

In the framework of the pseudopotential method and making use of phenomenological parameters, the temperature dependences of the energy extrema at highly symmetric points Γ , L, K, M, A, and H of the Brillouin zone in hexagonal zinc oxide, as well as the energies of the main interband transitions between them, have been calculated. The temperature dependence of the density of states has been also studied. The influence of the temperature on the electronic structure of ZnO was studied taking two factors into account: thermal expansion of the lattice and electron-phonon interaction. The temperature dependences of the energy levels, inter- and intraband transitions, and the density of states have been analyzed in detail. The results obtained are in good agreement with experimental data.

1. Introduction

Wurtzite-like zinc oxide is a direct-band-gap semiconductor with a favorable combination of useful electrical, optical, and acoustical properties, which makes it applicable in various branches ranging from optoelectronics to heterogeneous catalysis (see review [1]). It is an inexpensive, ecologically safe, and easily workable material which has high enough conductivity of the electron type and can be readily rolled out into a thin layer without addressing high-temperature technologies.

Optical properties of ZnO are similar to those of widely used gallium nitride. A wide energy gap $E_g \approx 3.30$ eV at T = 300 K (for comparison, in GaN, $E_g \approx 3.4$ eV at the same temperature) and a high exciton binding energy $E_{\rm eb} \approx 60$ meV (for GaN, $E_{\rm eb} \approx 26$ meV), together with a large absorption coefficient, make ZnO a promising material for the wide application in optoelectronics. For example, zinc oxide crystals comprise the basis for manufacturing blue and UV light-emitting diodes, UV detectors, electroluminescence and piezoelectric devices, solar cells, flat cathodes in ray tubes. On the basis of ZnO, the first transparent transistor has been created, which can cardinally enhance the quality of liquid crystal displays by making their screens brighter and sharper.

In works [1, 2], the stimulated emission caused by exciton transitions in ZnO at room temperature was observed for the first time. ZnO films fabricated by the method of molecular-beam epitaxy were used to create an UV laser with optical pumping. It has been demonstrated that the quantum yield of texturized ZnOfilms can be higher than that in gallium nitride, so that these films could be a material for the next generation of optoelectric devices.

In recent years, the interest in zinc oxide has grown again. This happened after the reports had been made about a capability to create high-quality substrates on its basis and the discovery of p-type conductivity in it, as well as ferromagnetism which arises after the doping of ZnO crystals with transition metals. Nevertheless, these properties still provoke discussions in the literature. The main obstacle on the way to expand the range of ZnObased devices is the poor reproducibility of crystals of the p-type with a low specific resistance [1].

In order to understand the origin of the phenomena that occur in ZnO-based crystals and films and to optimize materials intended for relevant processes and applications, one has to possess a reliable knowledge concerning, in particular, the exact quantitative characteristics of the ZnO electron structure and their temperature dependences. The band structure of a single-crystalline hexagonal ZnO was studied by many authors in the framework of the various theoretical and experimental methods. In many works [4], lowtemperature photoluminescence spectra were studied in detail, although there is no consensus on the interpretation of those spectra, in particular, with respect to an unambiguous correspondence between some sharp emission peaks and the definite intra- or interband transitions. ZnO was studied experimentally,

ISSN 0503-1265. Ukr. J. Phys. 2007. V. 52, N 5

making use of various methods: x-ray photoemission spectroscopy, UV reflection and absorption, angleresolved photoelectron spectroscopy, and synchrotronradiation spectroscopy.

The method of two-photon spectroscopy under hydrostatic pressure up to 7.3 GPa and at a temperature of 6 K was used in work [5] to study the baric dependences of three lowest energy gaps, the exciton binding energy, spin-orbit coupling, and crystal-field splitting in a wurtzite ZnO.

