PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980 J. PHYS. SOC. JAPAN 49 (1980) SUPPL. A p. 745-748

MICROSCOPIC DESCRIPTION OF PRESSURE INDUCED PHASE TRANSITIONS IN ZINCBLENDE TYPE SEMICONDUCTORS

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The pressure induced phase transition of ZnSe from the zincblende to the rocksalt structure is studied in the framework of the selfconsistent pseudopotential method. The calculated bandstructures indicate that ZnSe remains a semiconductor even after the phase transition. Total energies are calculated for both structures at various lattice constants. We find that it is the electron - ion interaction which is responsible for the structural change.

Under moderate hydrostatic pressure (100 - 200 kbar) semiconductors with zincblende (zb) structure transform into structures with 6-fold coordination like the rocksalt (rs) or the white tin structure. The transition is accompanied by an abrupt change of the atomic density of about 20% [1,2]. In this paper we present a selfconsistent pseudopotential study of this phase transition for the case of ZnSe whose structure under pressure is most probably rs [3,4]. Our aim is to understand the basic mechanism which drives the phase transition. The calculations are based on the local soft-core pseudopotentials for Zn^{2+} and Se^{6+} proposed by Hamann [5], which are of the same form as the Si⁴⁺ potentials described in [6].

Energy bands and charge densities were calculated selfconsistently for both the zb and the rs structures at various lattice constants.



Fig. 1 Valence charge densities in ZnSe for a=5.65% and a=5.1%.

The exchange - correlation potential was approximated by a Wigner type expression [7]. Our results for the bandstructures predict that ZnSe remains semiconducting even after the phase transition with an indirect gap of about l.leV [8]. The charge densities for the zb structure are shown in Fig.(1) for a = 5.65 Å and a = 5.1 R. It is seen that the bond charge decreases rapidly with the lattice constant. This indicates a destabilization of the zb lattice with increasing atomic density.

In order to investigate the mechanism of the phase transition, we have calculated the total energy for both structures at various lattice constants. The total energy can be written as

$$E_{tot} = T + E_{ei} + E_{H} + E_{ii} - E_{xc}^{(2)},$$
 (1)

(-)

where T is the kinetic energy of the valence electrons, E_{ei} , E_{H} and E_{ii} describe the electron - ion interaction, the Hartree energy and the ion - ion interaction energy, respectively, and $-E_{XC}(2)$ is the exchange - correlation contribution to the total energy. The result of the calculations is shown in Fig.(2). In agreement with experiment we find that for small lattice constants the total energy is smaller for the rs structure than for the zb structure, whereas for large lattice constants the total energy is smallest for the zb structure. However, two serious discrepancies exist

- i) the predicted equilibrium lattice constant for the zb structure is too small (5.1 Å against 5.65 Å)
- ii) the absolute minimum of the total energy is found for the rs structure rather than for the zb structure.

Both discrepancies are due to a wrong behaviour of the electron - ion interaction $\rm E_{ei}$ as a function of the lattice constant. $\rm E_{ei}$ can be written as

$$E_{ei} = 8 \widetilde{V}_{ion} (K = 0) + \sum_{n}^{\prime} \int d^{3}rn(r) V_{ion} (K_{n}) e^{iK_{n}r}, \qquad (2)$$

where \overline{V}_{ion} contains only the pseudopart of the ion potential and n(r) is the valence charge density. The second part of the above expression is correct, if the relative bandstructure (i.e. energy gaps, bandwidths) is correct, which we can assume in our case. The term \overline{V}_{ion} (K = 0), however, depends crucially on the pseudopotential model as was already pointed out by Ihm and Cohen [9] for the case of Si. As it is proportional to the reciprocal unit cell volume, it strongly influences the predicted equilibrium lattice constant. After a 30% change of \overline{V}_{ion} (K = 0) we obtain the total energy curves in Fig.(3). We see that this change does not only give the correct equilibrium lattice constant for the zb structure, but also the zb structure.



Fig. 2 Total energies of ZnSe in the zb and rs structure as a function of the lattice constant



Fig. 3 Corrected total energies of ZnSe in the zb and the rs structure as a function of the lattice constant

ture is now predicted to be the stable one. It should be noted that this modification of \tilde{V}_{ion} (K = 0) does not alter the bandstructures and charge densities.

The theoretical transition pressure which can be obtained from Fig.(3) is 285 kbar. This is about twice as large as the experimental value of 137 kbar [3]. According to our calculation the lattice constant changes from 5.25 % to 4.85 % at the transition, which corresponds to a volume change of 21%. Experimentally one finds a = 5.08 \pm 0.03 % for the rs structure after the phase transition [4]. This comparison with the experimental values shows that our description of the phase transition is only a qualitative one, which, however, is sufficient to discuss the driving mechanism of the transition.

In order to analyse the relative role played by the different single contributions to the total energy we have shown in Fig.(4) the quantities

$$x = x (rs) - x (zb)$$
,

as a function of the lattice constant. x denotes the different terms in eq.(1). These energy differences are not affected by our variation of $\widetilde{V}_{\text{ion}}$ (K = 0). As shown in Fig.(4), the electron - ion interaction Eei and the exchange - correlation interaction favor the zb structure, whereas all other terms favor the rs structure. Comparison of the different terms shows that it is the electron - ion interaction which is responsible for the observed phase transition : its respective contribution decreases rapidly with increasing atomic densi-



Fig. 4 Differences between the single contributions to the total energy of the rs and the zb structure as a function of the lattice constant ty and thus causes the destabilization of the zb configuration. This decrease of E_{ei} can be explained by the decrease of the bond charge with the lattice constant, Fig.(1). The pressure dependence of the bond charge allows also to understand the experimentally observed softening of the TA(X) - modes under hydrostatic pressure [3].

(3)

To obtain a more quantitative theoretical understanding, more accurate ionic pseudopotentials are needed. Work on these lines is now in progress.

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