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Optical and structural properties of III-nitrides compounds

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Self-consistent linear muffin-tin-orbital band-structure calculations are used to investigate the optical and structural properties of III-V semiconducting nitrides under hydrostatic pressure. The pressure behavior of the energy band structures is discussed in the context of the postulated chemical trends in III-V semiconductors. The regions in k space of dominant interband contributions to the elements of structure in the dielectric functions are identified. The total-energy calculations suggest that all the nitrides under pressure transform to the semiconducting rocksalt phase. The calculated transition pressures are 21.6 GPa (InN), 51.8 GPa (GaN), 16.6 GPa (AlN), and 850 GPa (BN). Experimental values that agree well with this have been found for the first three compounds. The fact that GaN and AlN have such different transition pressures in spite of their very similar ionicities is explained by the presence of *3d* states on Ga.

Keywords: Nitrides; Optical; Structural.

1. INTRODUCTION

The aim of this paper is to examine the physical properties of the III-V nitrides, GaN, AlN, lnN, and BN, with emphasis on their dependence on hydrostatic pressure. The nitrides form a specific subgroup of the III-V com- pounds characterized by high ionicity, very short bond lengths, low compressibility, and high thermal conductivity. These properties make them interesting and very useful. The III-V nitrides may, for example, find ap- plication in blue-light-emitting diodes and lasers operating in the blue and ultraviolet regime. They may also become important materials in high temperature diodes and transistors. Since the properties of electronic devices based on large-gap II-VI semiconductors tend to degrade with time, more and more attention is paid to the III-V nitrides. This is related to the fact that the formation energy of defects in these materials is very high [1-5].

Many physical properties of semiconductors can be scaled with material parameters such as atomic volume and ionicity. The theory proposed by Van Vechten[1] was based on this, and gave a qualitatively good classification of a large number of tetrahedrally coordinated semiconductors. The analysis also includes pressure effects. It is particularly interesting to investigate the pressure behavior of the nitrides, which are the most ionic semiconductors in the III-V group and have a very small atomic volume. By means of experiments and first-principles calculations it is possible to examine, over a wider parameter range, the chemical trends in the family of III-V compounds as deduced from models. The nitrides are therefore also interesting to basic research [6-10].

We study here the optical and structural properties of the III-V nitrides by means of band-structure and total- energy calculations performed for different volumes and crystal structures. The calculations were made by means of the linear muffin-tin-orbital **(**LMTO**)** method[2] in its scalar-relativistic form in conjunction with the local density approximation (LDA) to the density-functional theory. In the following sections the results of the calculations are presented and compared with experimental data. In Sec. II the pressure dependence of the energy band structure is presented and discussed in the context of chemical trends. In Sec. III the band structures obtained for different pressures are used to evaluate the imaginary part of the dielectric function under pressure. This function is directly related to the electronic band structure and thus allows investigations of the effects of external perturbations. A comparison with experimental data is made. The high-pressure phases are investigated and discussed in Sec. IV. A summary of our results and conclusions is given in Sec. V, which also contains further discussions of the results. In particular, we there elaborate on the role of the Ga *3d* states in connection with the pressure-induced structural transition [11-15].

2. RESULTS AND DISCUSSION

The band structures of the III-V nitrides for several crystal structures were calculated by means of the LMTO method in its scalar-relativistic form, in conjunction with the local density approximation (LDA). Here we applied the simplest version of the LMTO method, the atomic-sphere approximation, (ASA) but the "combined correction" terms[2] were incorporated. The details of the LDA-LMTO calculations for zinc-blende-type semiconductors are given elsewhere. The wurtzite structure, in which GaN, AlN, and InN crystallize at ambient conditions, is somewhat more complicated for this kind of calculation. The unit cell contains four "real" atoms and four so-called "empty spheres.". The calculations were optimized by the choice of equal atomic-sphere radii for real atoms and different values for two types of empty spheres. Earlier calculations[6-8] of the electronic structure of GaAs, band offsets in semiconductor heterostructures, and structural properties of tin under pressure, have demonstrated the effects of including the "semi-core" *d* states as fully relaxed band states. Based on this experience we found it necessary also in the present work to include the Ga 3d and In *4d* states as band states. This is especially important for GaN, and we shall discuss in more detail how the Ga 3d states influence the pressure at which the B3 --+ Bl transition occurs. The calculations for wurtzite structures were performed under the assumption that the crystal structure was "ideal," meaning that the *c/a* ratio was taken as equal to 1.633 and the internal bond-length parameter *u* was 3/8. Experimental *c/a* values are 1.627, 1.600, and 1.612 for GaN, AlN, and InN, respectively.[9] X- ray diffraction measurements[10] have shown that *u=0.377* for GaN and 0.3821 for AlN. A detailed structural optimization was made earlier[11] for AlN, and the structural parameters obtained, c/a=l.596, u=0.3820, agree very well with the experimental values. The *u* parameter has, to our knowledge, not yet been determined for InN, but a theoretical value, u=0.380, was obtained by Yeh, Lu, Froyen, and Zunger.

The LDA energy band structures of the nitrides for three crystal structures, wurtzite, zinc-blende, and rocksalt, are shown in Figs. 1-4. For the rocksalt phase we include results corresponding to two different volumes, one being the (theoretical) equilibrium volume, the other being the volume at the transition pressure. The latter volume is also as derived from the calculations (for InN, GaN, and AlN the wurtzite--+rocksalt, and for BN the zinc-blende--+rocksalt transition). The calculated band gaps as well as their deformation potentials are summarized contain the coefficients for first- and second-order gap variations with lattice constant and pressure.