As far as we know, the theoretical calculations of the temperature dependence of the band structure in wurtzite-type crystals, including ZnO, are practically absent. The theory of the temperature dependences of semiconductor properties was reviewed in works [6,7]. In some papers [8–13], the dependences of E_g and other interband transitions, including exciton ones, on the temperature, as well as the temperature behaviors of the spin-orbit coupling magnitude and the spectral line broadening, were studied experimentally. It should be noted that, in almost all works, the results were analyzed either with the help of the Varshny empirical formula

$$E_g(T) = E_0 - \frac{\alpha T^2}{T + \beta},$$

where α and β are empirical constants, or making use of the phenomenological expression for the thermal widening of the gap $\Delta E_g(T)$. The latter dependence stems from the renormalization of electron states, which is caused by the interaction between phonons with average phonon frequency. The corresponding expression contains the Bose-Einstein statistical factor

$$\Delta E_g(T) = \frac{2a_B}{\exp(\Theta/T) - 1},$$

where Θ is the temperature that corresponds to the average phonon frequency, and the parameter a_B describes the strength of electron-phonon interaction.

In this work, we have made, for the first time, a theoretical analysis for the temperature dependences of the main interband transitions, one-electron energy levels, and the density of states of a hexagonal zinc oxide; the researches were carried out in the framework of the empirical pseudopotential method. In work [7], a similar study has been fulfilled for a number of hexagonal modifications of silicon carbide. Therefore, we shall not dwell on the history and the modern state of the problem, as well as on the calculation procedure which have been discussed in detail in work [7]. We only

ISSN 0503-1265. Ukr. J. Phys. 2007. V. 52, N 5

note that the influence of the temperature dependence of electron-phonon interaction on the crystal band structure was taken into account by introducing the temperature dependence of the Debye—Waller factors, and the thermal expansion of the lattice was taken into account by varying the scale of form-factors, namely, by multiplying the Fourier-components of the pseudopotential by $a^3(0)/a^3(T)$, where *a* is the lattice constant.

The complete variant of the theory makes allowance for another, third type of contribution to the dependence of the band structure on temperature – the so-called Fan self-energy [14]. The calculations of the temperature dependence of interband gaps in zinc-blende structure crystals showed [15] that, if the temperature is high, the dominant contribution is given by the Debye–Waller factors, because two other contributions, having signs that are opposite to each other, considerably compensate each other. The self-energy terms are specific to every electron state and every phonon; therefore, their calculation is rather complicated. As was demonstrated in work [16], the errors obtained while determining the Debye–Waller factors often exceed the corrections given by taking the Fan self-energy into account. Therefore, in this work, similarly to what was done in work [7], the self-energy contribution was neglected.

The Debye—Waller factor governs the temperature dependence of the intensity of x-ray scattering by a particle in the crystal,

$$I = I_0 \exp\left[-W_j(G,T)\right],$$

and can be determined from experimental data. While calculating the temperature dependence of the crystal band structure, their both experimental and theoretical values were used in the literature.

2. Calculation Results

In this work, we calculated the band structure and the density of states of hexagonal zinc oxide by applying the empirical pseudopotential method and using the expansion of the wave function in a series of 427 plane waves, which corresponds to the electron kinetic energy $E = |G_{\rm max}|^2 \approx 18.55$ Ry. The calculations were carried out at the points and along the directions of high symmetry in the Brillouin zone of the hexagonal lattice (Fig. 1). The initial values of form-factors for the pseudopotential in ZnO at room temperature were taken from work [17]. The band structure of ZnO at T = 300 K is depicted in Fig. 1, a, and the electron density of



Fig. 1. Band structure (a) and the electron density of states (b) in hexagonal ZnO

states at T = 0, 300, and 900 K in Fig. 1,*b*. The use of symmetrized combinations of plane waves for highsymmetry points allowed us to determine irreducible representations, by which the corresponding electron states are transformed.

The band structure of hexagonal ZnO was calculated making use of a lot of methods. These are listed in Table 1 for the sake of illustration, together with our results of calculations of the main interband gaps and the theoretical and experimental results of other authors, the latter being included for comparison.

It is known that first-principle calculations, which use the variants of the methods of the density functional theory, accurately describe the dispersion of valence bands, but often give underestimated – by 20–30% – values of interband gaps; whereas the Hartree—Fock method produces substantially overestimated values for those quantities (see Table 1). At the same time, the method of empirical pseudopotential allows one to obtain the dispersion laws for all valence and conduction bands in ZnO, as well as such band parameters as the effective charge carrier masses or the equivalent $\mathbf{k} - \mathbf{p}$ - parameters which are necessary in the simulation of devices.

As one can see from Table 1, the theoretical calculations, where 3d-levels of Zn were considered as the valence band states, have been carried out in recent years. In this case, the agreement with experimental data becomes considerably worse. In a plenty of calculations, 3d-electrons were regarded as core ones [1].

