



Bound and free excitons in ZnO. Optical selection rules in the absence and presence of time reversal symmetry

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ABSTRACT

The correlation between ionized donor bound exciton recombinations and neutral donor bound exciton recombinations in ZnO has been investigated. The experimental data obtained by means of magneto-photoluminescence (MPL) concerning charge state and localization energies of ionized and neutral donor bound excitons are in good agreement with theoretical predictions. The optical selection rules in absence and presence of time reversal symmetry (TRS) are investigated. It is shown that the inclusion of extra degeneracy due to TRS reveals a number of new states of the same symmetries and essentially does not change the existing optical selection rules.

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1. Neutral and ionized donor bound excitons

Lithium-doped ZnO epilayers were grown by chemical vapor deposition on ZnO substrates. Photoluminescence (PL) and magneto-photoluminescence (MPL) measurements were performed using a 325 nm HeCd laser. Fig. 1 displays the PL at 4.2 K in the energetic range of the free and bound excitons. The most prominent excitonic transition lines are the I_9 (3.3567 eV), I_8 (3.3598 eV), I_{6a} (3.3604 eV), I_2 (3.3674 eV), I_1 (3.3720 eV), and I_0 (3.3726 eV).

Previous studies have shown that I_9 , I_8 , and I_{6a} are neutral exciton complexes bound to an indium [1], gallium [2], and aluminum impurity, respectively [3]. These lines are accompanied by the higher energetic lines I_2 , I_1 , and I_0 [4]. The neutral bound exciton line I_9 is correlated to I_2 , I_8-I_1 , and $I_{6a}-I_0$. In fact, all investigated samples exhibit only I_0-I_2 excitons if the related excitons $I_{6a}-I_9$ are present as well. Due to a similar scaling in intensity and energetic position, it is likely that these correlated pairs of transition lines are excitons bound to an impurity of the same chemical identity but in a different charge state. Consequently, we attribute I_0 , I_1 , and I_2 to ionized donor bound excitons related to Al, Ga, and In impurities, respectively. Concerning the I_1 complex, this correlation is in agreement with the data published by Johnston et al. [2], who reported a simultaneous decrease in the I_8 and I_1 intensity for ZnO crystals doped with a radioactive Ga isotope. The various bound exciton complexes with

their localization energies and suggested chemical identities are summarized in Table 1.

The charge states of the bound exciton complexes are investigated by MPL spectroscopy. Excitons bound to ionized impurities can be distinguished from those bound to neutral impurities by a nonlinear splitting of energy levels in the magnetic field perpendicular to the c -axis of the crystal, while excitons bound to neutral impurities exhibit a linear splitting behavior for $\mathbf{B} \perp \mathbf{c}$ [5]. For ionized bound excitons at low magnetic fields, only a high energy Zeeman component, resulting from a Γ_5 state is visible, whereas the low energy component, originating from Γ_1 to Γ_6 transition is forbidden by selection rules (SRs). However, for larger magnetic fields, the SRs can be relaxed due to a spin–spin interaction of Γ_5 states with anti-parallel spin, mixed with Γ_6 states with parallel spin, thus allowing the appearance of a new line associated with the Γ_6 state. The extrapolation of the peak positions to $B = 0$ T reveals the presence of the zero-field splitting, ascribed to the spin–spin interaction energy. Such an interaction cannot occur in transition lines originating from excitons bound to neutral impurities, since the spin of the two equal particles are anti-parallel.

Evidently, we observe a linear Zeeman splitting for the $I_{6a}-I_8$ lines, whereas this is not the case for the bound excitons I_0 and I_1 (Fig. 2). Furthermore, an additional low energy transition due to the zero-field splitting appears for I_0 and I_1 if a magnetic field is applied. Similar results (not shown) were obtained for I_9 (linear Zeeman splitting) and I_2 (zero-field splitting) in accordance with the previously published measurements [6]. Consequently, following the previous discussion, the transition lines $I_{6a}-I_9$ originate from recombinations of neutral bound excitons, whereas I_0-I_2 are related to ionized bound exciton complexes.

