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Crystal lattice dynamics of various silicon-carbide polytypes

Stanisław Nowak

Technical University, Radom, Poland

ABSTRACT

A valence force field model with an added ionic interaction is applied to an explanation of phonon dispersion curves in 6H-SiC. The phonon dispersion curves in 3C-, 2H-, and 4H-SiC are calculated within the same model. Our results are compared with the published results of ab initio calculations. One can suppose that the present model may be applied for other polytypes of SiC. A phonon contribution to Helmholtz energy is determined for the simplest four polytypes. The results indicate a stability of hexagonal polytypes in relation to the cubic one at high temperatures.

Keywords: lattice dynamics, valence force field model, silicon carbide polytypes.

1. INTRODUCTION

Silicon carbide (SiC) is an interesting semiconducting material. It exists in numerous different structures called polytypes, built up by stacking identical SiC layers in different stacking sequences. In all structures every atom is tetrahedrally surrounded by four atoms of the other species. Some physical properties of SiC are strongly dependent on the crystal structure. The band gap varies from 2.42 eV in 3C-SiC to 3.33 eV in 2H-SiC. The mechanical and thermal stability of SiC is unique. These features imply the prospects for applications in various electronic and optoelectronic devices. Before SiC is generally applied in electronic devices, many technological problems have to be solved. Therefore, the insight into the basic physical properties of SiC is of great interest.

The physical properties of SiC are studied intensively. A great part of these investigations concentrates on the electronic structure of the pure and doped material, as well as on its optical properties. The results of these studies are summarised in a review article by Choyke and Devaty[1]. The crystal lattice dynamics investigation is important for the understanding of the phonon related properties and the polytypism of SiC. Feldman et al.[2,3] have reported the results of Raman spectroscopy of SiC. They have determined the dispersion relation for the direction of phonon wavevector parallel to the trigonal symmetry axe. Olego and Cardona[4,5] have reported the dependence on temperature and pressure of the optical phonons observed in Raman spectra. The absence of the dispersion relation for low symmetry directions has been stimulating theoretical studies. Progress of the density functional theory has enabled the calculation of the crystal structure of different polytypes and the dispersion relations for the simplest polytypes of SiC. Cheng et al.[6] and Käckell et al.[7] have determined the distortion of the hexagonal polytypes structure. Cheng et al.[8] have calculated some phonon frequencies using the frozen phonon method. On the basis of these calculations and the Feldman's experimental results, they have determined a shell model of the cubic SiC lattice dynamics. They have studied the problem of SiC polytypism[9,10], too. Karch et al.[11,12,13] have calculated the phonon dispersion relations in two simplest polytypes using the density functional perturbation theory (DFPT). Hofmann et al.[14] have presented a bond charge model of SiC lattice dynamics, determined on the basis of Feldman data and Karch calculations. Van Elsbergen et.al.[15] have reported the results of surface phonon investigation by means of a high energy resolution electron spectroscopy.

New experimental results have been reported in 1998. Dorner et al.[16] have measured the dispersion relations in 6H polytype by an inelastic neutrons scattering. They have determined the dispersion relation for two mutually perpendicular symmetry directions: along line Δ (Γ-A) and along line Σ (Γ-M). The results for line Δ confirmed the data of Feldman et al.[3]. The 36 nondegenerate phonon branches exist for line Σ, but the measurements of scattering have been performed in the plane of mirror symmetry, therefore 12 branches have been invisible. The results for the line Σ form a complicated structure of dispersion curves. No model of the dynamics has been presented. The authors have made the transformation of the dispersion curves of 3C-SiC to 6H-SiC structure, but the agreement with the experimental results is poor.

The aim of the present paper is to explain the dispersion relations in 6H-SiC. A phenomenological model of valence force field is used. The chemical bonds in SiC are treated as heteropolar covalent bonds, therefore the Madelung energy is included. This model operates with 11 parameters. These parameters are fitted by a least squares method. It is assumed that the interatomic interactions are identical in all SiC polytypes. The dispersion curves and phonon spectra of four

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simplest polytypes are determined. The phonon contribution to Helmholtz energy is calculated in the harmonic approximation on the basis of these results.