The comparison of the results of our calculations with experimental data and the results of calculations, which took a nonlocal pseudopotential into account, reveals a good agreement between them. However, it should be noted that our calculations are very sensitive to the choice of atomic form-factors and the magnitudes of lattice constants.

To obtain relatively reliable temperature dependences, the band structure was calculated for 20 sets of form-factors (see Table 2) determined in the temperature interval $0 \div 900$ K with a step of 50 K. We found how the temperature dependence $G^2(T)/4\pi = 3, 4, 8, 11, 12, 16/\{a_{\rm ZnO}^2(T)/a_0^2\}$ affects the accuracy of determination of the Zn and O form-factors following the method expounded in work [28].

ISSN 0503-1265. Ukr. J. Phys. 2007. V. 52, N 5

It turned out that the quantity $G^2(T)$ changes by no more than 0.25% in the interval $0 \div 900$ K. Therefore, the temperature variation in the $V(G_i^2(a_{\text{ZnO}}(T)))$ dependence can be neglected.

To make allowance for the variation of formfactors associated with the lattice thermal expansion, we used the functions a(T) and c(T) deduced from the temperature dependences of the linear coefficient of lattice thermal expansion [29].

Root-mean-square displacements of zinc and oxygen atoms at various temperatures were taken from work [29], where they were determined by the method of neutron diffractometry.

T a b l e $\,$ 1. Comparison of main interband transitions in hexagonal ZnO $\,({\rm eV})$

Γ_{1c} - $\Gamma_{6\nu}$	M_{1c} – $\Gamma_{6\nu}$	K_{2c} – $\Gamma_{6\nu}$	$A_{1,3c}-\Gamma_{6\nu}$	$L_{1,3c} - \Gamma_{6\nu}$	$H_{3c}-\Gamma_{6\nu}$
3.30^{*}	7.29^{*}	8.24*	6.09*	6.77*	7.91*
3.30[18]	7.16[20]	10.55[18]	6.11[18]	9.05[18]	9.74[18]
3.30[19]	5.34[20]	9.29[19]	6.15[19]	7.78[19]	8.30[19]
2.13[20]	6.49[20]		4.88[20]		
0.23[20]			3.02[20]		
1.58[20]			4.14[20]		
0.97[21]					
3.45[21]					
10.60[21]					
11.59[22]					
4.23[22]					
0.93[22]					
0.23[23]					
3.77[23]					
3.40[23]					
2.11[24]					
3.15[24]					
3.39[25]					
3.44[26]					
3.37[27]					

N o t e s: * - this work; [18] - semiempirical tight-binding method; [19] – pseudopotential method; [20] – nonlocal norm-conserving pseudopotential method in the Kleinman–Bilander separable form: 1) zinc 3d-electrons are considered as core ones, 2) zinc 3delectrons are considered as valence ones, and 3) calculations are made in the local density approximation; [21] - the LMTO-method in the approximations of 1) local density, 2) Green's function and the screened Coulomb potential, and 3) Hartree-Fock; [22] - a full-potential method of linearized augmented plane waves in the approximations of 1) Hartree-Fock, 2) Green's function and the screened Coulomb potential, and 3) local density; [23] - nonlocalpotential method in the approximations of 1) local density, 2) local density taking self-interaction corrections into account, and 3) experimental data; [24] - ab initio pseudopotential method in the approximations of 1) local density and 2) Green's function and the screened Coulomb potential; [25] - Green's function method; [26] optical absorption spectra at T = 4.2 K; [27] – photoluminescence spectra at T = 300 K.

3. Studies of the Temperature Coefficients for the Energies of Main Interband Transitions and One-electron Levels

Proceeding from the data on the band structure which were obtained in the previous section, we calculated the temperature dependences of one-electron energy levels (Fig. 2) and the main interband transitions (Table 3) in hexagonal zinc oxide and studied the main properties and characteristics of those dependences.