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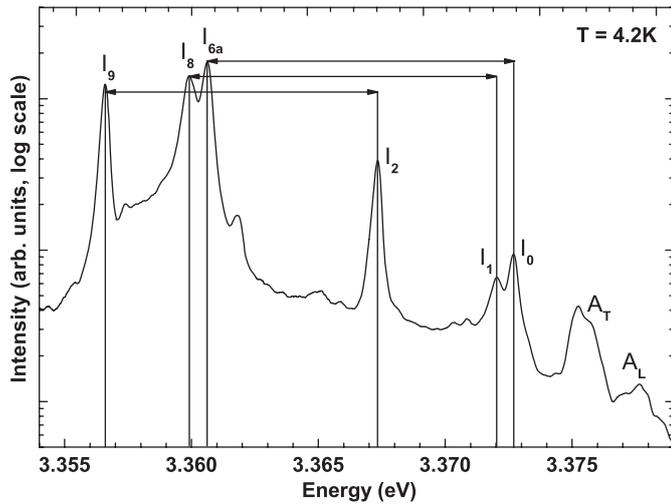


Fig. 1. PL spectra of lithium-doped high quality ZnO grown by CVD at a temperature of 4.2 K.

Table 1
Bound exciton complexes in ZnO

Line	E (eV)	E_b (meV)	Complex	Chem. element
I_9	3.3567	19.2	D^0X	In
I_8	3.3598	16.1	D^0X	Ga
I_{6a}	3.3604	15.5	D^0X	Al
I_2	3.3674	8.5	D^+X	In
I_1	3.3718	4.1	D^+X	Ga
I_0	3.3726	3.3	D^+X	Al

Energetic positions are given for $T = 4.2$ K.

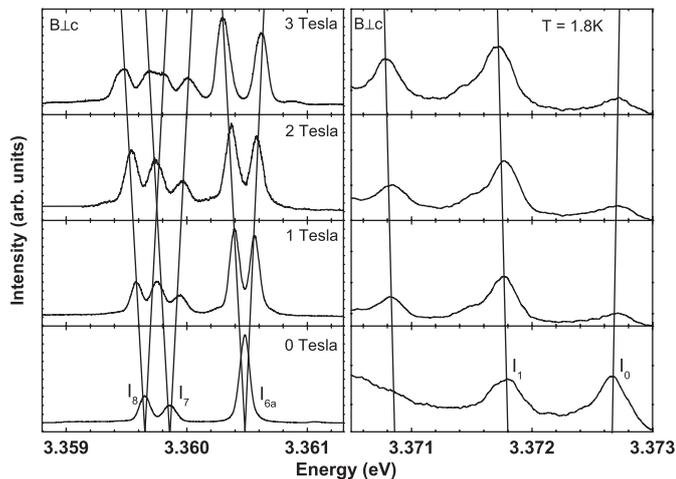


Fig. 2. Zeeman splitting of neutral and ionized donor bound excitons for magnetic fields of 0–3 T. Spectra are taken at 1.8 K in Voigt geometry ($\vec{B} \perp \vec{c}$).

2. Band structure and SRs for optical transitions in the absence and presence of time reversal symmetry

Large magnetic fields and high spectral resolutions better than 50–100 μeV reveal the presence of additional transition lines due to the lifting of degeneracy [7]. The new transitions are related to the absorption and emission of free and bound excitons, which depend on the structure and symmetry of the conduction band (CB) and valence band (VB). In order to understand the origin of

the optical transitions, we recall and modify the theory of band structures and SRs for wurtzite compounds with the C_{6v}^4 space group. Possible reason for additional transition lines could be related to excited states, non-zero hole g -values, hyperfine structure splittings, or time reversal symmetry (TRS) splittings. The following theoretical discussion intends to clarify, if the inclusion of TRS in the group theoretical consideration can explain the additional degeneracy and optical transitions.

2.1. Band structure

The band structure of wurtzite compounds has been investigated by many authors [8,9]. However, to our best knowledge the effect of TRS has not been considered. Disregarding the spin-orbit (S–O) interaction, crystalline field (CF) and TRS effect, the free electrons occupy S-like CB states and free holes P (P_x, P_y, P_z) VB states. The S-like states transform according to irreducible representation (irrp) Γ_1^c of the C_{6v} -ZnO point group, while the P (P_x, P_y, P_z) hydrogenic-like orbitals transform like X, Y, Z according to the so-called vector representation $V(x, y, z)$.

