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Thermal Expansion of Some Crystals with the Diamond Structure

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The linear coefficient of thermal expansion of silicon, germanium, and indium antimonide has been measured in the range 4.2°K–300°K using an interferometric method. In the cases of silicon and germanium, these values are used to calculate the variation in Grüneisen's factor γ with temperature and the result is compared with the predictions of T. H. K. Barron. Silicon and indium antimonide have negative values for γ at low temperatures and some of the requirements for a structure to behave in this manner are suggested, namely, fourfold coordination in the lattice, covalent bonding, and openness of structure.

INTRODUCTION

SINCE semiconductors are important for solid state devices their physical properties are of great interest. In addition, silicon was reported[1] to have a negative value for the coefficient of thermal expansion below approximately 100°K. It is one of the few solids known to have this unusual property. It was decided, therefore, to investigate the coefficient of thermal expansion of three semiconductors, namely, silicon, germanium, and the III-V compound indium antimonide in order to see if this anomaly was present in other solids with the diamond cubic structure.

EXPERIMENTAL TECHNIQUE

The interferometric technique used in this study is based on that described by Nix and MacNair.[2] The interferometer consists of two optical flats separated by three specimens, in a triangular array, of the material to be investigated. The specimens are in the form of cones ~6 mm high and 2–3 mm in diameter at base. The apparatus was designed[3] to cover the range 4.2–300°K by placing the interferometer in a chamber at the base of a thin-walled stainless steel tube which could be lowered into a helium Dewar. The temperature of the interferometer could be controlled to within ±0.05°K by a constantan wire heater surrounding the interferometer. Above 20°K the temperature was measured with a copper-constantan thermocouple and below 20°K with a calibrated carbon resistor thermometer. In order to maintain stable thermal equilibrium, it was necessary to allow helium gas at a pressure ~1 mm Hg in the interferometer chamber. A helium discharge tube was used as a source of monochromatic light, the He 5878A line being isolated by a Baird interference filter. In all cases, the specimen heights were adjusted to give 2 to 3 fringes across the upper optical flat which was 1 cm in diameter. The interferometer was kept at constant temperature for 20 minutes in order to attain thermal equilibrium before the fringe system was photographed on 35-mm Kodak Tri X Pan. It was found possible to measure the position of the fringes with respect to a fiducial mark engraved upon the upper optical flat to within 1/20 of a fringe spacing, which corresponds to a change in length of approximately 150 A.

MATERIALS

In addition to the semiconductors, it was decided to measure the expansion of an annealed single-crystal specimen of aluminum to check the apparatus and compare with previous measurements on the coefficient of expansion of aluminum. The aluminum was 99.99% pure and the axis of the cones was a ⟨111⟩ direction.

Silicon.—Because it was suspected that the growing technique affected thermal behavior, single crystals prepared by three different techniques were measured.

(1) A crystal was grown by the crystal-pulling technique and the crystal was rotated during growth. This crystal contained electrically active impurities with a concentration of $\sim 10^{15}$/cc and an oxygen concentration of 9×10^{17} atoms/cc. Two crystals were prepared, one with a ⟨100⟩ growth direction and the other, a ⟨111⟩ growth direction. The axis of each set of cones was the growth direction.

(2) A crystal was grown by the crystal-pulling technique without rotation of the crystal during growth. This crystal contained electrically active impurities with a concentration of $\sim 10^{15}$/cc and an oxygen concentration of 3×10^{17} atoms/cc. The axis of the cones was a ⟨100⟩ direction.

(3) A crystal was grown by the floating-zone technique. This crystal contained electrically active impurities with a concentration of $\sim 2\times10^{13}$/cc and an oxygen concentration of $<10^{15}$ atoms/cc. The cone axis was a ⟨100⟩ direction.

Germanium.—The crystal was grown by the crystal-pulling technique in vacuo and contained electrically active impurities corresponding to a concentration of 10^{14}/cc. The cone axis was a ⟨100⟩ direction.

Indium Antimonide.—Two crystals were obtained by the crystal pulling technique. The crystals contained electrically active impurities of 10^{14} and 10^{16}/cc, respectively. In each case the cone axis was a ⟨100⟩ direction.

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[1] H. E. V. Erfling, Ann. Physik **41**, 467 (1942).

[2] F. C. Nix and D. MacNair, Rev. Sci. Instr. **12**, 66 (1941).

[3] The author is indebted to M. E. Fine, who was responsible for the initial design of the apparatus.

EXPERIMENTAL RESULTS

In all cases the reported coefficient of linear thermal expansion was obtained graphically from a plot of the expansivity $[\Delta l/l_{272.2}]$ with temperature. The probable error in expansivity is $<0.5\%$ and in the expansion coefficient is greater but $<1.5\%$.