The analysis of the temperature dependences of energy levels in the conduction and valence bands at highly symmetric points Γ , K, H, A, M, and L of the Brillouin zone in a wurtzite lattice showed that the temperature factor $\alpha_T = dE/dT$, which characterizes the rate of one-electron-level and interband-gap variations with temperature, is positive for the levels from the upper valence band and, on the average, 3.4 times greater by absolute value than the negative temperature factor for the levels from the lower conduction band within the temperature interval $0 \div 900$ K. Hence, if the temperature increases, the levels in the conduction and valence bands come closer and the widths of interband gaps between the upper valence and bottom conduction bands become narrower. The average rates of the changes of 12 one-electron energy levels and 12 interband transitions within each of the temperature intervals 0 - 300, 300 - 600, 600 - 900, and 0 - 900 K are listed in Table 4.

In Fig. 2, the temperature dependences of six oneelectron energy levels from the valence band (panel a) and six energy levels from the conduction band (panel b) at the high-symmetry points in the Brillouin zone of ZnO are depicted. It is evident from the figure that the levels in the conduction band smoothly descend, while the levels in the valence band smoothly – but at a rate that is several times higher – ascend as the temperature grows:

$$\alpha_T^{\nu} = \left\langle \frac{dE_{\nu}}{dT} \right\rangle = 3.22 \times 10^{-4} \text{ eV/K},$$
$$\alpha_T^c = \left\langle \frac{dE_c}{dT} \right\rangle = -0.959 \times 10^{-4} \text{ eV/K},$$
$$\frac{\langle \alpha_T^{\nu} \rangle \left(0 \div 900 \text{ K}\right)}{\langle \alpha_T^c \rangle \left(0 \div 900 \text{ K}\right)} = 3.36.$$

With respect to the degree of mobility increase, our calculated levels range in the following order: Γ_{1c} , $A_{1,3c}$, $L_{1,3c}$, M_{1c} , H_{3c} , K_{2c} , $K_{3\nu}$, $L_{1,3\nu}$, $H_{3\nu}$, $M_{4\nu}$, $A_{5,6\nu}$, and

ISSN 0503-1265. Ukr. J. Phys. 2007. V. 52, N 5

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Fig. 2. Temperature dependences of the energy levels in the upper valence (a) and lower conduction (b) bands of hexagonal ZnO

 $\Gamma_{6\nu}$. Therefore, the top of the valence band turns out the most mobile level, which is in agreement with the literature data on the temperature dependence of the band structure of cubic semiconductors [6].

The analysis of data in Table 4 showed that the temperature coefficient for the levels in the upper valence band grows as the temperature increases within the studied temperature interval 0-900 K, i.e.

T a b l e 2. Temperature dependences of the pseudopotential form-factors for Zn and O atoms in ZnO (Ry)