The CF splits the P_x, P_y, P_z states into P_x, P_y ($\Gamma_5(x, y)$) and P_z ($\Gamma_1(z)$) states. The vector representation for ZnO is reducible to Γ_1 and Γ_5 irrps $V = \Gamma_1(z) \oplus \Gamma_5(x, y)$.

The inclusion of the S–O interaction results in further splittings: $\Gamma_1^c \otimes D_{1/2} = \Gamma_7^c$, $\Gamma_5^v \otimes D_{1/2} = \Gamma_7^v \oplus \Gamma_9^v$, and $\Gamma_1^v \otimes D_{1/2} = \Gamma_7^v$. The free electrons in the CB and holes in VBs are classified according to double-valued irrps [10].

2.2. The effect of TRS on band structure and classification of states

Replacing t by $-t$ and taking the complex conjugate of any time-dependent Schrödinger equation we obtain $\Psi_i^*(\vec{r}, -t)$ wave functions which are also eigenfunctions of \hat{H}_{Sch} together with the $\Psi_i(\vec{r}, t)$. The Ψ_i are the basis of the D irrp of the group of \hat{H}_{Sch} while Ψ_i^* are the basis of D^* . When D and D^* are complex [11] the state of a system (energy term) will be classified by the joint $D \oplus D^*$ irrps. Clearly, the degeneracy of a state increases twice. In order to determine whether or not the TRS is present in a system, one has to find all complex irrps of a symmetry group of a Hamiltonian. Fröbenius and Schur [12] showed that it is sufficient to know only the characters of irrps to determine whether a representation (rep) is real or complex. The characters of the 32 crystallographic point groups and 230 space groups are readily available in CDML tables [13]. We have tested all irrps of the C_{6v} -ZnO group. The following irrps are TRS degenerate:

Single-valued irrps for classification of spinless particle states (like phonons): $A_{1,2,3,4,5,6}$, $\Delta_{1,2,3,4,5,6}$, $H_{1,2}$, $L_{1,2,3,4}$, $U_{1,2,3,4}$, $P_{1,2,3}$, and $S_{1,2}$ of high symmetry points.

Double-valued irrps for particles with $S = \frac{1}{2}, \frac{3}{2}, \dots$ (spinors): $\Gamma_{6,7,8}$ of point and space groups. The double-valued irrps of the 32 crystallographic point groups and 230 space groups are normally complex and therefore TR degenerated. Consequently, the states of free electrons and holes at $\mathbf{k} = \mathbf{0}$ in ZnO suppose to be classified by joint irrps: $\Gamma_7^c \oplus (\Gamma_7^c)^*$, $\Gamma_9^v \oplus (\Gamma_9^v)^*$, and $\Gamma_7^v \oplus (\Gamma_7^v)^*$. Fig. 3 displays the effect of TRS on the band structure.

2.3. SRs for optical transitions in wurtzite structure in the absence of TRS

In the absence of accidental degeneracy and TRS, the matrix elements of a perturbation \hat{f} between CB and VB states is of the form: $\int (\Psi_i^c)^* \hat{f} \varphi_j^v d\vec{r}$, which is non-zero when the corresponding Kronecker product $\Gamma^c \otimes D^f \otimes \Gamma^v$ contains the unit rep normally denoted as Γ_1 or A_1 [13].

