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THERMAL EXPANSION BEHAVIOR OF SILICON AT LOW TEMPERATURES

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Lattice parameters, thermal expansion coefficients and Grüneisen parameters of silicon are determined by an X-Ray diffraction method in the temperature range of 180–40 K without the use of liquid gases. Thermal expansion of silicon becomes negative below 120 K which is discussed in terms of its lattice vibrations and crystal structure.

1. INTRODUCTION

Thermal expansion behavior of elements in the fourth group of the periodic table – silicon, germanium, gray tin and $A^{II} B^{IV}$ compounds is peculiar. These tetrahedrally bonded substances exhibit negative thermal expansion coefficients for temperatures $T \leq 0.2\theta$ where θ is the Debye characteristic temperature. Theories have been proposed by Barron^{1,2} to explain how the negative thermal expansion of a solid comes about but no clear treatment of this problem is available at present.

The agreement between the thermal expansion data obtained by dilatometric methods and those obtained by X-Ray diffraction techniques is not always good.³ This is probably due to the fact the dilatometric methods use bulk samples which contain a variety of micro and macro defects affecting the expansivity results. Whereas the X-Ray method is independent of such errors since it

measures the size of the crystal unit cell directly.

Batchelder and Simmons⁴ have studied the thermal expansion of a single crystal of silicon in an X-Ray back reflection, rotating camera. They found that the thermal expansion of silicon becomes zero at 117 K and negative below this temperature. All the other thermal expansion studies on silicon were made by dilatometric methods. Gibbons⁵ observed the thermal expansion of silicon single crystals by an interferometric technique. His measurements show that the thermal expansion of silicon was zero at 120 K and negative upon further cooling. Carr *et al.*⁶ determined the thermal expansion of silicon by a dilatometric technique, finding negative thermal expansion of silicon below 130 K but to a much smaller extent than that reported by Batchelder and Simmons.

2. EXPERIMENTAL TECHNIQUE AND RESULTS

Lattice parameter measurements in the present investigation were made in a symmetrical back-reflection focusing X-Ray diffraction camera in

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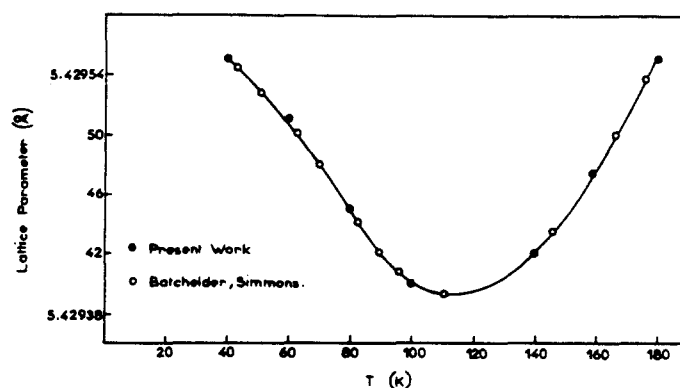


FIG. 1. Lattice parameters of silicon as a function of temperature.

the temperature range of 180–40 K. Cooling was achieved by means of a Joule–Thompson pump eliminating the use of liquid gases. Necessary film shrinkage and refraction corrections were made. The detailed description of the experimental apparatus appears elsewhere.⁷

Silicon powder of 99.999 per cent purity was obtained from Koch Labs., England. Particle sizes of 20μ or less were needed to obtain uniform and sharp diffraction patterns. Lattice parameters were calculated by using the high angle reflection $(444)a_1$ produced by copper $K_{\alpha(1)}$ radiation ($\text{Cu } K_{\alpha(1)}\lambda = 1.54051 \text{ \AA}$). The standard deviation of the lattice parameters was $\pm 5.7 \times 10^{-6} \text{ \AA}$. These results are compared with those of Batchelder and Simmons in Fig. 1. From Fig. 1 it is evident that the lattice parameters obtained by our method agree very well with those found in a different laboratory, by a different method, different temperature calibrations and measurement procedures. This agreement in turn confirms the accuracy of the measurement and control of temperature in our low temperature camera.