Aluminum.—Table I gives the value of expansivity $\beta=[\Delta l/l_{273.2}]$ and coefficient of thermal expansion, $\alpha=[(1/l_{273.2})(dl/dT)_P]$ at 10°K intervals from 20°K–300°K. The values in the table are the averages of three separate runs, all of which agreed within the small experimental error. The value of β at 80°K is within 0.3% of that reported by Nix and MacNair.[4] The results of Bijl and Pullan[5] do not agree so well and are about 2% greater than those reported here in the range 20–200°K.

TABLE I. Aluminum.

T°K	$\beta=\frac{\Delta l}{l_{273.2}}\times10^3$	$\alpha=\frac{1}{l}\left(\frac{dl}{dT}\right)_p\times10^6$
20	−3.659	0.06
30	−3.657	0.68
40	−3.645	1.87
50	−3.619	3.21
60	−3.581	4.83
70	−3.524	6.82
80	−3.444	9.00
90	−3.344	10.99
100	−3.231	12.65
110	−3.107	14.05
120	−2.968	15.11
130	−2.817	16.00
140	−2.653	16.84
150	−2.484	17.61
160	−2.314	18.25
170	−2.127	18.82
180	−1.933	19.43
190	−1.740	19.86
200	−1.539	20.34
210	−1.340	20.70
220	−1.130	21.04
230	−0.918	21.36
240	−0.704	21.63
250	−0.486	21.90
260	−0.282	22.10
270	−0.069	22.25
280	+0.146	22.39
290	+0.369	22.49
300	+0.597	22.59

Silicon.—Experimentally no difference in expansivity was observed among any of the specimens tested. Table II gives the value of β and α between 40°K and 300°K and is the average of six runs. At 300°K the reported value of α is $\sim$1.5% higher than that given by Fine.[6] The temperature at which α becomes zero is 119.5°K, which is 11°K higher than that reported by Fine. However, the agreement is quite good when one considers the very low expansivity of silicon.

TABLE II. Silicon.

T°K	$\beta=\frac{\Delta l}{l_{273.2}}\times10^3$	$\alpha=\frac{1}{l}\left(\frac{dl}{dT}\right)_p\times10^6$
40	−0.168	−0.05
50	−0.169	−0.20
60	−0.172	−0.41
70	−0.177	−0.59
80	−0.184	−0.77
90	−0.192	−0.51
100	−0.195	−0.31
110	−0.198	−0.15
120	−0.199	+0.01
130	−0.197	+0.16
140	−0.195	+0.31
150	−0.191	+0.47
160	−0.186	+0.65
170	−0.178	+0.84
180	−0.169	+1.05
190	−0.157	+1.28
200	−0.143	+1.49
210	−0.127	+1.67
220	−0.111	+1.83
230	−0.093	+1.97
240	−0.070	+2.07
250	−0.052	+2.16
260	−0.030	+2.22
270	−0.007	+2.27
280	+0.015	+2.30
290	+0.039	+2.31
300	+0.062	+2.33

Germanium.—Table III gives the values of β and α at 10°K intervals from 40°K–300°K and is the average of three separate runs. The values for β reported are on the average 10% less than those of Fine[7] in the range he covered, namely, 80°K–300°K. D. MacNair (private communication) covered the range 150°K–300°K and his values are approximately 2% larger than those reported in this paper.

TABLE III. Germanium.

T°K	$\beta=\frac{\Delta l}{l_{273.2}}\times10^3$	$\alpha=\frac{1}{l}\left(\frac{dl}{dT}\right)_p\times10^6$
40	−0.811	0.07
50	−0.810	0.20
60	−0.808	0.39
70	−0.803	0.67
80	−0.794	1.05
90	−0.782	1.54
100	−0.763	2.20
110	−0.739	2.79
120	−0.708	3.25
130	−0.675	3.62
140	−0.638	3.91
150	−0.609	4.12
160	−0.559	4.29
170	−0.516	4.45
180	−0.472	4.58
190	−0.425	4.70
200	−0.376	4.82
210	−0.328	4.93
220	−0.279	5.03
230	−0.229	5.13
240	−0.178	5.23
250	−0.126	5.32
260	−0.072	5.42
270	−0.018	5.50
280	+0.037	5.59
290	+0.094	5.67
300	+0.151	5.75

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[4] F. C. Nix and D. MacNair, Phys. Rev. **60**, 597 (1941).

[5] D. Bijl and H. Pullan, Physica **21**, 253 (1955).

[6] M. E. Fine, J. Chem. Phys. **21**, 1427 (1953).

[7] M. E. Fine, J. Appl. Phys. **24**, 338 (1953).

TABLE IV. Indium antimonide.

