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# The pressure dependence of the intrainpurity absorption and the charge transfer process of ZnS:Ni and ZnSe:Ni

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**Abstract.** The absorption spectra of ZnS:Ni and ZnSe:Ni were measured at 100 K under hydrostatic pressure up to 10 GPa. Two kinds of optical transition were investigated: (i) the d–d transitions between crystal field levels of Ni<sup>2+</sup> in the tetrahedral field of the host lattice and (ii) a charge transfer band that occurs when an electron is transferred from the valence band to the Ni<sup>2+</sup> ion. The pressure dependence of the crystal field parameter  $Dq$  and of the Racah parameter  $B$  were determined and a revised assignment of the d–d transitions was obtained. The charge transfer can be considered as a deep-acceptor transition. In this case the Ni acceptor level may be used as an energy reference, which enabled us to determine the hydrostatic deformation potential of the valence band.

## 1. Introduction

This work is concerned with the optical spectra of Ni<sup>2+</sup> in ZnS and ZnSe. The Ni<sup>2+</sup> ion has a 3d<sup>8</sup> configuration and substitutes the metal site in II–VI semiconductors as do all of the 3d transition metal ions, which usually act as deep impurities. Investigations of these impurities under hydrostatic pressure are interesting for two reasons. (i) There is the possibility to identify the observed internal d–d transitions by their pressure shifts within the framework of crystal field theory. (ii) Transition metal impurities form deep levels, which lie in the band gap and may be used as energy references.

This surprising property was first noted by Langer *et al* [1] and Caldas *et al* [2], who noticed that the sequence of deep acceptor or deep donor levels remains constant within a family of isovalent semiconductors. Based on this observation it has been proposed that these levels may serve as a probe in the determination of absolute pressure coefficients of the conduction and valence band edges [1, 3]. This information is especially useful to stimulate an experiment with Ni<sup>2+</sup> in large-gap II–VI semiconductors that allows a separate determination of the conduction and the valence band pressure shift, whereas in a high-pressure measurement of undoped semiconductors only the sum of the above mentioned contributions is accessible.

ZnS and ZnSe have been chosen by us not only because of their transparency in the spectral range of the Ni<sup>2+</sup> transitions but also because of a renewed interest in these substances as active material for blue LEDs and injection lasers. We measured the transmission spectra of ZnS:Ni and ZnSe:Ni in a diamond anvil cell at 100 K up to 10 GPa. The experimental details are given in section 2. In subsection 3.1 the observed internal transitions are compared with a crystal field model [4]; in 3.2 the pressure shift of the charge transfer threshold is presented and from these data the absolute deformation potentials of the valence and conduction bands are determined.

## 2. Experiment

Optical absorption measurements under pressure up to 10 GPa were performed in a gasketed diamond anvil cell [5]. Details of the set-up have been published elsewhere [6]. A 4:1 methanol:ethanol mixture was used as pressure transmitting medium. The pressure was measured by the ruby fluorescence technique [7]. Polycrystalline ZnS:Ni and ZnSe:Ni samples were grown by chemical transport and were kindly provided to us by Professor W Giriat of the Instituto Venezolano de Investigaciones Científicas, Caracas, Venezuela. The ZnSe crystals are of a pure zincblende structure whereas the ZnS samples have a mixed structure of zincblende and wurtzite. The crystals, containing an Ni concentration between 1% and 5%, were polished to thicknesses between 20  $\mu\text{m}$  and 60  $\mu\text{m}$ . The absorption spectra were measured at 100 K in a spectral energy range from 1 eV to 2.8 eV.

## 3. Results and discussion

### 3.1. Intraimpurity absorption

Figures 1 and 2 show the absorption spectra for two different pressure values. The absorption pattern of the d-d transitions is found at the low-energy side of the spectra. The steep absorption threshold at the high-energy side is due to a charge transfer process and will be discussed below.