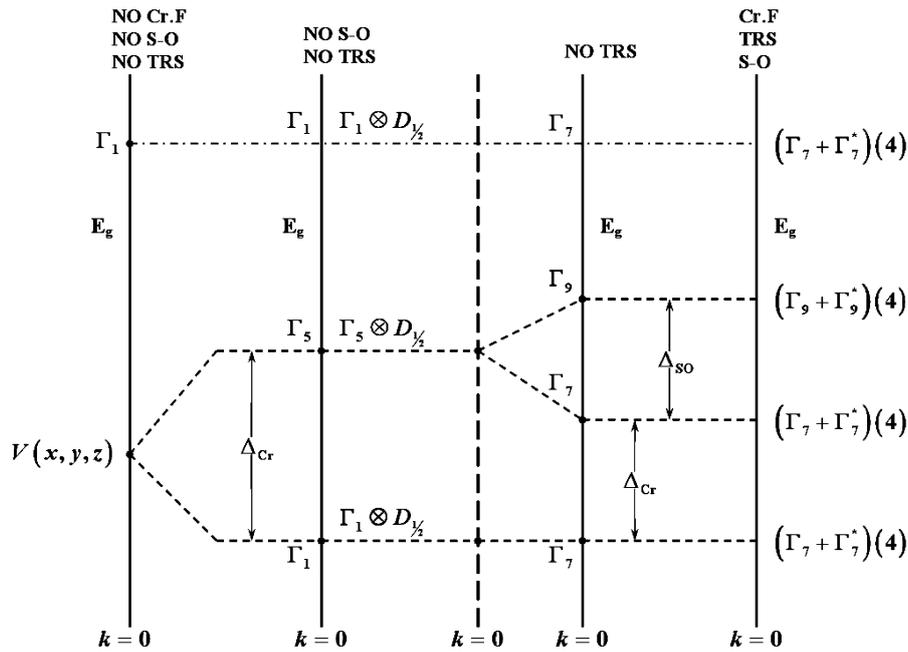


Fig. 3. Band structure and selection rules for wurtzite compounds at the Γ symmetry point ($\mathbf{k} = \mathbf{0}$). The V stands for 3×3 dimensional vector representation, which is reducible to $\Gamma_1(z) + \Gamma_5(x, y)$. There are a number of wurtzite compounds for which the above band structure is valid. In some of them the crystalline field is rather negligible. For them the very first left diagram of band structure can be relevant. Our figure can be directly compared with Fig. 1 in Ref. [8]. Birman assigned the top VB of a zinc-blende structure by Γ_4 rep. The Γ_4 rep is one of the irrops of the zinc-blende space group and it is simultaneously vector representation of the group. For wurtzite structures, a similar assignment on Birman's figure is missing. It should be mentioned that for the here used valence band structure of ZnO, the ordering of the uppermost valence bands has to be reversed.

The D^f is a rep (not necessary irreducible) according to which the perturbation operator transforms. In case of absorption (emission) of electromagnetic radiation, the dipole moment operator $\hat{f} = \hat{d}$ for the electric dipole radiation transforms like X, Y, Z (vector rep $V = \Gamma_1(z) \oplus \Gamma_5(x, y)$) in ZnO. In order to discuss the SRs we have to establish the ordering of the VBs. Following the ordering of Thomas and Hopfield [14] in agreement with recent MPL studies [6] we attribute the uppermost A VB to consist of hole states with Γ_7 symmetry.

For $\tilde{\mathbf{E}} \parallel \mathbf{c}$ (c -hexagonal axis along z) the SRs are:

$$\Gamma_7^c \otimes \Gamma_1(z) \otimes \Gamma_7^v = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_5 \text{ (allowed transitions for A- and C-excitons).}$$

$$\Gamma_7^c \otimes \Gamma_1(z) \otimes \Gamma_9^v = \Gamma_5 \oplus \Gamma_6 \text{ (B-excitons, forbidden transition since the Kronecker product does not contain } \Gamma_1 \text{ rep).}$$

For $\tilde{\mathbf{E}} \perp \mathbf{c}$, we have:

$$\Gamma_7^c \otimes \Gamma_5(x, y) \otimes \Gamma_7^v = \Gamma_1 \oplus \Gamma_2 \oplus 2\Gamma_5 \oplus \Gamma_6.$$

$$\Gamma_7^c \otimes \Gamma_5(x, y) \otimes \Gamma_9^v = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_6 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5.$$

For $\tilde{\mathbf{E}} \perp \mathbf{c}$ polarization all transitions for A-, B-, and C-excitons are allowed and observed experimentally [15,16].

2.4. SRs in the presence of TRS

As mentioned the electron and hole states are TR degenerated and therefore their states are classified according to the joint reps: $D \oplus D^*$. Consequently, the respective SRs are:

For $\tilde{\mathbf{E}} \parallel \mathbf{c}$: $(\Gamma_7^c \oplus (\Gamma_7^c)^*) \otimes \Gamma_1(z) \otimes (\Gamma_9^v \oplus (\Gamma_9^v)^*)$. The decomposition of the KPs reveals $4\Gamma_5$ and $4\Gamma_6$ states. All the states have different basis functions and those can be obtained by Clebsch-Gordan coefficients methods. The B-excitons are still forbidden as in the absence of TRS.