2. SILICON CARBIDE POLYTYPES

It is well known that close packed spheres form a face centred cubic structure or a hexagonal close packed structure. The repetition period contains three layers in the fcc structure and two layers in the hcp structure. More complicated structures exist with a longer period of repetition. The phenomenon of forming different crystal structures by stacking identical layers in different sequences is called the polytypism[17].

SiC crystals are built from layers of Si and C atoms. The stacking of SiC layers in different sequences causes the polytypism. The simplest polytype, called 3C, has the cubic structure of sphalerite. The polytype 2H has the hexagonal structure of wurtzite. The primitive unit cells of 3C and 2H polytypes contain one and two SiC molecules respectively. The hexagonal polytypes 4H and 6H unit cells contain four and six molecules respectively. Many other hexagonal polytypes denoted by the symbol nH, and rhombohedrall polytypes denoted by symbol nR, exist. Their structure is more complicated. The Landolt-Börnstein Tables[18] contain the crystallographic data for many polytypes of SiC with the explanation of structure. The ratio of lattice constants *c/a* is equal to $\sqrt{8/3}$ for the 2H structure if the nearest neighbours of each atom form a regular tetrahedron, like in the cubic 3C structure. The ratio c/a is equal to integer multiplicity of this value for other hexagonal polytypes. The lattice constants of four examined polytypes are given in Table 1. One can see that the divergence from the perfect symmetry is very small.

Table 1. Lattice parameters of SiC polytypes at room temperature and distances between nearest neighbours and valence angles

Polytype	a [Å]	c [Å]	Ratio c/a		Bond lengths	Valence angles
			in real structure	in perfect structure	R_0	α
3C	4.3596	-	-	-	1.888	109.47°
2H	3.0763	5.0480	1.6409	1.633	1.885	109.38°
					1.893	109.56°
4H	3.073	10.053	3.2714	3.266	1.882	109.44°
					1.885	109.50°
6H	3.0806	15.1173	4.9073	4.899	1.887	109.44°
					1.889	109.50°

3. VALENCE FORCE FIELD MODEL OF INTERATOMIC INTERACTION IN SILICON CARBIDE

The valence force field method (VFFM) of crystal lattice dynamics has been formulated by McMurry et al.[19]. The bond lengths and interbond angles are used as valence co-ordinates. The potential energy of crystal lattice is expressed in terms of valence co-ordinates changes. VFFM operates with a set of parameters, called valence force constants (VFC).

It is assumed that the short range interaction in SiC originates in the covalent bonds between nearest neighbours. This interaction is expressed in the VFFM. The long range interaction is ionic in nature and expressed in the form of Madelung energy of rigid ions interaction. This interaction is described by the parameter q^2, where q denotes the absolute value of the ion charge. The set of VFC used for description of SiC lattice potential energy is listed in Table 2. The perfect symmetry of crystal, with the lattice constants c equal to $(24)^{1/2}a$, is assumed. This assumption is quite well realised. The phonon dispersion curves of 6H-SiC[16] are used to determine q^2 and the VFC values by the least squares method. The value of ion charge determined in this way equals

$$q = 1.028 \pm 0.010 \text{ e}.$$

The VFC values are presented in Table 2. The value of the first VFC is determined from the condition of equilibrium between Coulomb forces and the repulsive covalent force. One can deduce, from the values of some parameters, that the carbon atoms are negatively charged and silicon atoms are positively charged. It agrees with the ab initio calculations of Karch et al.[11].

Table 2. Valence force constants of 6H-SiC with the explanation. R_0 is the equilibrium distance between nearest neighbours.

