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Figure 1

Figure 1: Figure 1

Abstract

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FREQUENCY SPECTRUM OF VIBRATIONS OF THE SILICON LATTICE

The problem of determining the frequency (phonon) spectrum of ion vibrations in the lattice of crystals is among the most important problems of the physics and physical chemistry of the solid state. The fundamental significance of knowledge of the phonon spectrum of solids is evident already from the fact that the temperature dependence of the lattice part of the heat capacity and of other thermodynamic functions, as well as many phenomena of transport and scattering in solids, are determined by the vibrational spectrum of the lattice and by its features. Nevertheless, up to the present time the experimental and theoretical determination of the frequency spectrum of elastic vibrations of the lattice of crystals has been carried out only for a few substances and with comparatively low accuracy.

The aim of the present investigation was to calculate the phonon spectrum of silicon and to determine its principal thermodynamic functions from experimentally determined elastic constants. The calculations were carried out on electronic computers using the Monte Carlo method (ˆ2). The calculation is based on solutions of systems of equations of motion and of the dynamical matrix, first considered by M. Born and von Karman (ˆ3). Subsequently H. Smith (ˆ4) and others determined the dynamical matrix for the diamond structure (ˆ1), in particular, considered in our previous publications (ˆ5).

In the calculations of the phonon spectrum of silicon, there were used—

Fig. 1. Spectra of different types of vibrations of the silicon lattice: three acoustic branches $g_1(\nu)$, $g_2(\nu)$, $g_3(\nu)$, and three optical branches $g_4(\nu)$, $g_5(\nu)$, $g_6(\nu)$.

Fig. 2. Phonon spectra of silicon at temperatures 73° K (a) and 296° K (b)

Figure 2: Fig. 2. Phonon spectra of silicon at temperatures 73° K (a) and 296° K (b)

the elastic constants and the Raman frequency determined from neutronographic data (6) were used. Table 1 gives the values of the elastic constants used at different temperatures and the force constants calculated from them.

Table 1

T, °K	Elastic constants, 10^{11} dyn · cm^{-2}	Elastic constants, 10^{11} dyn · cm^{-2}	Elastic constants, 10^{11} dyn · cm^{-2}	ν_R, cm^{-1}	Force constants, 10^5 g · sec^{-2}	Force constants, 10^5 g · sec^{-2}	Force constants, 10^5 g · sec^{-2}
	C_{11}	C_{12}	C_{44}		α	β	ψ
73	16.75	6.488	8.007	517	0.5550	0.3734	0.0443
293	16.57	6.39	7.96	517	0.5550	0.3698	0.0431

In calculating the phonon spectrum, the components of the frequency distribution density $g(\nu)$ were determined separately by polarizations both for the acoustic (1-3) and for the optical (4-6) branches ($g_i(\nu)$, where $i = 1, 2, \ldots, 6$). In this case the distribution density is defined, as usual, as the derivative of the number of oscillator degrees of freedom with respect to frequency,

$$g(\nu) = \frac{dz}{d\nu} = \lim_{\Delta\nu \to 0} \frac{z(\nu + \Delta\nu) - z(\nu)}{\Delta\nu},$$

where $z(\nu)$ is the number of frequencies less than ν.

Fig. 2. Phonon spectra of silicon at temperatures 73° K (*a*) and 296° K (*b*)

In the calculation, series of computations were carried out on electronic computers, in which the data obtained were smoothed by the method of least squares, and also without smoothing. The resulting dependences $g(\nu)$ obtained in both cases practically coincide. The calculation was performed for frequency intervals (calculation step) corresponding to 1/32, 1/64, and 1/128 of the limiting frequency value. For silicon these steps were, respectively, $0.4853 \cdot 10^{12}$; $0.242 \cdot 10^{12}$; $0.1213 \cdot 10^{12}$ sec^{-1}.

Since the unit cell of silicon, corresponding to the diamond structure, has two structurally nonequivalent positions, the total number of acoustic and optical types of vibrations of different polarizations is equal to 6. As is known, for P

Fig. 3

Figure 3: Fig. 3

structurally nonequivalent positions in the unit cell the total number of vibration types will be $3P$, of which 3 will be acoustic and $3P-3$ optical.

Figure 1 gives the spectra of vibrations by polarizations separately for the acoustic and optical branches. According to the results obtained, the areas under each of the curves are equal to one another.

Figure 2 gives the resulting phonon spectra of silicon, calculated for different temperatures, normalized to the total number of vibrations $3N$ as to unity. It is seen from the figure that for silicon, at least in the interval 73–296° K, the resulting spectrum changes only slightly.

Examination of the low-frequency part of the spectrum indicates that, within the range from 0 to $0.19 \cdot 10^{13}$, the function $g(\nu)$ can be approximated

by the law $A\nu^m$, with the exponent close to the Debye value. However, the m of the initial segment of the resulting curve of the vibrational spectrum is in fact determined by the total course of the curves of the three spectra differing in polarizations: $g_i(\nu) = A_i \nu^{m_i}$, where $i = 1, 2, 3, 4, 5, 6$.

The contribution of the spectra of the optical branches in the low-frequency interval is equal to zero. As is seen from Fig. 2, the largest component in this region is the curve $g_1(\nu)$, corresponding to longitudinal vibrations, which in the very initial segment determines the course of the resulting spectrum curve. The change in the distribution densities of longitudinal and transverse vibrations can also be described by power functions, whose exponents are respectively $m_1 = 1.93$; $m_2 = 3.19$; $m_3 = 2.23$.

The phonon spectrum found makes it possible to determine the temperature dependence of the heat capacity and of other thermodynamic functions. In Fig. 3 the curve, calculated from the phonon spectrum found by us, of the change in the heat capacity of silicon at constant volume c_v is shown, and experimental points are indicated ([7–12]).

Fig. 3. Temperature dependence of the specific heat c_v of silicon and of the Debye characteristic temperature $\theta(T)$ of silicon. The experimental points are taken from the works: a–([7]), b–([8]), v–([9]), g–([10]), d–([11]), e–([12]).

Also shown in Fig. 3 is the curve of the dependence of the Debye characteristic temperature θ on temperature. The heat-capacity curve c_v constructed from our data is comparatively close to the experimental one. The deviation of the behavior of θ from the horizontal straight line for the case $\theta(T) = \text{const}$ indicates that the Debye function is only a rough approximation to reality.

Fig. 4. Temperature dependence of the internal energy $U(T)$ and the Gibbs free energy $F(T)$

Fig. 4

Figure 4: Fig. 4

In Fig. 4 are shown the curves, calculated from the phonon spectrum found by us, of the change in the internal energy $U(T)$ and the Gibbs free energy $F(T)$.

Thus, the complete phonon spectrum of silicon obtained in the present work makes it possible to find the temperature dependences of the principal thermodynamic functions, as well as of a number of quantities that determine the temperature dependence of many physical properties of silicon.

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