped with Mn^{2+} ions have additional peaks in the long-wavelength region. At liquid nitrogen temperature, both pure and Mn^{2+}-doped samples have only the intrinsic peak (figure 2). The intrinsic peak shifts to shorter wavelength at liquid nitrogen temperature because the band gap becomes larger.
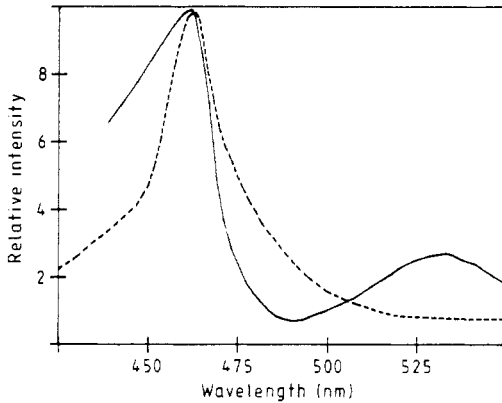

Figure 1. The excitation spectra of the photoconductivity of (dotted curve) ZnSe and (full curve) ZnSe:Mn at room temperature.
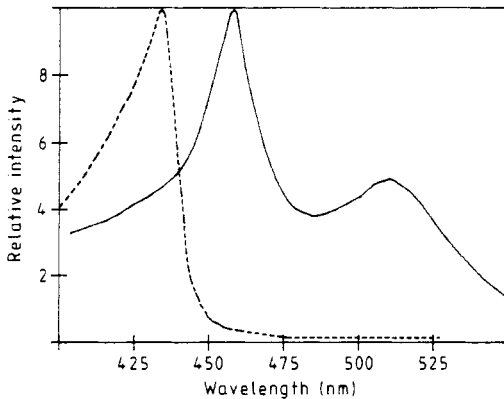

Figure 2. The excitation spectra of the photoconductivity of $ZnS_xSe_{1-x}:Mn^{2-}$ ($x = 0.02$) at (full curve) room temperature and (broken curve) liquid nitrogen temperature .

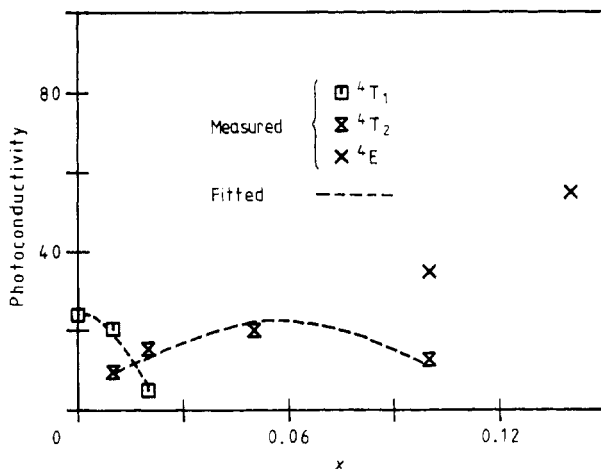**Figure 3.** The excitation spectra of the photoconductivity of ZnS$_x$Se$_{1-x}$:Mn^{2-} at room temperature.

The photoconductivity excitation spectra of ZnS$_x$Se$_{1-x}$:Mn^{2+} ($x = 0$, 0.01, 0.02, 0.05, 0.10, 0.14) were measured at room temperature (see figure 3).

The peak positions and the relative intensities of the decomposed bands (the intensity of the intrinsic band is taken as 100) are listed in table 1. From table 1 we can see that there are three bands, peaking around (1) 5300 Å for $x = 0$, 0.01, 0.02, (ii) 5000 Å for $x = 0.01$, 0.02, 0.05, 0.10 and (iii) 4650 Å for $x = 0.10$, 0.14. All samples have the intrinsic bands in the shorter-wavelength side. The peaks of the intrinsic bands shift to the shorter wavelength with increase of x. The variation of the relative intensities of the three bands in the long-wavelength region with x is shown in figure 4. The intensity of the 5300 Å band decreases with x. The intensity of the 5000 Å band increases first, reaches a maximum around $x = 0.05$ and then decreases. The intensity of the 4650 Å band becomes stronger when x increases from 0.10 to 0.14.