VFC	Explanation	Value [N/m]
$R_0^{-1}\cdot(\partial\Phi/\partial R)$	R = distance between nearest neighbours	-15.24±0.29
$\partial^2\Phi/\partial R^2$	R = distance between nearest neighbours	269.42±8.37
$R_0^{-2}\cdot\left(\partial^2\Phi/\partial\alpha^2\right)$	α = C-Si-C angle	9.55±2.75
$R_0^{-2}\cdot\left(\partial^2\Phi/\partial\alpha^2\right)$	α = Si-C-Si angle	21.66±5.66
$\partial^2\Phi/\partial R'\partial R''$	R′,R″ = lengths of Si-C bonds with common Si	-15.17±2.83
$\partial^2\Phi/\partial R'\partial R''$	R′,R″ = lengths of Si-C bonds with common C	34.99±3.62
$R_0^{-1}\cdot\left(\partial^2\Phi/\partial R\,\partial\alpha\right)$	α = angle C-Si-C, R = one leg of α	11.33±0.87
$R_0^{-1}\cdot\left(\partial^2\Phi/\partial R\,\partial\alpha\right)$	α = angle Si-C-Si, R = one leg of α	5.18±0.78
$R_0^{-2}\cdot\left(\partial^2\Phi/\partial\alpha'\,\partial\alpha''\right)$	α′,α″ = angles Si-C-Si, C-Si-C with common leg but not common apex; all atoms are coplanar and the bonds form zigzag structure	1.59±0.31
$R_0^{-2}\cdot\left(\partial^2\Phi/\partial\alpha'\,\partial\alpha''\right)$	α′,α″ = angles C-Si-C with common leg and apex	-2.48±1.15
$R_0^{-2}\cdot\left(\partial^2\Phi/\partial\alpha'\,\partial\alpha''\right)$	α′,α″ = angles Si-C-Si with common leg and apex	2.30±2.32

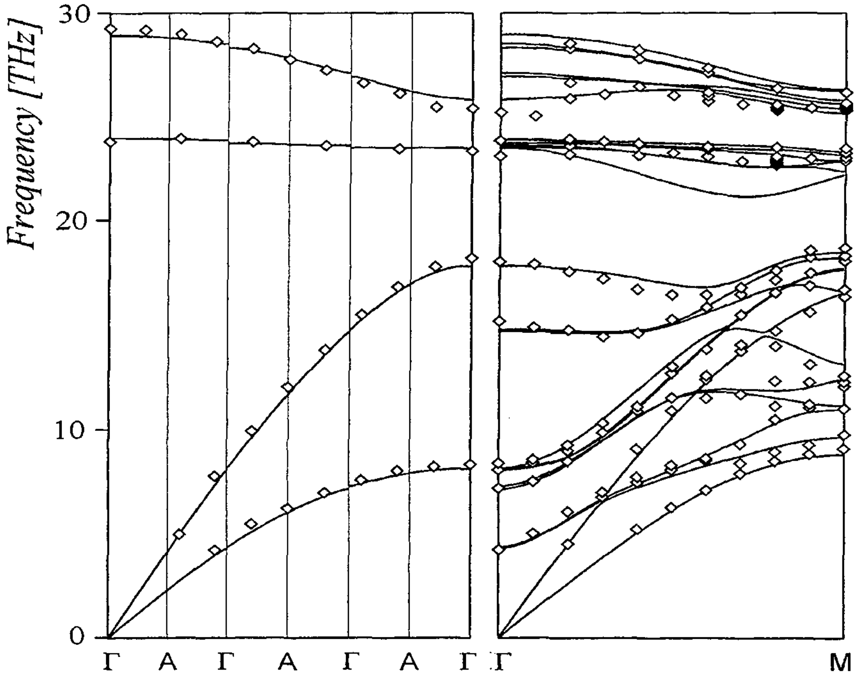

Fig.1.Phonon dispersion curves in 6H-SiC. Diamonds represent the experimental points determined by Dorner et al[16]. The dispersion relations in the hexagonal direction are shown in an extended zones scheme. The curves for phonons measured experimentally are only shown for the ΓM direction.