T, K	$V_{\rm Zn}(3)$	$V_{\rm Zn}(4)$	$V_{\rm Zn}(8)$	$V_{\rm Zn}(11)$	$V_{\rm Zn}(12)$	$V_{\rm Zn}(16)$	$V_{\rm O}(3)$	$V_{\rm O}(4)$	$V_{\rm O}(8)$	$V_{\rm O}(11)$	$V_{\rm O}(12)$	$V_{\rm O}(16)$
0	-0.6546	-0.4010	-0.0325	0.0101	0.0156	-0.0906	-0.0101	0.0209	0.1339	0.1322	0.1174	0.0212
50	-0.6542	-0.4007	-0.0324	0.0101	0.0156	-0.0904	-0.0101	0.0209	0.1337	0.1320	0.1173	0.0211
100	-0.6534	-0.4002	-0.0324	0.0101	0.0156	-0.0902	-0.0101	0.0208	0.1335	0.1317	0.1170	0.0211
150	-0.6527	-0.3997	-0.0323	0.0101	0.0155	-0.0899	-0.0101	0.0208	0.1332	0.1314	0.1167	0.0210
200	-0.6519	-0.3992	-0.0322	0.0101	0.0155	-0.0896	-0.0100	0.0208	0.1329	0.1310	0.1164	0.0209
250	-0.6510	-0.3985	-0.0322	0.0100	0.0154	-0.0893	-0.0100	0.0207	0.1326	0.1306	0.1160	0.0208
300	-0.6500	-0.3979	-0.0321	0.0100	0.0154	-0.0890	-0.0100	0.0207	0.1321	0.1300	0.1154	0.0207
350	-0.6489	-0.3972	-0.0320	0.0100	0.0153	-0.0887	-0.0100	0.0206	0.1316	0.1293	0.1147	0.0206
400	-0.6478	-0.3964	-0.0319	0.0099	0.0153	-0.0883	-0.0100	0.0206	0.1309	0.1285	0.1139	0.0204
450	-0.6466	-0.3956	-0.0318	0.0099	0.0152	-0.0879	-0.0099	0.0205	0.1301	0.1274	0.1129	0.0201
500	-0.6454	-0.3947	-0.0317	0.0099	0.0152	-0.0874	-0.0099	0.0204	0.1291	0.1262	0.1118	0.0199
550	-0.6441	-0.3938	-0.0316	0.0098	0.0151	-0.0869	-0.0098	0.0203	0.1280	0.1248	0.1104	0.0196
600	-0.6427	-0.3928	-0.0315	0.0098	0.0150	-0.0864	-0.0098	0.0202	0.1267	0.1231	0.1088	0.0192
650	-0.6411	-0.3918	-0.0314	0.0097	0.0150	-0.0858	-0.0098	0.0201	0.1262	0.1224	0.1082	0.0190
700	-0.6397	-0.3908	-0.0313	0.0097	0.0149	-0.0852	-0.0098	0.0201	0.1256	0.1217	0.1075	0.0189
750	-0.6381	-0.3896	-0.0311	0.0096	0.0148	-0.0845	-0.0097	0.0200	0.1250	0.1210	0.1068	0.0187
800	-0.6364	-0.3884	-0.0310	0.0096	0.0147	-0.0838	-0.0097	0.0200	0.1244	0.1202	0.1060	0.0186
850	-0.6347	-0.3872	-0.0308	0.0095	0.0146	-0.0830	-0.0097	0.0199	0.1237	0.1194	0.1053	0.0184
900	-0.6329	-0.3859	-0.0306	0.0094	0.0145	-0.0822	-0.0097	0.0198	0.1231	0.1186	0.1045	0.0182

<i>Т</i> , К	$L_{1,3c} - \Gamma_{6\nu}$	M_{1c} – $\Gamma_{6\nu}$	$\Gamma_{1c} - \Gamma_{6\nu}$	$A_{1,3c}$ – $\Gamma_{6\nu}$	$H_{3c}-\Gamma_{6\nu}$	$K_{2c}-\Gamma_{6\nu}$	$L_{1,3c} - L_{1,3\nu}$	$M_{1c}–M_{4\nu}$	$E_g^{\text{ind }*}$	$A_{1,3c} - A_{5,6\nu}$	$H_{3c}-H_{3\nu}$	K_{2c} - $K_{3\nu}$
0	6.8490	7.3729	3.3648	6.1622	7.9920	8.3472	8.4780	8.2215	6.3932	6.6557	9.1803	10.9115
50	6.8405	7.3646	3.3581	6.1550	7.9832	8.3366	8.4701	8.2134	6.3845	6.6487	9.1721	10.9026
100	6.8268	7.3516	3.3478	6.1436	7.9691	8.3199	8.4575	8.2007	6.3706	6.6375	9.1590	10.8883
150	6.8137	7.3387	3.3375	6.1326	7.9555	8.3035	8.4451	8.1881	6.3572	6.6266	9.1461	10.8741
200	6.7994	7.3246	3.3265	6.1205	7.9408	8.2857	8.4315	8.1741	6.3426	6.6146	9.1319	10.8583
250	6.7823	7.3078	3.3132	6.1061	7.9232	8.2644	8.4153	8.1575	6.3251	6.6003	9.1150	10.8396
300	6.7659	7.2912	3.3001	6.0921	7.9063	8.2436	8.3995	8.1410	6.3081	6.5862	9.0985	10.8210
350	6.7469	7.2720	3.2849	6.0759	7.8867	8.2195	8.3812	8.1218	6.2885	6.5700	9.0793	10.7996
400	6.7287	7.2531	3.2699	6.0603	7.8680	8.1960	8.3633	8.1026	6.2694	6.5541	9.0606	10.7783
450	6.7090	7.2323	3.2532	6.0432	7.8478	8.1703	8.3438	8.0814	6.2487	6.5366	9.0402	10.7550
500	6.6884	7.2103	3.2354	6.0253	7.8267	8.1431	8.3234	8.0588	6.2267	6.5182	9.0187	10.7305
550	6.6681	7.1881	3.2173	6.0075	7.8060	8.1160	8.3028	8.0356	6.2050	6.4997	8.9970	10.7054
600	6.6456	7.1632	3.1968	5.9877	7.7831	8.0857	8.2801	8.0097	6.1806	6.4790	8.9732	10.6778
650	6.6163	7.1347	3.1738	5.9632	7.7530	8.0494	8.2532	7.9821	6.1505	6.4550	8.9451	10.6476
700	6.5880	7.1070	3.1512	5.9395	7.7239	8.0142	8.2272	7.9551	6.1213	6.4316	8.9179	10.6182
750	6.5554	7.0754	3.1252	5.9123	7.6905	7.9739	8.1978	7.9248	6.0876	6.4051	8.8873	10.5857
800	6.5224	7.0434	3.0989	5.8847	7.6567	7.9330	8.1680	7.8939	6.0535	6.3783	8.8562	10.5526
850	6.4868	7.0091	3.0705	5.8551	7.6202	7.8891	8.1363	7.8611	6.0166	6.3495	8.8231	10.5177
900	6.4489	6.9726	3.0400	5.8236	7.5814	7.8423	8.1028	7.8263	5.9773	6.3191	8.7882	10.4810