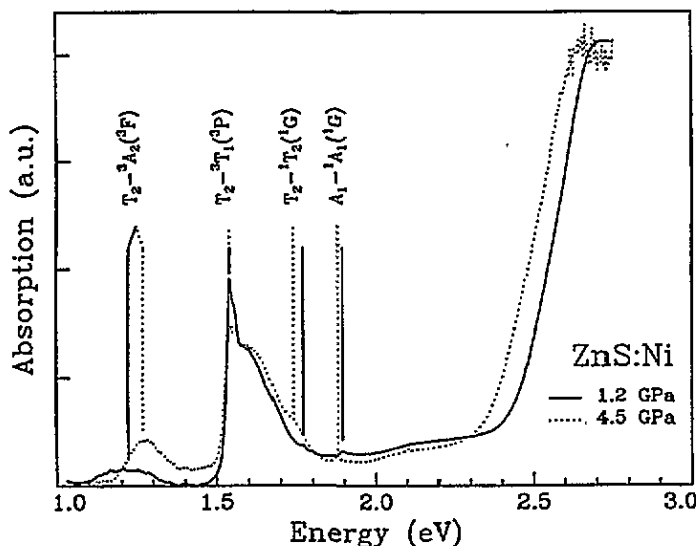


Figure 1. The intraimpurity absorption due to  $\text{Ni}^{2+}$  in ZnS at  $T = 100$  K and two different pressures, together with the energy positions due to the best fit to the crystal field model.

In figure 3 the splitting of the free ion states of the  $d^8$  configuration is shown under the action of the  $T_d$  crystal field without and with spin-orbit interaction together with the transitions observed in this work. The energy levels have been calculated by diagonalizing the weak-field energy matrices following the work of Liehr and Ballhausen [11]. The Racah parameter  $B$  [12] and crystal field parameter  $Dq$  that give a best fit of the observed

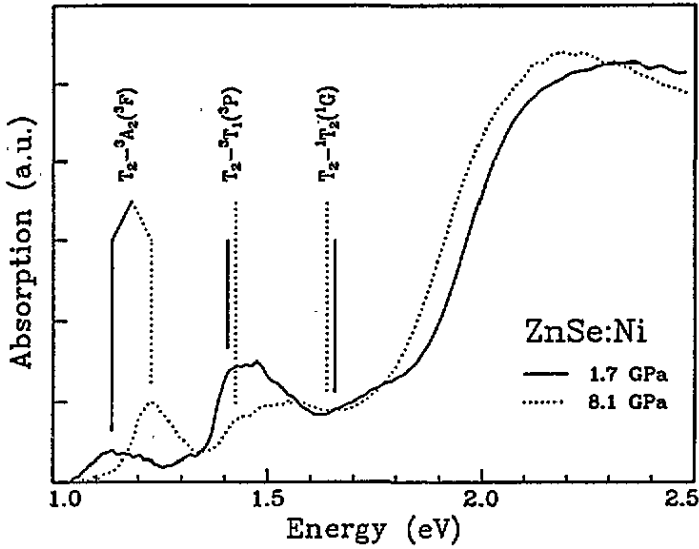


Figure 2. The intrapurity absorption due to Ni<sup>2+</sup> in ZnSe at T = 100 K and two different pressures, together with the energy positions due to the best fit to the crystal field model.

transitions for vanishing pressure are given in table 3 below. For the spin-orbit parameter  $\lambda$  we used a value of  $250 \text{ cm}^{-1}$  [8] and a B:C ratio of 35:9 [11]. The positions of the calculated levels are marked in figures 1 and 2. The dominant structure is due to the transition from the  $A_1-^3T_1(^3F)$  ground state to the  $^3T_1(^3P)$  excited states (see also figure 3). Here the low-energy peak has its origin in the  $T_2$  spin-orbit level with E,  $T_1$  and  $A_1$  levels and phonon replica at the high-energy side of the peak. The latter could not be resolved at T = 100 K, therefore we use from this band only the first peak to fit the crystal field model.

Table 1. The hydrostatic pressure shift of the intrapurity absorption in ZnS:Ni at T = 100 K.