Dorner et al.[16] have divided the measured phonons into three groups. The phonons with frequency below 19 THz are called "acoustic", the ones with frequency between 20 and 24 THz are called "transverse optical", and with frequency above 25 THz are called "longitudinal optical". Figure 1 presents the experimental points of Dorner et al.[16], and the phonon dispersion relation calculated within VFFM. The data for the line Δ (Γ-A) are shown in an extended zones scheme. One can see from the right part of this figure that the splitting of the "transverse optical" branches is very small and cannot be resolved experimentally. The "optical" phonons for the line Σ (Γ-M) are excluded from the estimation of VFC, but the agreement of the dispersion curves with the experimental points is satisfactory, excepting one curve for "transverse optical phonons".

The dispersion curves calculated for the line Δ (Γ-A) have discontinuities at two "inner" Γ-points. These gaps have been determined by Feldman et al.[2]. The agreement of calculated and measured gaps is within 10%-50% accuracy. This agreement is satisfactory, taking into account that experimental errors are of the same order.

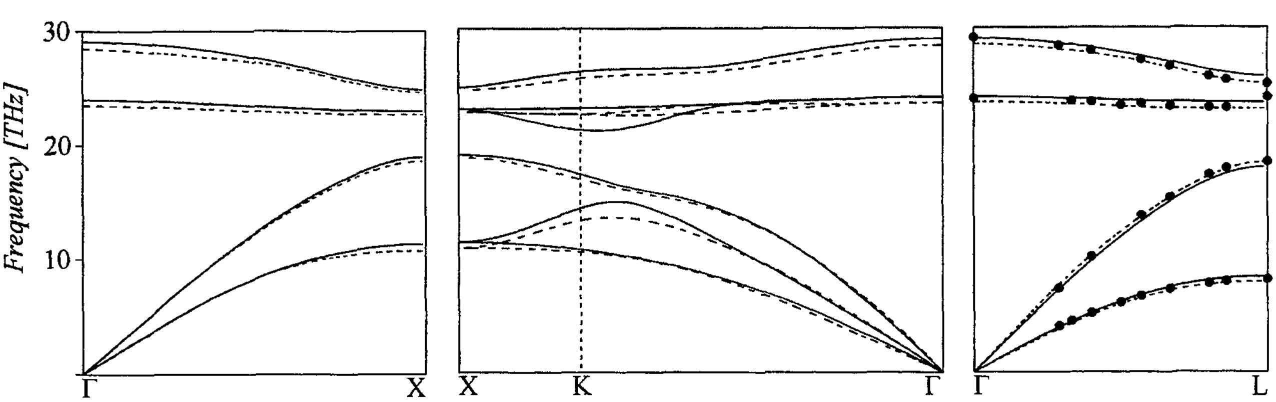

Fig.2. Phonon dispersion relation in 3C-SiC: solid lines - determined within VFFM, dashed lines - determined from DFPT by Karch et al[11]. Circles represent the experimental data of Feldman et al[3].