Table 1. The peak positions λ(Å) and the relative intensities I of the decomposed excitation bands of the photoconductivity of ZnS$_x$Se$_{1-x}$:Mn^{2-}.

x	0	0.01	0.02	0.05	0.10	0.14
λ	5313	5305	5284			
(I)	(24.0)	(20.5)	(5.0)			
λ		5000	5018	4988	5000	
(I)		(9.6)	(15.4)	(20.0)	(12.7)	
λ					4670	4598
(I)					(35.0)	(55.0)
λ	4657	4600	4556	4488	4430	4405
(I)	(100)	(100)	(100)	(100)	(100)	(100)

Figure 4. The relative intensity of the photoconductivities of different bands of $ZnS_xSe_{1-x}:Mn^{2+}$ versus x.

In figure 5 excitation spectra of $ZnS_xSe_{1-x}:Mn^{2+}$ are shown. Three characteristic excitation peaks located around 5300, 5000 and 4650 Å can be seen clearly. The monitored luminescence is at 5850 Å. The band width of the detected luminescence is 10 Å.

4. Discussion

In the photoconductivity excitation spectra of $ZnS_xSe_{1-x}:Mn^{2+}$ samples there are three bands besides the intrinsic band. From table 1 and figure 5 we find that the peak positions of these three bands coincide with peaks of the characteristic excitation bands of the Mn^{2+} luminescence. The excitation bands at 5300, 5000 and 4650 Å in figure 5 correspond to the transitions from $^6A_1$ to $^4T_1$, $^4T_2$ and ^4E of Mn^{2+} respectively. Therefore the three long-wavelength bands in table 1 must be related to the transitions from $^6A_1$ to $^4T_1$, $^4T_2$ and ^4E of Mn^{2+} in ZnS_xSe_{1-x}. This is also supported by the fact that the pure ZnS_xSe_{1-x}
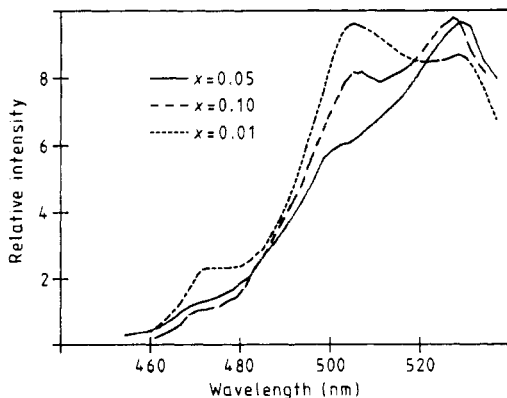

Figure 5. The excitation spectra of $ZnS_xSe_{1-x}:Mn^{2+}$ monitoring 5850 Å.

samples do not have these bands. As has been explained in previous work (Jiang Xueyin *et al* 1983), the electrons are excited from $^6A_1$ to the excited states ($^4T_1$, $^4T_2$ or ^4E) by photo-excitation, then thermally excited to the conduction band at room temperature and then produce photoconductivity. At liquid nitrogen temperature, the temperature is too low to allow thermal excitation to the conduction band, so the bands related to the excited states of Mn^{2+} do not appear.
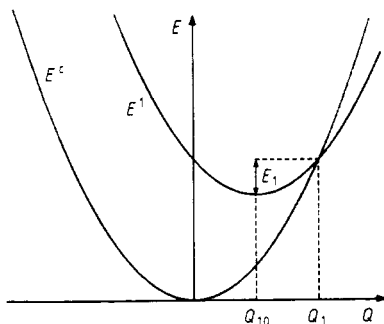

Figure 6. The configuration curves of the manganese centre in ZnS_xSe_{1-x}. For the notation, see the text.

In order to explain the variation of the relative intensity of photoconductivity shown in figure 4 and to deduce the positions of Mn^{2+} levels relative to the conduction band of ZnS_xSe_{1-x} we use the configuration model shown in figure 6. Q denotes the configuration coordinate characterising the configuration of the manganese centre (the Mn^{2+} ion with its environment) in ZnS_xSe_{1-x}. The configuration curve E^i represents the sum of the electronic energy of a electron in the ith excited state of Mn^{2+} and the elastic energy of the manganese centre. The configuration curve E^c represents the sum of the electronic energy of a electron in the conduction band and the elastic energy of the centre. This model is similar to the model used by Lang and co-workers (Lang and Logan 1977, Henry and Lang 1977).