Transition	Energy (eV)	Pressure coefficient (meV GPa <sup>-1</sup> )
$A_1-^3T_1(F) \Rightarrow A_1-^1A_1(^1G)$	$1.90 \pm 0.02^a$	$-4.4 \pm 0.5^a$
$^3T_1(F) \Rightarrow ^1T_2(^1G)$	$1.901^b$	$-4.84 \pm 0.1^b$
$A_1-^3T_1(F) \Rightarrow T_2-^1T_2(^1G)$	$1.78 \pm 0.03^a$	$-8.7 \pm 0.7^a$
$A_1-^3T_1(F) \Rightarrow T_2-^3T_1(^3P)$	$1.540 \pm 0.002^a$	$-0.1 \pm 0.3^a$
	$1.533^b$	$-0.26 \pm 0.01^b$
$A_1-^3T_1(F) \Rightarrow T_2-^3A_2(^3F)$	$1.19 \pm 0.03^a$	$+15.7 \pm 0.6^a$
	$1.080^b$	$+12.8 \pm 0.4^b$

<sup>a</sup> Present work.

<sup>b</sup> Results at 5 K, up to 1.2 GPa [9].

From figures 1 and 2 it is evident that under hydrostatic pressure a shift of the d-d transitions can be readily observed and is in most cases negative. The obtained pressure coefficients are given in tables 1 and 2 together with values from Wasik *et al* [9,10] for comparison. The values of this work obtained for ZnS agree well within the experimental errors with those of [9] with the exception of the low-energy band at 1.19 eV. For ZnSe our data are mostly at variance with those of [10]. The deviation may be due to the fact that the pressure range used in [9] and [10] was limited to 1.2 GPa whereas in the present work

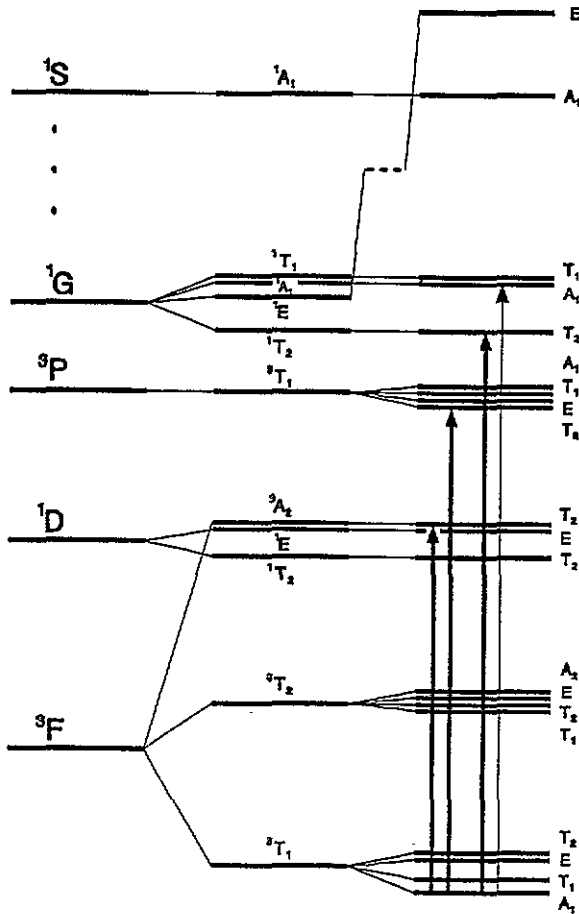
free ion +  $T_d$  crystal field + spin-orbit coupling

Figure 3. A schematic energy level diagram for the  $d^8$  configuration in a crystal field of  $T_d$  symmetry, together with the observed transitions ( $\uparrow$ ) in ZnS:Ni and ZnSe:Ni. The bold arrows denote the allowed and the thin arrow the forbidden transitions [8].

Table 2. The hydrostatic pressure shift of the intraimpurity absorption in ZnSe:Ni at  $T = 100$  K.