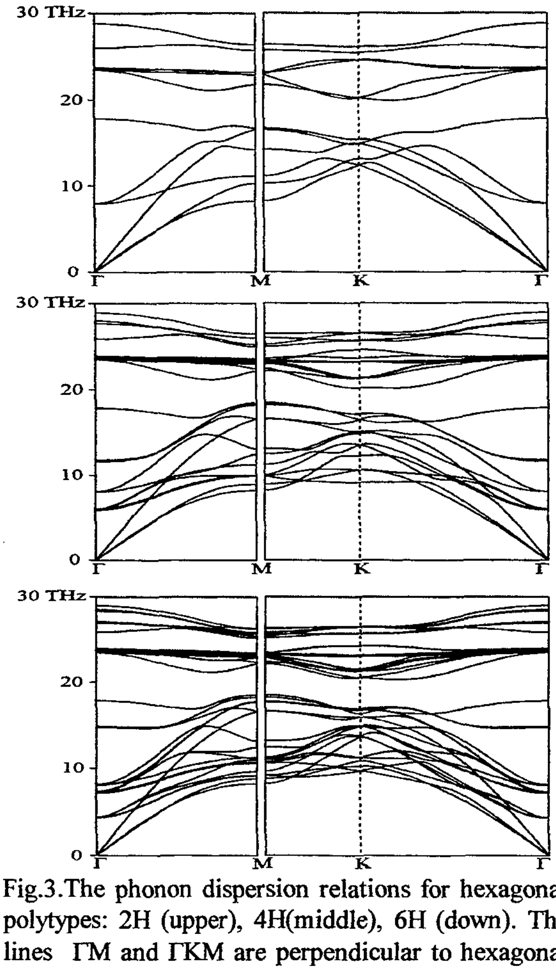

Fig.3.The phonon dispersion relations for hexagonal polytypes: 2H (upper), 4H(middle), 6H (down). The lines ΓM and ΓKM are perpendicular to hexagonal axis and mutually one to another.

The presented VFFM contains eleven independent VFC. The shell model[8] and the bond charge model[14] of 3C-SiC dynamics contain ten parameters each. The bond charge model of 6H-SiC dynamics[14] contains sixteen parameters. It is clear that the number of the present model parameters is reasonable.

A comparison of the different SiC polytypes structure suggests that in all polytypes the chemical bonds and the interatomic interaction are identical. Therefore, it is assumed that in other polytypes the crystal lattice potential has the form of VFFM with the same values of VFC. The phonon dispersion curves for 3C- , 2H-, and 4H-SiC polytypes are calculated. The results are shown in Fig.2 and Fig.3.

The experimental results of Feldman[3], the results of DFPT calculation[11] and dispersion relation determined within VFFM for 3C-SiC are presented in Fig.2. One can see that all the presented result are in satisfactory agreement.

The dispersion relation along the line Δ (Γ-A) in all hexagonal polytypes, presented in the extended zones scheme, is similar to the dispersion relation along the line Λ (Γ-L) for the 3C-SiC. Figure 3 presents the dispersion relations along lines Σ (Γ-M) and T (Γ-K-M) for three simplest hexagonal polytypes. Karch and et.[11] have calculated, by means of DFPT, the dispersion relations in 2H-SiC along line T. Those results agree with ours very well.

Figure 4 presents the frequency dependence of the phonon density of states for four SiC polytypes under examination. One can see that the phonon spectra are similar, but some small differences are noticeable. The spectrum of 3C can be divided into the "acoustic", "transverse optical" and "longitudinal optical" phonons. The "transverse" and "longitudinal optical" phonons in the spectra of hexagonal polytypes are inseparable.

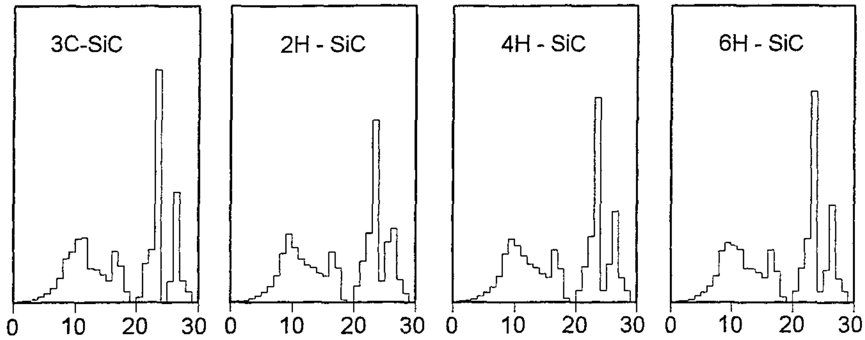

Fig.4. Phonon density of states for different polytypes of SiC

4. PHONON CONTRIBUTION TO FREE ENERGY AND POLYTYPISM

We have determined the crystal lattice dynamics of SiC, therefore we are able to calculate the different thermodynamic quantities related to phonons within the harmonic approximation. The free energy is important in understanding the polytypism phenomenon. It is calculated according to the formula[20]:

$$F_{ph}=\sum_{q,j}\left[\frac{1}{2}h\cdot\nu_{q,j}+k_BT\cdot\ln\left(1-e^{-\frac{h\cdot\nu_{q,j}}{k_BT}}\right)\right]$$