The electrons excited to the state E^i will relax to the bottom of the curve E^i quickly, then will be thermally excited into the conduction band overcoming the barrier E_i and will then produce photoconductivity. When x increases, the curve E^i moves downwards relative to the curve E^c, and the barrier E_i becomes lower. When the minimum of the curve E^i falls on the curve E^c, the probability of thermal excitation to the conduction band reaches its maximum and so does the photoconductivity. When x increases further, the curve E^i moves downwards further, the point where the curves E^c and E^i cross is to the left of the minimum of the curve E^i, the barrier E^i increases with x, the probability of thermal excitation becomes smaller, and the photoconductivity becomes weaker. When the barrier is so high that thermal excitation is disallowed, the corresponding excitation band of photoconductivity will disappear. The behaviour of the three photo-conductivity bands shown in figure 4 can be explained by the above model.

When x increases from 0 to 0.02, the photoconductivity decreases: this implies that the configuration curve of $^4T_1$ moves downwards, the barrier becomes higher, and the photoconductivity becomes weaker. The intensity of the $^4T_2$ photoconductivity band increases with x for $x = 0.01$ and 0.02; this means that the point where the $^4T_2$ curve and

the curve E^c cross is to the right of the minimum of the $^4T_2$ curve. The photoconductivity reaches maximum around $x = 0.05$ and this indicates that the minimum of the $^4T_2$ curve approaches the curve E^c. When x increases further, the point where the $^4T_2$ curve and the curve E^c cross is to the left of the minimum of the $^4T_2$ curve, the barrier becomes higher and the photoconductivity becomes weaker. When $x = 0.10$ and 0.14, the point where the ^4E curve and the curve E^c cross is to the right of the minimum of the ^4E curve and the photoconductivity increases with x.

The parameters of the configuration curves E^i for different values of x can be deduced from the experimental data as follows.

When an electron is in the conduction band,

$$E^c = \tfrac{1}{2}kq^2.$$

When an electron is in $^4T_1$,

$$E^1 = E_{10} + \tfrac{1}{2}k_1(q - q_{10})^2.$$

When an electron is in $^4T_2$,

$$E^2 = E_{20} + \tfrac{1}{2}k_2(q - q_{20})^2.$$

Assume $k = k_1 = k_2$. Let $k^{1/2}q = Q$; then the above formulae have following forms:

$$E^c = \tfrac{1}{2}Q^2 \tag{1}$$

$$E^i = E_{i0} + \tfrac{1}{2}(Q - Q_{i0})^2 \qquad i = 1, 2. \tag{2}$$

When the curve E^c and the curve E^i cross at Q_i,

$$\tfrac{1}{2}Q_i^2 = E_{i0} + (Q_i - Q_{i0})^2. \tag{3}$$

Assuming E_{i0} varies linearly with x in the range $x = 0\text{--}0.10$,

$$E_{i0} = \tfrac{1}{2}Q_{i0}^2 - \alpha(x - x_{i0}) \qquad i = 1, 2 \tag{4}$$

where α and x_{i0} are constants.

From (4) and (3), we obtain

$$Q_i = Q_{i0} - (x - x_{i0})\alpha/Q_{i0} \tag{5}$$

$$E_i = \tfrac{1}{2}(Q_i - Q_{i0})^2 = \tfrac{1}{2}[(x - x_{i0})\alpha/Q_{i0}]^2. \tag{6}$$

The dynamical equation in the stationary case is

$$\mathrm{d}n_i/\mathrm{d}t = I_i - n_i f_{i0}\exp(-E_i/kT) - n_i F_i = 0 \tag{7}$$

where n_i represents the number of electrons in the excited state E^i, I_i is the excitation intensity from $^6A_1$ to E^i, f_i is the thermal excitation probability from E^i to E^c;

$$f_i = f_{i0}\exp(-E_i/kT).$$

F_i is the probability of radiative and/or non-radiative transitions from E^i. The electrons thermally excited to the conduction band will move away from the manganese centres quickly, so the probability of recapture of the electrons by the manganese centres is neglected.

From (7), we obtain

$$n_i = I_i/[f_{i0}\exp(-E_i/kT) + F_i]. \tag{8}$$

The photoconductivity

$$\sigma \propto n_i f_{i0} \exp(-E_i/kT).$$

That is

$$\sigma \propto \exp(-E_i/kT)/[\exp(-E_i/kT) + F_i/f_{i0}]. \tag{9}$$

E_i varies with x, so the photoconductivity varies with x. If

$$F_i \ll f_{i0} \exp(-E_i/kT)$$

the photoconductivity will not vary with x significantly. This is not the case for experimental results. Thus

$$F_i \gg f_{i0} \exp(-E_i/kT)$$

is a better approximation to the real case. Under this approximation

$$\sigma \propto \exp(-E_i/kT) = \llbracket \exp -\{[(x - x_{i0})/(2kT)^{1/2}]\alpha/Q_{i0}\}^2 \rrbracket \tag{10}$$

σ varies with x as a gaussian function.