T a b l e 3. Temperature dependences of interband transition energy in hexagonal ZnO (eV)

*The indirect energy gap width E_g^{ind} corresponds to a transition from point (0,0.82,0.29) along LM-direction into point $\Gamma_{6\nu}$

T a b l e 4. Temperature coefficients ($\alpha_T \times 10^4$ K) of one-electron energy levels and interband transitions in a ZnO crystal

$\Delta T, K$	$L_{1,3\nu}$	$M_{4\nu}$	$\Gamma_{6\nu}$	$A_{5,6\nu}$	$H_{3\nu}$	$K_{3\nu}$	$L_{1,3c}$	M_{1c}	Γ_{1c}	$A_{1,3c}$	H_{3c}	K_{2c}
0 - 300	+1.58	+1.69	+1.74	+1.71	+1.61	+1.30	-1.04	-0.99	-0.42	-0.603	-1.12	-1.72
300-600	+3.17	+3.31	+3.20	+3.30	+3.27	+2.71	-0.803	-1.07	-0.24	-0.273	-0.9	-2.06
600-900	+4.76	+5.17	+5.40	+5.26	+4.85	+3.85	-1.15	-0.947	+0.177	-0.067	-1.32	-2.71
0 - 900	+3.17	+3.39	+3.45	+3.43	+3.24	+2.62	-0.999	-1.001	-0.161	-0.314	-1.114	-2.163
ΔT , K	$L_{1,3c}$ – $\Gamma_{6\nu}$	M_{1c} – $\Gamma_{6\nu}$	$\Gamma_{1c} - \Gamma_{6\nu}$	$A_{1,3c}$ – $\Gamma_{6\nu}$	$H_{3c}-\Gamma_{6\nu}$	K_{2c} – $\Gamma_{6\nu}$	$L_{1,3c} - L_{1,3\nu}$	$M_{1c}-M_{4\nu}$	E_g^{ind}	$A_{1,3c} - A_{5,6\nu}$	$H_{3c}-H_{3\nu}$	$K_{2c}-K_{3\nu}$
0 - 300	-2.77	-2.72	-2.16	-2.34	-2.86	-3.45	-2.62	-2.68	-2.84	-2.32	-2.73	-3.02
300-600	-4.01	-4.27	-3.44	-3.48	-4.11	-5.26	-3.98	-4.38	-4.25	-3.57	-4.18	-4.77
600-900	-6.56	-6.35	-5.23	-5.47	-6.72	-8.11	-5.91	-6.11	-6.78	-5.33	-6.17	-6.56
0 - 900	-4.45	-4.45	-3.61	-3.76	-4.56	-5.61	-4.17	-4.39	-4.62	-3.74	-4.36	-4.78

$$\langle d\alpha_T^{\nu}/dT \rangle > 0,$$

$$\frac{\langle \alpha_T^{\nu} \rangle \left(300 \div 600 \,\mathrm{K} \right)}{\langle \alpha_T^{\nu} \rangle \left(0 \div 300 \,\mathrm{K} \right)} = 1.96$$

and

$$\frac{\left<\alpha_T^\nu\right>(600\div900\,\mathrm{K})}{\left<\alpha_T^\nu\right>(300\div600\,\mathrm{K})}=1.54,$$

but the rate of growth becomes slower.