For $\tilde{\mathbf{E}} \parallel \mathbf{c}$: $(\Gamma_7^c \oplus (\Gamma_7^c)^*) \otimes \Gamma_1(z) \otimes (\Gamma_7^v \oplus (\Gamma_7^v)^*) = 4\Gamma_1 \oplus 4\Gamma_2 \oplus 4\Gamma_5$. The transitions are also allowed as in the absence of TRS.

For $\tilde{\mathbf{E}} \perp \mathbf{c}$: $(\Gamma_7^c \oplus (\Gamma_7^c)^*) \otimes \Gamma_5(x, y) \otimes (\Gamma_9^v \oplus (\Gamma_9^v)^*) = (\Gamma_5 \oplus \Gamma_6) \otimes \Gamma_5 \oplus \dots$. The transition is allowed for an B-exciton, since the KP $\Gamma_1 \in \Gamma_5 \otimes \Gamma_5$.

For $\tilde{\mathbf{E}} \perp \mathbf{c}$: $(\Gamma_7^c \oplus (\Gamma_7^c)^*) \otimes \Gamma_5(x, y) \otimes (\Gamma_7^v \oplus (\Gamma_7^v)^*) = 4(\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5 \oplus \Gamma_6)$. Again these transitions are allowed.

Clearly the TRS does not change the existing SRs. It introduces only a number of new states of the same symmetries. All the states are based on different wave functions, which correspond to different energy levels. Further splitting due to TRS is possible. The effect of TRS on phonons and TR splitting has been experimentally observed [18]. Recent studies of the electronic band structure of ZnO by means of first-principles calculations and density-functional theory [17] clearly evidence the existence of TRS on high symmetry point A and Δ line in ZnO and other wurtzite compounds.

3. Discussions and conclusion

From the first part of this paper, it follows that magneto-photoluminescence studies can clearly identify the origin of the neutral and ionized bound exciton transitions shown in Figs. 1 and 2. We observe a linear splitting of I_{6a} – I_8 corresponding to neutral excitonic complexes and a non-linear zero-field splitting for the ionized donor bound excitons I_0 – I_2 . It is suggested, that these ionized donor bound excitons are related to the same chemical impurity as their correlated neutral donor bound excitons I_{6a} , I_8 , and I_9 .

The selections rules discussed in Section 2 are related to absorption (emission) transitions observed by reflectivity measurements [19,20]. Our results are in good agreement with early and recently reported experimental data [21]. The ordinary photoluminescence (PL) technique can only probe A-excitons at $\mathbf{k} = \mathbf{0}$ of symmetries Γ_5 and Γ_6 ($\Gamma_7^c \otimes \Gamma_9^v = \Gamma_5(\uparrow\downarrow) \oplus \Gamma_6(\uparrow\uparrow)$). The shoulder lines at around 3.3750 and 3.3775 eV might be

related to the Γ_5 (anti-parallel spins) and Γ_6 (parallel spins) free excitons.

As discussed in Section 1, the transition lines I_{6a} , I_8 , and I_9 originate from the recombination of bound excitons at neutral donor complexes such as Al, Ga, and In. The atomic ground states of the elements listed in Table 1, including Li, are: Li ($n = 2$, $^2S_{1/2}$), Al ($n = 3$, $^2P_{1/2}$), Ga ($n = 4$, $^2P_{1/2}$), In ($n = 5$, $^2P_{1/2}$); see Fig. 5.2, p. 87 and Fig. 8.1, p. 115 in Ref. [22], where n is the principal quantum number. These states are doublets ($2S + 1 = 2$) and therefore exhibit anomalous Zeeman splitting. Their spectral terms can also be found in [22]. In ZnO these dopants become shallow donors to which the excitons of symmetries $\Gamma_7^c \oplus \Gamma_7^v(A)$, $\Gamma_7^c \oplus \Gamma_9^v(B)$, and $\Gamma_7^c \oplus \Gamma_7^v(C)$ are bound. The excitons bound to the dopant states do not contribute to the spin states of complexes. Therefore, these complexes remain doublets ($S = \frac{1}{2}$, $2S + 1 = 2$), $m_s = -1/2, +1/2$. In a magnetic field, the Zeeman effect of these states can be observed and the g -values obtained.