Transition	Energy (eV)	Pressure coefficient (meV GPa $^{-1}$ )
$A_1-{}^3T_1(F) \Rightarrow T_2-{}^1T_2({}^1G)$	$1.660 \pm 0.01^a$	$-3.0 \pm 0.4^a$
	$1.660^b$	$-5.7 \pm 0.1^b$
$A_1-{}^3T_1(F) \Rightarrow T_2-{}^3T_1({}^3P)$	$1.400 \pm 0.01^a$	$+3.8 \pm 0.4^a$
	$1.390^b$	$-2.85 \pm 0.01^b$
$A_1-{}^3T_1(F) \Rightarrow T_2-{}^3A_2({}^3F)$	$1.10 \pm 0.03^a$	$+19.7 \pm 0.6^a$
	$1.100^b$	$+9.1 \pm 0.4^b$

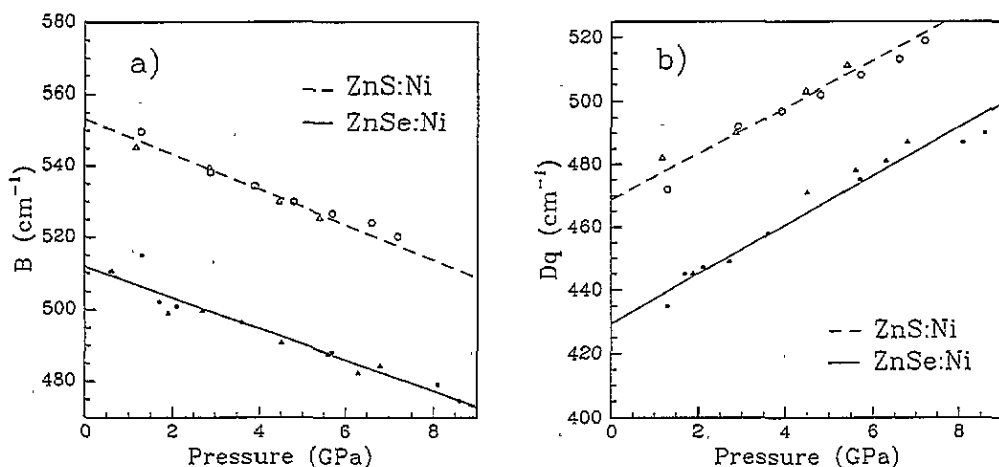
<sup>a</sup> Present work.

<sup>b</sup> Results at 10 K, up to 1.1 GPa [10].

the maximum pressure was about 10 GPa. This pressure is sufficiently high to decouple the three mixed states under the 1.2 eV band,  $T_2-{}^1T_2({}^1D)$ ,  $E-{}^1T_2({}^1D)$  and  $T_2-{}^3A_2({}^3F)$ , and only the allowed transition  $T_2-{}^3A_2({}^3F)$  is left strong enough to be observed. In ZnSe the high-energy wing of this band almost coincides above 5 GPa with the  $T_2-{}^3T_1({}^3P)$  peak, which is a result of the different pressure coefficients of these transitions.

**Table 3.** The variation of the Racah parameter  $B$  and the crystal field parameter  $Dq$  with hydrostatic pressure.

Material, parameter	Value ( $\text{cm}^{-1}$ )	Pressure coefficient ( $\text{cm}^{-1} \text{GPa}^{-1}$ )
ZnS:Ni, $Dq$	469 <sup>a</sup>	$+7.4 \pm 0.7^a$ $+7.42^b$
ZnS:Ni, $B$	554 <sup>a</sup>	$-5.0 \pm 0.4^a$ $-5.21^b$
ZnSe:Ni, $Dq$	429 <sup>a</sup>	$+7.8 \pm 0.5^a$ $+7.8^c$
ZnSe:Ni, $B$	512 <sup>a</sup>	$-4.3 \pm 0.3^a$ $-5.8^c$

<sup>a</sup> Present work.<sup>b</sup> Results at 5 K, up to 1.2 GPa [9].<sup>c</sup> Results at 10 K, up to 1.1 GPa [10].**Figure 4.** The variation of (a)  $B$  (the Racah parameter) and (b)  $Dq$  (the crystal field parameter) with pressure. The different symbols denote different samples.