Linear thermal expansion coefficients, $\alpha = a^{-1}(\partial a/\partial T)_p$ for silicon were calculated from equation 1 which relates the lattice parameter, $a(\text{\AA})$ as a function of temperature, $T(\text{K})$ from 180–40 K range. The present results of thermal expansion coefficients

$$a(\text{\AA}) = 5.42926 + 1.56 \times 10^{-5} T - 3.15 \times 10^{-7} T^2 + 2.15 \times 10^{-9} T^3 - 4.68 \times 10^{-12} T^4 \dots \quad (1)$$

compare favorably with those of Batchelder and

Simmons but the agreement with the data obtained by dilatometric methods of Carr *et al.* and Gibbons is only fair (Fig. 2). We observe that thermal expansion of silicon becomes zero at 120 K and negative below this temperature. The maximum magnitude of the negative thermal expansion is found to be -0.60×10^{-6} at 70 K.

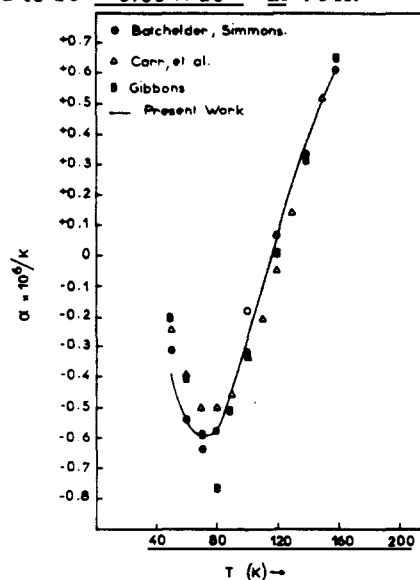


FIG. 2. Linear thermal expansion coefficients of silicon as a function of temperature.

The Grüneisen parameters, $\gamma = 3 \alpha K_T / C_v$, where α is the coefficient of linear thermal expansion, K_T is the isothermal bulk modulus, C_v is the specific heat at constant volume and V the molar volume, were calculated by using our results for α and V and literature data for C_v^0 and K_T .⁹ These calculations for γ are listed in Table 1 together with the thermal expansion coefficients.

Table 1. Linear thermal expansion coefficients and Grüneisen parameters of silicon at low temperatures.

T (K)	$\alpha \times 10^6$ (K ⁻¹)	γ
160	0.63	0.18
140	0.48	0.16
120	0.12	0.05
100	- 0.28	- 0.14
90	- 0.44	- 0.25
80	- 0.56	- 0.38
70	- 0.60	- 0.50
60	- 0.54	- 0.60
50	- 0.38	- 0.61

3. DISCUSSION

The negative thermal expansion of silicon below 120 K can be easily explained in terms of its Grüneisen parameters and the crystal structure. Since thermal expansion in silicon is clearly related to the Grüneisen parameter, all the discussion pertaining to Grüneisen parameters will also correspond to its thermal expansion behavior. The Grüneisen parameter, γ , is a weighted average of the Grüneisen parameters of various lattice vibrational modes, γ_i

$$\gamma = \frac{\sum_{i=1}^{3N} \gamma_i C_i}{\sum_{i=1}^{3N} C_i} \dots \quad (2)$$

where

$$\gamma_i = -(\partial \log \omega_i / \partial \log V)_T \dots \quad (3)$$

and C_i are the contributions to the specific heat

(C_v), from the i th mode. Now, usually in the crystal, all the γ_i will be positive yielding a positive Grüneisen parameter, γ . That is what is generally expected that, as the volume of a crystal decreases, the frequency of vibration increases giving rise to positive γ_i for different lattice vibrational modes. However, if some of the γ_i for certain modes are negative and if they dominate over the positive γ_i upon cooling, the weighted average γ will be negative and the thermal expansion will also become negative. At low temperatures only the transverse acoustic modes are important and some of these for silicon must be negative and dominating over the rest of the positive modes to give rise to negative Grüneisen parameters for silicon below 120 K.

An intuitive insight can be obtained if one relates the negative thermal expansion of silicon to its crystal structure.⁵ The negative thermal expansion is also exhibited by many tetrahedrally bonded covalent substances like InAs, GaAs, InSb, GaSb, α -Sn, Ge and vitreous silica, etc, which either possess a diamond cubic or a zincblende type structure. In each of these cases, the atoms have a fourfold coordination, and they are loosely packed structures. Because of loose packing, the restoring forces for the transverse modes of the bonds may be weak, and these factors may be responsible for the negative γ_i 's for certain transverse modes dominating over the positive ones.

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Nous avons déterminé, par diffraction des rayons X, les paramètres, les coefficients de dilatation thermique et les coefficients de Grüneisen du silicium, entre 40 et 180 K, sans employer de gaz liquide. Les coefficients de dilatation thermique du silicium sont négatifs en-dessous de 120 K. Nous considérons ses vibrations de réseau et sa structure cristalline pour discuter cette anomalie.