For phonons in ZnO and GaN the extra time reversal degeneracy has already been proven by experiments [19,20]. Clearly, the phonons at the high symmetry line Δ and point A experience time reversal symmetry (TRS) degeneracy. However, the time reversal splitting of electronic states has, to the best of our knowledge, never been observed. Since the inclusion of TRS has no effect on the optical selection rules, but only introduces additional states of the same symmetry, this fact is in agreement with our theoretical calculations.

In conclusion we have demonstrated a correlation between ionized and neutral donor bound excitons of the same chemical identity. For high resolution and high magnetic field spectra additional transition lines can be observed. Rigidly derived selection rules are in good agreement with the experimental data. The inclusion of TRS as possible origin has been studied. It could be proven that the inclusion of TRS does not change the existing selection rules compared to those in the absence of

TRS. It only introduces new states of the same symmetry. By the strict derivation of the selection rules, it could be concluded that the inclusion of TRS should not affect the observable optical transition.

References

- [1] S. Müller, D. Stichtenoth, M. Uhrmacher, H. Hofsäuss, C. Ronning, J. Röder, Appl. Phys. Lett. 90 (2007) 012107.
- [2] K. Johnston, M.O. Henry, D. McCabe, E. McGlynn, M. Dietrich, E. Alves, M. Xi, Phys. Rev. B 73 (2006) 165212.
- [3] B.K. Meyer, H. Alves, D.M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straburg, M. Dworzak, U. Haboek, A.V. Rodina, Phys. Status Solidi 241 (2004) 231.
- [4] B.K. Meyer, J. Sann, S. Lautenschläger, M.R. Wagner, A. Hoffmann, Phys. Rev. B 76 (2007) 184120.
- [5] D.G. Thomas, J.J. Hopfield, Phys. Rev. Lett. 7 (1961) 316.
- [6] A.V. Rodina, M. Strassburg, M. Dworzak, U. Haboek, A. Hoffmann, A. Zeuner, H.R. Alves, D.M. Hofmann, B.K. Meyer, Phys. Rev. B 69 (2004) 125206.
- [7] M.R. Wagner, A. Hoffmann, A. Rodina, B.K. Meyer, to be published, 2008.
- [8] J. Birman, Phys. Rev. Lett. 2 (1959) 4.
- [9] W.R.L. Lambrecht, A.V. Rodina, S. Limpjumnong, B. Segall, B.K. Meyer, Phys. Rev. B 65 (2002) 075207.
- [10] M. Hamermesh, Group Theory and its Application to Physical Problems, Pergamon Press, New York, 1962.
- [11] G.F. Koster, J.O. Dimmock, R.G. Wheeler, H. Statz, Properties of the Thirty-Two Point Groups, MIT Press, Cambridge, MA, 1963.
- [12] G. Frobenius, I. Schur, Berl. Ber. 186 (1906).
- [13] A.P. Cracknell, B.L. Davis, S.C. Miller, W.F. Love, Kronecker Product Tables, vol. 4.IFI/Plenum Press, New York, Washington, London, 1979.
- [14] J.J. Hopfield, J. Phys. Chem. Solids 15 (1960) 97.
- [15] Y.S. Park, C.W. Litton, T.C. Collins, D.C. Reynolds, Phys. Rev. 143 (1966) 512.
- [16] P. Erhart, K. Albe, A. Klein, Phys. Rev. B 73 (2006) 205203.
- [17] J. Serrano, A.H. Romero, F.J. Manjon, R. Lauck, M. Cardona, Rubio, Phys. Rev. B 69 (2004) 094306.
- [18] D.C. Thomas, J.J. Hopfield, Phys. Rev. 128 (1962) 2135.
- [19] K. Thoma, B. Dorner, G. Duesing, W. Wegener, Solid State Commun. 15 (1974) 1111.
- [20] A.W. Hewat, Solid State Commun. 8 (1974) 187.
- [21] D.C. Reynolds, C.W. Litton, T.C. Collins, Phys. Rev. 140 (1965) A1726.
- [22] H.E. White, Introduction to Atomic Spectra, McGraw-Hill, New York, London, 1934.