All the calculations are performed using the lattice constants from Table 1. The temperature dependence of the 3C-SiC phonon free energy is presented in the Fig.5. Similar dependencies can be drawn for other polytypes, the differences are very small. Fig.6 presents the phonon free energy of hexagonal polytypes relative to cubic polytype, i.e. $F_{ph}(nH,T)-F_{ph}(3C,T)$.

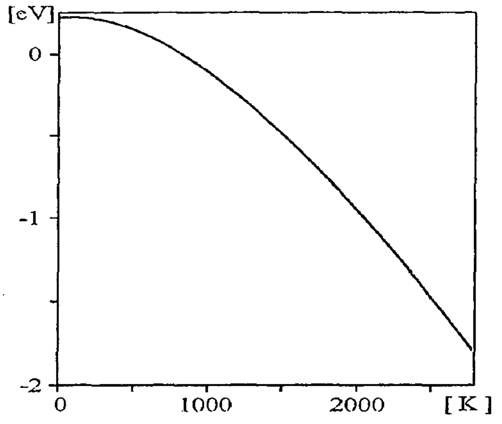

Fig.5.Phonon free energy of cubic silicon carbide (per one molecule SiC)

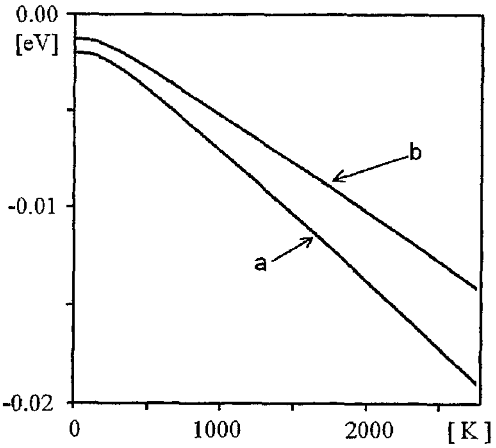

Fig.6. Phonon free energy of hexagonal polytypes relative to the cubic one in electronovolts per one molecule. The curve denoted with the letter *a* stands for 2H, the curve with the letter *b* for 4H and 6H polytypes

Over one hundred SiC polytypes are known[17]. The polytype with the lowest free energy is stable (at low pressure). To solve the problem, one has to take into account other contributions to the free energy. According to results of Käckell et. al. calculation[7] the cohesive energy of 2H polytype is the lowest, which means that the electronic free energy is the highest. Our results suggest that at low temperatures the 2H-SiC is in the nonequlibrium state. The wurtzite structure of SiC is preferred at very high temperatures only. The sphalerite structure of SiC is preferred at low temperatures, according to the analysis of Käckell and our data. The polytypes 6H is stable at middle temperatures. Unfortunately, this conclusion is uncertain within the precision of these calculations. The free energy differences of various polytypes are smaller than the thermal energies at the crystal growth. Therefore, the nonequlibrium effects related to growth can play an important role.

5. CONCLUSIONS

The VFFM has been successfully applied to the calculation of phonon dispersion relations in 6H-SiC. The same potential of interatomic interaction describes the dispersion relations in 2H- and 3C-SiC. The presented agreement between the results of ab initio calculations for 3C and 2H polytypes and our results proves the identity of interatomic interaction in all examined polytypes of SiC. DFPT has a great potential but is restricted to simple structures at present. Thus, a marriage of experiment, ab initio methods and phenomenological models is very useful. The phonon contribution to the free energy stabilises the 6H-SiC structure at middle and high temperatures.

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