For photoconductivity related to the $^4T_1$ state of Mn^{2+}, we know (table 1)

$$x = 0 \qquad\qquad \sigma = 24.0$$

$$x = 0.01 \qquad\qquad \sigma = 20.5$$

$$x = 0.02 \qquad\qquad \sigma = 5.0.$$

Fitting formula (10) to the data, we obtain

$$x_{10} = 0.0029 \qquad \alpha/Q_{10} = 15.4 \text{ eV}^{1/2}. \tag{11}$$

For photoconductivity related to $^4T_2$,

$$x = 0.01 \qquad\qquad \sigma = 9.6$$

$$x = 0.02 \qquad\qquad \sigma = 15.4$$

$$x = 0.05 \qquad\qquad \sigma = 20.0$$

$$x = 0.10 \qquad\qquad \sigma = 12.7.$$

Fitting experimental data, we obtain

$$x_{20} = 0.057 \qquad \alpha/Q_{20} = 4.23 \text{ eV}^{1/2}. \tag{12}$$

The energy difference between the zero-phonon lines of $^4T_1$ and $^4T_2$ of Mn^{2+} is 0.195 eV (Langer and Richter 1966). According to the definition given as formula (4),

$$\alpha = [0.195 - (\tfrac{1}{2}Q_{20}^2 - \tfrac{1}{2}Q_{10}^2)]/(x_{20} - x_{10}). \tag{13}$$

Using the data $x_{10} = 0.0029$, $x_{20} = 0.057$, $\alpha/Q_{10} = 15.4$ and $\alpha/Q_{20} = 4.23$, from (13) we have

$$\alpha = 1.895 \qquad Q_{10} = 0.123 \qquad Q_{20} = 0.448.$$

Now all the parameters determining the configuration curves for different values of x have been obtained. The calculated relative positions of the configuration curves and barrier heights at room temperature are summarised in table 2.

In previous work (Jiang Xueyin *et al* 1983), from the temperature behaviour of the photoconductivity the barrier height for thermal excitation from the $^4T_1$ state of Mn^{2+}

Table 2. The parameters Q_1, Q_2, E_{10}, E_{20} and barrier heights E_1, E_2 for the configuration curves of $ZnS_xSe_{1-x}:Mn^{2-}$.

x	Q_1 (eV$^{1/2}$)	Q_2 (eV$^{1/2}$)	E_1 (eV)	E_2 (eV)	E_{10} (eV)	E_{20} (eV)
0	0.168	0.689	0.001	0.029	0.013	0.208
0.01	0.0137	0.647	0.006	0.020	−0.006	0.189
0.02	−0.140	0.605	0.035	0.012	−0.025	0.171
0.05	−0.602	0.478	0.263	0.0004	−0.082	0.114
0.10	−1.372	0.266	1.118	0.017	−0.177	0.018

to the conduction band in ZnSe was determined to be about 0.054 eV. Using the parameters for the configuration curves obtained in this work, the barrier height for thermal excitation from E^1 to E^c can be derived and compared with the previous result.

The photoconductivity excitation spectra of ZnSe:Mn^{2+} at 293 and 77 K were measured. The peak of the intrinsic photoconductivity is at 4658 Å at 293 K, and 4420 Å at 77 K. Assuming a linear temperature dependence of the energy gap in the range of 77–293 K, the temperature coefficient of the energy gap is -6.6×10^{-4} eV K^{-1}. Grimmeiss *et al* (1976) found that the position of the ground state of Mn^{2+} relative to the valence band of ZnSe is independent of temperature. The relative positions between the ground state and the excited state of Mn^{2+} in ZnSe are also independent of the temperature, so the configuration curve E^c must move upwards relative to the configuration curve E^1 when the temperature decreases. The barrier height E_1 will vary with temperature. Here we give a few calculated values of E_1 for different temperatures:

$$E_1 = 0.043 \text{ eV} \qquad T = 230 \text{ K}$$

$$E_1 = 0.060 \text{ eV} \qquad T = 220 \text{ K}$$

$$E_1 = 0.103 \text{ eV} \qquad T = 200 \text{ K}$$

$$E_1 = 0.622 \text{ eV} \qquad T = 77 \text{ K}.$$

The previous value of 0.054 eV cannot be compared directly with the above results since in the previous work the temperature dependence of the barrier height was not taken into consideration. However, if we consider 0.054 eV to be the barrier height around the temperature where the photoconductivity reaches its maximum ($T \simeq 200$ K), the agreement is reasonable (see figure 7(a)).

