Crystal stability and band structure

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A local criterion of structural stability is discussed. The PT diagrams are calculated for a number of crystals. The possibility is considered of determining the stability regions (from the pseudopotential parameters) and of determining the changes of the symmetry type during a crystal transition in the zinc blende structure.

The universally employed approach to the determination of stable crystal structures reduces to calculation and comparison of the values of free energy. As a rule, the accuracy of these calculations does not make it possible to separate the stable structure. It is of interest to consider a different approach, based on a local criterion. The semimetal–dielectric phase transition in[1,2] was used to analyze the phonon instability that arises in the case of overlap of the direct or indirect gap. In the present paper, the stability limits of semiconductor crystals with zinc blende structure were determined from the instant of the collapse of the indirect gaps of the real band structure.

We calculated the energy spectrum of the electrons with continuous variation of the pseudopotential parameters, of the temperature, and of the pressures. The relations between the energies of the single-electron state at the high symmetry points X, Γ, and L of the Jones band with pseudopotential form factors were used to construct the PT diagrams of Si, InSb, and CdTe. The equilibrium line was determined from the instant of the overlap of the indirect gaps Γ-X and L-Γ. The dependence of the form factors of the pseudopotential on the temperature was taken into account by the Debye-Waller factor. The change of the lattice period with changing pressure and temperature also alters the form factors, and this can be expressed in terms of the change in the reduced radius of the ion core and of the normalization factor. The diagrams are shown in Figs. 1, 2, and 3, which contain also the experimental data and the results of[3], where the diagrams for Si and InSb were constructed on the basis of the minimum of the free energy. The much better agreement observed between the results of these calculations and experiment, compared with the results of the usual energy calculations, together with the relative simplicity of the procedure, can be regarded as a preliminary justification of the applicability of the local criterion of stability besides the usual integral criterion. A similar procedure was used to analyze the tendencies of the band structures in the series of $A_N B_{8-N}$ compounds in the zinc blende structure. The tendency in the band structure, as a function of the pseudopotential parameters, is such that a collapse of the indirect L-Γ gaps takes place with increasing ionicity (on going over to compounds with rock-salt structure).

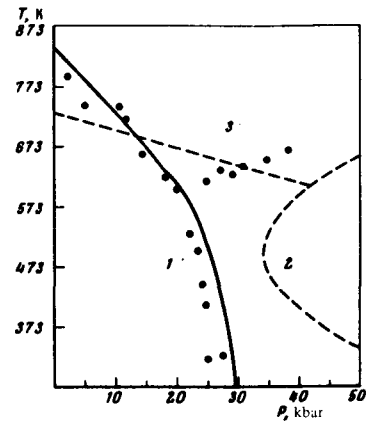

FIG. 2. InSb; the points show the experimental data of[4], dashed—calculations of[3], solid—our calculations.

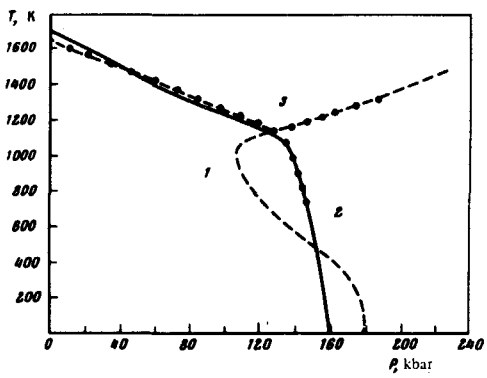

FIG. 1. Silicon; the points show the experimental data of[3], the dashed curve shows the theoretical calculations of[3], and the solid line shows our calculations.

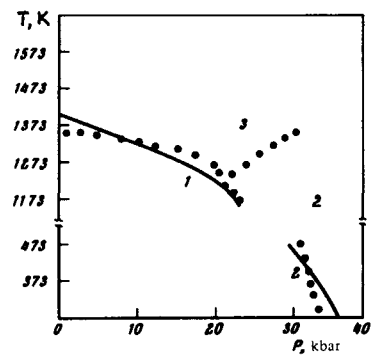

FIG. 3. CdTe; the points show the experimental data of[5], and the solid curves show our calculations; 1—low-pressure phase, 2—high-pressure phase, 3—liquid phase.

The described procedure is not intended for the analysis of the mechanism of structural transitions, but by comparing the type of overlap of the forbidden band with the character of the rearrangement of the structure it is possible to predict the formation of a definite structure modification. Thus, in $A_N B_{8-N}$ structures the pressure and temperature transitions from the covalent structure to A_2B_6 proceed with overlap of the Γ-X gap (this corresponds to a change in the sign of the form factor close to the first zero of $V(220)$), and terminates in formation of a structure of the gray-tin type, whereas the overlap of the L-Γ gap (corresponding to a change in the sign of the first structure form factor of cation $V(111)$) causes a transition to the sodium-chloride structure. Simultaneous overlap of the indirect gap and of the direct gap (for example, at the point Γ) can lead to a change in the type of symmetry or to an incomplete transition of the tetrahedral distortion type (InBi).

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