The temperature coefficients for the different levels from the lower conduction band behave differently as the temperature grows; in particular,

$$\left\langle \frac{d\left|\alpha_{T}^{c}(K_{2c})\right|}{dT}\right\rangle >0$$

and

$$\left\langle \frac{d \left| \alpha_T^c(A_{1,3c}) \right|}{dT} \right\rangle < 0$$

ISSN 0503-1265. Ukr. J. Phys. 2007. V. 52, N 5

in the whole temperature interval. At the same time, the temperature coefficients for other levels in the conduction band change their signs when the temperature varies.

The average rate of the direct-band-gap variation is $dE_g^{\rm dir}/dT = -3.61 \times 10^{-4} \text{ eV/K}$ in the temperature interval 0 – 900 K. In the interval from 0 to 300 K, it is $dE_g^{\rm dir}/dT = -2.16 \times 10^{-4} \text{ eV/K}$, which is in good agreement with an experimentally measured value of about $-2 \times 10^{-4} \text{ eV/K}$ [4]. Table 4 also demonstrates that all interband gaps decrease with increase in the temperature; the higher the temperature, the quicker the reduction.

In Fig. 1, b, the electron density of states n(E) at temperatures of 0, 300, and 900 K is shown. One can see that, if the temperature becomes higher, the curve of the density of states in the valence band shifts towards higher energies, whereas the curve of the density of states in the conduction band towards lower energies, in full agreement with a general tendency for interband gaps to diminish as the temperature grows. Figure 1, *b* also demonstrates that the maxima and the minima of the dependence n(E), besides being subjected to a common shift, vary differently by a value which is most likely associated with differences between the individual temperature coefficients of energy levels.

4. Conclusions

We have carried out the theoretical calculations of the influence of the temperature on the electron energy spectrum and the density of states in hexagonal zinc oxide. The influence of the temperature dependence of the electron-phonon interaction on the band structure in a crystal was taken into account by introducing the temperature dependence of the Debye—Waller factors, and the contribution of the linear expansion of the lattice by introducing the temperature dependence of the linear expansion coefficient.

The results of calculation showed that the widths of all interband transitions between the upper valence band and the lower conduction one become narrower as the temperature increases; and the rate of narrowing is quicker, if the temperature is higher (Table 4). The level that corresponds to the top of the valence band turned out most sensitive to the temperature variation. This level gives the dominant contribution to the variation rate of the fundamental gap with temperature. Some interesting features in the temperature dependences of the temperature coefficients for the conduction band levels have been found (Table 4). Probably, they may be associated with fine effects of the interaction between electrons and optical or acoustical phonons. They may also be due to our neglect of the Fan self-energy terms [14].

It is worth noting that the information obtained in this work can be useful in the design of various ZnObased optical devices.

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Received 05.10.06. Translated from Ukrainian by O.I. Voitenko

ISSN 0503-1265. Ukr. J. Phys. 2007. V. 52, N 5

РОЗРАХУНОК ТЕМПЕРАТУРНИХ ЗАЛЕЖНОСТЕЙ ЗОННОЇ СТРУКТУРИ ТА ЩІЛЬНОСТІ СТАНІВ ГЕКСАГОНАЛЬНОГО ОКСИДУ ЦИНКУ

Т.В. Горкавенко, С.М. Зубкова, Л.Н. Русіна, В.А. Макара, В.Л. Бекеньов

Резюме

Методом псевдопотенціалу з використанням феноменологічних параметрів розраховано температурні залежності актуальних екстремумів енергії у високосиметричних точках Γ, L, K, M, A, H зони Бріллюена та енергії основних міжзонних переходів між ними у гексагональному оксиді цинку, а також досліджено температурну залежність щільності електронних станів. Дослідження впливу температури на електронну структуру ZnO проведено з урахуванням двох факторів: теплового розширення ґратки та електронфононної взаємодії. Проведено детальний аналіз температурних залежностей енергетичних рівнів, міжзонних та внутрішньозонних переходів; проаналізовано поведінку кривої щільності станів при зміні температури. Результати розрахунків добре узгоджуються з експериментальними даними.