In the next step the parameters of the crystal field theory are obtained by a best fit of the d-d transitions at various pressures. For this purpose the spin-orbit coupling  $\lambda$  and the ratio of the Racah parameter  $B:C$  are kept constant. Thus the pressure dependence is completely described by  $B(P)$  and  $Dq(P)$  given in table 3. The decrease of  $B$  with increasing pressure may be due to the increasing covalency of the ligand-metal bond [2]. Furthermore the observed increase of  $Dq$  is usually described by the variation of the crystal field with the interatomic distance [13]:

$$Dq = \frac{1}{6}(q/R^5)\bar{r}^4 \quad (1)$$

where  $\bar{r}^4$  is the radial integral,  $q$  the effective charge of the surrounding host atoms and  $R$  the impurity-host atom distance. The validity of this relation for  $Dq$  in ZnS:Ni and ZnSe:Ni seems to be well verified as can be seen in figure 5(a) and (b).

The present measurements enable us to reassign the observed crystal field transitions according to the energy matrix used. There is no agreement in the literature on whether

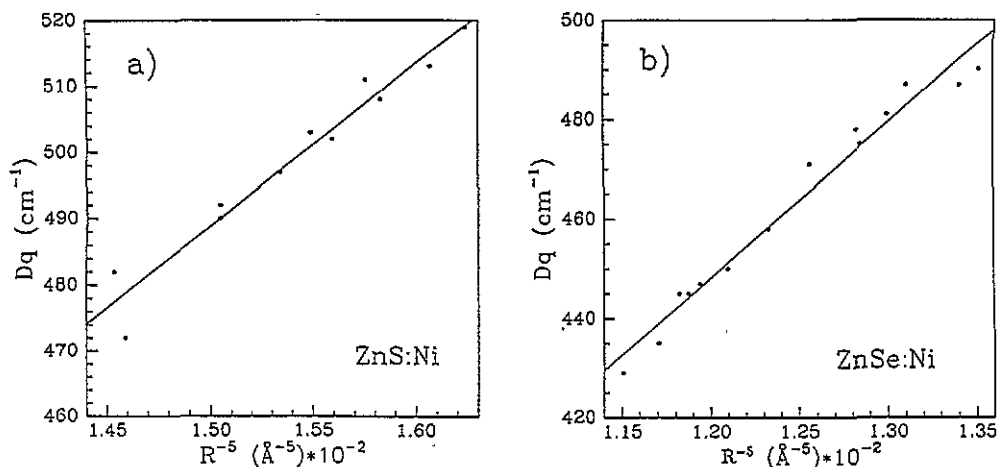
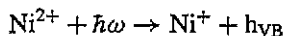


Figure 5. The variation of  $Dq$  with the interatomic distance in (a) ZnS and (b) ZnSe.

the  $T_2-{}^3A_2({}^3F)$  level lies above [14–16] or below [8, 17, 18] the levels due to the atomic  ${}^1D$  level. In the last mentioned case the observations lead to an increase of  $B$  and  $Dq$  with pressure. This would be in contradiction to (1) and experimental results obtained with other substances [19, 20], which show a decrease of  $B$  but an increase in  $Dq$  with pressure. Assuming the level sequence of the first case we obtain the correct pressure dependence of  $B$  and  $Dq$ . Moreover the deviation of the experimental level positions from the fit is in that case smaller by a factor of 50.

### 3.2. Charge transfer

In order to derive the absolute pressure shifts of the band edges we have investigated the pressure dependence of the onset of charge transfer from the valence band to the Ni ion. The strong absorption near 2.5 eV and 2.0 eV in figures 1 and 2 respectively is interpreted in terms of the following process:



where  $h_{VB}$  denotes a hole in the valence band [24].

According to Masut and Penchina [21] the spectral dependence near the absorption threshold is given by

$$\alpha(\hbar\omega) \propto (\hbar\omega - E_i)^\beta$$

$$\beta = \frac{1}{2} \text{ for allowed transitions}$$

$$\beta = \frac{3}{2} \text{ for forbidden transitions.}$$

The observed transitions are allowed since the initial state is a p-like valence band and the final states are d-like transition metal states. This assignment is confirmed by the sharp onset of the absorption and by a sufficiently good fit with  $\beta = \frac{1}{2}$  as shown in figure 6. The experimental pressure coefficients of the threshold energy obtained from the spectra shown in figure 6 are given in table 4 together with values published by Wasik *et al* [9, 10]. The latter authors used samples with low Ni concentration and observed at 10 K the zero-phonon line of the charge transfer band, which they used to determine the pressure coefficient. Their