The energy difference between the zero-phonon line and the maximum of the absorption band of ZnSe:Mn^{2+} is 0.105 eV for the transition $^6A_1$–$^4T_1$ and 0.052 eV for $^6A_1$–$^4T_2$ (Langer and Richter 1966). If the configuration coordinate of the minimum of the configuration curve of $^6A_1$ is taken as 0.7 eV$^{1/2}$ in our model, the calculated energy differences between the zero-phonon line and the maximum of the corresponding absorption band of ZnSe:Mn^{2-} are 0.166 eV for $^6A_1$–$^4T_1$ and 0.032 eV for $^6A_1$–$^4T_2$, which are not unacceptable.

If the configuration curve E^A of the ground state of the manganese centre in ZnSe and the configuration curve E^V of the manganese centre with an electron in the valence band are assumed to have the same curvature as the configuration curve E^c, the position of E^A relative to E^V can be found. The band gap of ZnSe at room temperature is 2.66 eV. The coordinate of the minimum of E^A is taken as 0.7 eV$^{1/2}$. The zero-phonon line of the transition from $^6A_1$ to $^4T_1$ is at 2.23 eV (Langer and Richter 1966). The calculated
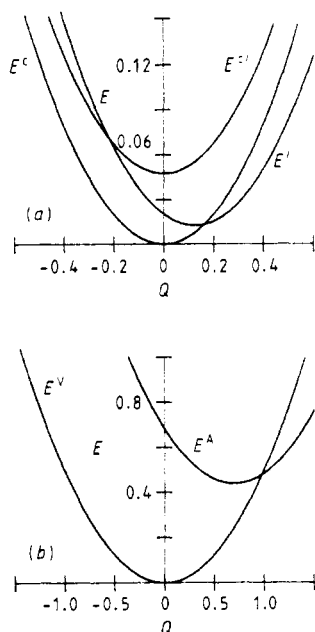
Figure 7. The configuration curves of the manganese centre in ZnSe. E^c represents the position of the configuration curve E^c at 220 K. See the text for the other notation.

coordinate of the point where E^A and E^V cross is $0.98\,\text{eV}$[1,2] (see figure 7(b)). The calculated barrier height for thermal excitation from the valence band to the ground state is 0.48 eV. The barrier height for thermal excitation from E^A to E^V is 0.039 eV. The minimum of the configuration curve ${}^6A_1$ is 0.44 eV above that of the valence band. The threshold energy E_0 for optical excitation from E^V to E^A is 0.69 eV. This value is very close to the optical threshold energy 0.68 eV from the valence band to the ground state of Mn²⁺ in ZnSe reported by Grimmeiss *et al* (1976).

5. Conclusion

The photoconductivity peaks related to the excited states ${}^4T_1$, ${}^4T_2$ and ${}^4E$ of Mn²⁺ in ZnS_xSe_{1-x} ($x = 0, 0.01, 0.02, 0.05, 0.10, 0.14$) have been found. Their relative intensities vary with x. The positions of the energy states of Mn²⁺ in ZnS_xSe_{1-x} relative to the conduction band were determined systematically for the first time by fitting experimental data to the configuration model. Comparing the calculated results with some independent experimental data shows that our model is acceptable. The results show that ZnS_xSe_{1-x}:Mn²⁺ is a valuable system for deep-level study in which the positions of the energy states of Mn²⁺ relative to the conduction band and barrier height for thermal excitation of the photoconductivity can be adjusted by x.

References

Braun S, Grimmeiss H G and Allen J W 1972 *Phys. Status Solidi* a **14** 527

Grimmeiss H G, Ovren C and Allen J W 1976 *J. Appl. Phys.* **47** 1103

Henry C H and Lang D V 1977 *Phys. Rev.* B **15** 989

Jiang Xueyin, Yu Jiaqi, Yang Baojun, Feng Shufen and Hai Ying 1983 *Luminescence and Display Devices* vol 1, p 1 (in chinese)

Jones G and Woods J 1973 *J. Phys. D: Appl. Phys.* **6** 1640

Lang D V and Logan R A 1977 *Phys. Rev. Lett.* **39** 635

Langer D W and Richter H J 1966 *Phys. Rev.* **146** 554

Ozsan M E and Woods J W 1975 *Solid State Electron.* **18** 519