Since the semiconductor band gaps derived from LDA eigenvalues are too small, we performed, for InN, GaN, and AlN, additional calculations where the gaps were ad justed by inclusion of some external potentials.[3] These results are listed in the column headed by "adjusted." It should be noted, however, that the experimental data available are not sufficiently detailed to allow an accurate determination of the parameters of the adjusting potential. This statement reflects experience obtained from calculations on several compound semiconductors, e.g., as in Ref. 36, and is further supported by theory.[37],[38] A very recent calculation by Palummo *et al.* of gap corrections using the *GW* method for cubic GaN indicates that the LDA gap in that case is too small by 0.97 eV. The same work also estimates the correction to the deformation potential (which is one-third of their[29] linear coefficient *ai)* of the minimum gap at r. Within the LDA the deformation potential *a* is found[29] to be -6.95 eV, in good agreement with our value -7.4 eV. Inclusion of the *GW* correction yields *a*= -8.96 eV. This may indicate that some precaution should be taken when it is assumed in general that LDA errors do not show up in the gap deformation potentials.

The gap values, 2.34 eV and 2.03 eV, given in square brackets for GaN were obtained from a calculation that uses the same potentials as the other calculations, but where coupling to the low-lying (Ga 3d) as well as to the high-lying (Ga *4d) d* states were simultaneously taken into account. Gaps given without brackets were GaN and InN two-panel calculations obtained directly from the upper-panel calculation, i.e., where the coupling is to the higher *d's* only. {All two-panel calculations for GaN and InN do of course treat the low-lying *d* states as relaxed band states, and their major influence on the potential is thus taken into account). It follows that for GaN we find that the gap in the wurtzite structure exceeds the value of the zinc-blende phase by 2.34-2.03= 0.31 eV. This is slightly overestimated because the band structure of wurtzite GaN was calculated for the ideal structure. In the case of AlN we found[11] that changing *c/a* and *u* from the ideal values to those resulting from a total-energy optimization (close to the observed values) causes a reduction of the wurtzite-AlN gap at r by 0.21 eV. Using, for GaN, the experimental structural parameters given above leads to a gap that is only 0.03 eV below the one obtained for the ideal structure. This smaller shift reflects the fact that for GaN the actual structure is closer to the ideal than is the case for AlN. In InN the structural relaxation reduces the gap at r by 0.06 eV. When reading, it should be borne in mind that structural relaxations may change the gaps by amounts that are typically of the order of one-half to two-tenths of an eV. Thus, our best LDA gap at r for AlN is not the 4.73 eV given, but rather 4.52 eV. Also, the gap deformation potentials are somewhat affected by structural relaxation. For AlN we found, for the gap at r, *a*= -9.l eV if the structure is assumed to be ideal, but changing the atomic coordinates to their optimized values we obtained *a*= -7.6 eV. In the cubic structures there are, of course, no corrections to be made for structure relaxations.

The pressure behavior of the energy gaps has in gen- eral a sublinear character. The values of the deformation potentials for the wurtzite and zinc- blende structures vary usually between -3 and -10 eV. Only for the r ***v-Kc*** gaps in the wurtzite and the r *v-Xc* gaps in the zinc-blende structure is a weaker, and almost linear, pressure dependence found. These gaps have deformation potentials which are small in magnitude. The deformation potentials in the rocksalt phase are large in magnitude, approaching the value of 19.3 eV for BN at the r point. The variation of the energy gap with pressure, as calculated here and measured by Perlin *et al.,* is shown in Fig. 5 for GaN in the wurtzite structure. For the conventional III-V compounds the value of the pressure coefficient of the direct gap at the r point varies from 100 to 150 meV /GPa. For all the nitrides these coefficients are much smaller, ranging from 11 to 40 meV /GPa. This contradicts the empirical rule formulated by Paul[40] that pressure coefficients of electronic band-to-band transitions should be the same for all III-V compounds. Rather, it appears that the lattice constant as well as the ionicity should be taken into account in a description of the trends. We find that dE_9/dP in- creases with the lattice constant and decreases with ionicity. This behavior is illustrated in Fig. 6, where we present the pressure coefficients for the III-V compounds as a function of the ratio of lattice constant and ionicity. The ionicities were estimated by Van Vechten[1] and the values for the nitrides are somewhat higher (0.4-0.6) than typical values for other III-V semiconductors (0.2- 0.3). Our ionicity values were obtained as in Ref. 42. The results, together with calculated and experimental lattice constants are summarized. The ionicities calculated here are higher than those obtained by Van Vechten and much higher than ionicities of other III-V.

3. CONCLUSIONS

It has been attempted here to give a rather comprehensive presentation of the results that we have obtained so far within the LDA for the III-V nitrides. When these are compared to experiments one should of course recall the known "deficiencies" of the LOA-eigenvalue spectrum. But it is also important to observe that most quantities are sensitive to structural data, especially to the volume. Some samples used in experiments are grown on lattice-mismatching substrates, and as a result the volume and strain state may not easily be specified. Such complications occur, for example, in the case of GaN in the zinc- blende form. The experimental data of wurtzite GaN are probably more reliable because in that case crystals of good quality can be produced without evaporation onto a substrate. Also, comparing different theoretical calculations it is essential that results for identical structures and volumes are compared. This seems obvious, but one should be aware, for example, that "equilibrium" in some cases is taken to mean "theoretical equilibrium" and in other "experimental equilibrium.". The electronic band structure, its pressure dependence, the dielectric functions, and pressure-induced structural phase transitions have been calculated. By comparing the pressure coefficients of the gaps in several semiconductors we find that trends in the dE_9/dP values cannot be established by considering them to depend only on the bond lengths. The ionicities must be included also in order to obtain a systematic description.

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