**Table 4.** The hydrostatic pressure shift of the charge transfer threshold in ZnS:Ni and ZnSe:Ni.

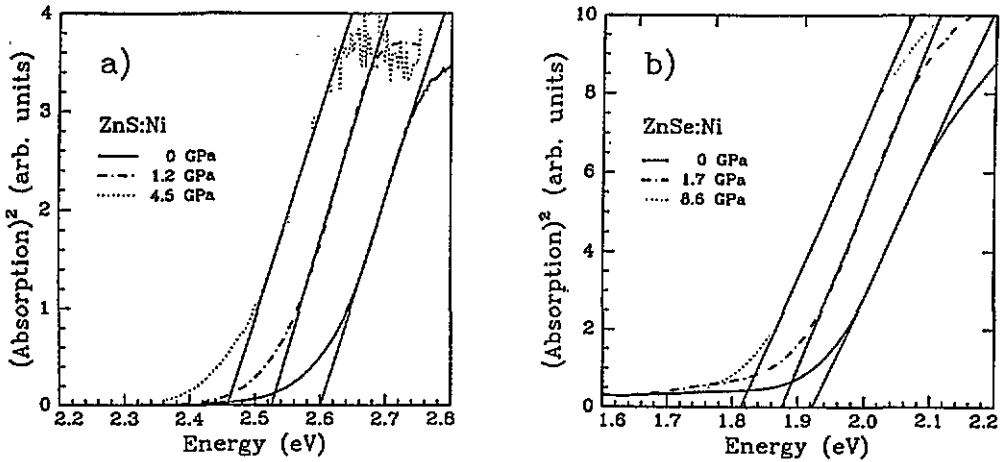
$Ni^{2+}h\nu \rightarrow Ni^+ + h\nu_B$	Energy	Pressure coefficient (meV GPa <sup>-1</sup> )
ZnS:Ni	2.46 ± 0.05 <sup>a</sup>	-23.5 ± 0.8 <sup>a</sup>
	2.48 <sup>b</sup>	-12.8 <sup>b</sup>
	2.458 <sup>c</sup>	
ZnSe:Ni	1.94 ± 0.01 <sup>d</sup>	-13.3 ± 0.8 <sup>a</sup>
	1.85 <sup>d</sup>	-13.0 ± 0.4 <sup>d</sup>
	1.855 <sup>c</sup>	

<sup>a</sup> Present work.

<sup>b</sup> Results at 5 K, up to 1.2 GPa [9].

<sup>c</sup> Results at 77 K for ZnSe and 6 K for ZnS [24].

<sup>d</sup> Results at 10 K, up to 1.1 GPa [10].



**Figure 6.** The pressure shift of the charge transfer threshold of Ni<sup>2+</sup> in (a) ZnS and (b) ZnSe.

results for ZnSe are in good agreement with the values from this work. However there is disagreement for ZnS, for reasons that are not yet clear.

Knowing the Ni charge transfer threshold we have a reference level that enables us e.g. to determine valence band offsets. As an example we calculate the valence band offset  $\Delta_v$  of ZnS/ZnSe to be  $0.52 \pm 0.06$  eV at zero pressure. This is in good agreement with the value  $\Delta_v = 0.56$  eV given by Langer *et al* [1].

**Table 5.** The deformation potentials of the charge transfer threshold in ZnS:Ni and ZnSe:Ni and of the band gap in ZnS and ZnSe and calculated from these, the absolute deformation potentials of the valence and conduction band ( $a_v, a_c$ ) of ZnS and ZnSe (with  $a = a_c - a_v$ ).

	ZnS:Ni	ZnSe:Ni	ZnS	ZnSe
$a$ (eV)	1.8 ± 0.1 <sup>a</sup>	1.0 ± 0.1 <sup>a</sup> 1.4 ± 0.2 [10]	-5.0 [23]	-4.9 ± 0.2 [25]
$a_v$ (eV)	—	—	-1.8 ± 0.1	-1.0 ± 0.1
$a_c$ (eV)	—	—	-6.8 ± 0.1	-5.9 ± 0.3

<sup>a</sup> Present work.

The deformation potentials of the Ni threshold in ZnS and ZnSe given in table 5 are



calculated using the Murnaghan equation for the volume–pressure relation

$$\varepsilon = (1 + (B'_0/B_0)P)^{-(1/3)B'_0} - 1 \quad (2)$$

with  $B_0 = 62.4$  GPa,  $B'_0 = 4.77$  for ZnSe [22] and  $B_0 = 75$  GPa,  $B'_0 = 4$  for ZnS [23]. Under the 'reference level assumption' we use these values to determine the absolute deformation potential of the valence band  $a_v$  (see table 5). Since the band gap deformation potentials of ZnSe and ZnS are well known [23, 25] we can use  $a_v$  to calculate the deformation potentials of the conduction band  $a_c$ , which are also listed in table 5.

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## References

- [1] Langer J M, Delure C, Lannoo M and Heinrich H 1988 *Phys. Rev. B* **38** 7723
- [2] Caldas M J, Fazzio A and Zunger A 1984 *Appl. Phys. Lett.* **45** 671
- [3] Nolte D D, Walúkiwicz W and Haller E E 1987 *Phys. Rev. Lett.* **59** 501
- [4] Tanabe Y and Sugano S 1954 *J. Phys. Soc. Japan* **9** 753, 766
- [5] Hawke S, Syassen K and Holzapfel W J 1974 *Rev. Sci. Instrum.* **45** 1548
- [6] Lindner M, Schötz G F, Link P, Wagner H P, Kuhn W and Gebhardt W 1992 *J. Phys.: Condens. Matter* **4** 6401
- [7] Mao H K and Bell P M 1978 *Science* **200** 1145  
Noack R A and Holzapfel W B 1979 *Proc. 6th AIRAPT Int. High Pressure Conf. (Boulder, CO, 1977) High Pressure Science and Technology* vol 1, ed K D Timmerhaus and M S Barber (New York: Plenum) p 748
- [8] Weakliem H A 1962 *J. Chem. Phys.* **36** 2117
- [9] Wasik D, Liro Z and Baj M 1988 *Proc. 19th Int. Conf. on Physics of Semiconductors (Warsaw, 1988)* ed W Zawadzki (Warsaw: Inst. Phys.) p 1107
- [10] Wasik D, Liro Z and Baj M 1990 *J. Cryst. Growth* **101** 466
- [11] Liehr A D and Ballhausen C J 1959 *Ann. Phys., NY* **6** 134
- [12] Racah G 1942 *Phys. Rev.* **62** 438
- [13] Schläfer H L and Gliemann G 1969 *Basic Principles of Ligand Field Theory* (London: Wiley Interscience)
- [14] Bouhelal A and Albert J P 1989 *Solid State Commun.* **69** 713
- [15] Fazzio A, Caldas M and Zunger A 1984 *Phys. Rev. B* **30** 3430
- [16] Roussos G and Schulz H-J 1980 *Phys. Status Solidi* b **100** 577
- [17] Bishop S G, Dean P J, Porteous P and Robbins D J 1980 *J. Phys. C: Solid State Phys.* **13** 1331
- [18] Wray E M and Allen J W 1971 *J. Phys. C: Solid State Phys.* **4** 512
- [19] Zahner J C and Drickamer H G 1961 *J. Chem. Phys.* **35** 1483
- [20] Stephens D R and Drickamer H G 1961 *J. Chem. Phys.* **35** 429
- [21] Masut R and Penchina C M 1985 *Phys. Status Solidi* b **130** 737
- [22] Ves S, Strössner K, Christensen N E, Chul Koo Kim and Cardona M 1985 *Solid State Commun.* **56** 479
- [23] Ves S, Schwarz U, Christensen N E, Syassen K and Cardona M 1990 *Phys. Rev. B* **42** 9113
- [24] Noras J M and Allen J W 1980 *J. Phys. C: Solid State Phys.* **13** 3511
- [25] Schötz G F, Griebel E, Stanzl H, Reisinger T and Gebhardt W 1994 *Proc. European Workshop on II–VI Semiconductors (Linz, Austria, 1994) Materials Science Forum* (Switzerland: Trans. Tech.) at press