T°K	$\beta=\frac{\Delta l}{l_{273.2}}\times 10^3$	$\alpha=\frac{1}{l}\left(\frac{dl}{dT}\right)_p\times 10^6$
10	−0.739	< −0.06
20	−0.746	−0.10
30	−0.764	−1.72
40	−0.777	−0.82
50	−0.782	−0.33
60	−0.784	+0.28
70	−0.778	+0.89
80	−0.766	+1.50
90	−0.748	+2.18
100	−0.724	+2.76
110	−0.694	+2.22
120	−0.659	+2.48
130	−0.625	+3.67
140	−0.588	+3.83
150	−0.563	+3.96
160	−0.510	+4.08
170	−0.470	+4.17
180	−0.428	+4.27
190	−0.395	+4.35
200	−0.341	+4.43
210	−0.296	+4.51
220	−0.250	+4.58
230	−0.204	+4.64
240	−0.158	+4.71
250	−0.112	+4.78
260	−0.064	+4.83
270	−0.016	+4.89
280	+0.033	+4.95
290	+0.082	+5.00
300	+0.133	+5.04

Indium antimonide.—No difference was observed in the results from the two samples and Table IV gives the values of β and α at 10°K intervals from 10°K–300°K. This table is the average of four separate runs. The only data available on indium antimonide are reported by Potter,[8] who lists average values for α between 83–213°K, 212–253°K, and 253–293°K as being 3.9×10^{-6}, 4.4×10^{-6}, and 4.7×10^{-6}, respectively.

If we calculate an equivalent set of average values from the values of β in Table IV, we obtain 3.8×10^{-6}, 4.5×10^{-6} and 4.9×10^{-6}. Further comment is not warranted because of the limitation imposed by the averaging process.

DISCUSSION

Figure 1 shows the variation of expansivity $\beta=[\Delta l/l_{273.2}]$ with temperature for silicon, germanium, and indium antimonide. Silicon and indium antimonide have a minimum in the expansivity at 119.5°K and 56°K, respectively; below this temperature the coefficient of linear expansion is negative. A discussion of this unusual behavior is best approached by a consideration of the Grüneisen factor.

From statistical mechanics[9] a factor γ_j can be derived for each vibrational frequency ν_j, where

$$\gamma_j=-\partial\ln\nu_j/\partial\ln V. \tag{1}$$

If one assumes that the frequency spectrum is determined entirely by the limiting frequency $\nu_{\max}$, characterized by the Debye θ, then the γ_j's are the same and equal to

$$\gamma=-\partial\ln\nu_{\max}/\partial\ln V. \tag{2}$$

By using thermodynamic relationships, it can be shown that

$$\gamma=\alpha V/\chi C_v, \tag{3}$$

where α is the volume coefficient of thermal expansion, V the volume per gram atom, χ the compressibility, and C_v the specific heat at constant volume. The γ defined in Eq. (3) may be identified with a γ_G which was originally obtained by Grüneisen from an empirical equation of state and shown to be a constant. However, it has been realized for many years that γ_G need not be a constant and the assumptions which were made have been discussed recently by Barron.[10] From Eq. (2) it can be seen that γ is a measure of the variation of vibrational frequency with volume. The validity of the assumptions can be tested by observing if γ is independent of temperature according to Eq. (3).

Contrary to Grüneisen's original thesis, Bijl and Pullan[5] were the first to show from experimental measurements that the Grüneisen factor is not a constant for aluminum and copper in the temperature range 20°K–300°K. The assumption that the γ_j's can be represented by an average value is therefore incorrect and $\gamma(T)$ obtained from Eq. (3) really represents the variation of γ, the integral of the γ_j's over all modes

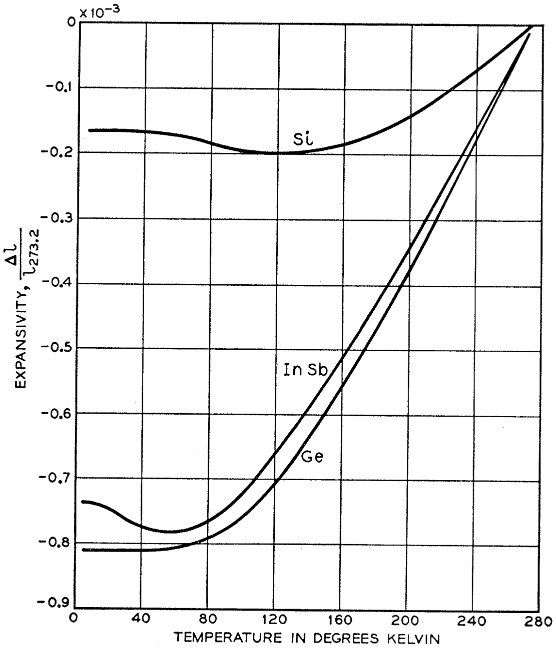

FIG. 1. Variation of expansivity with temperature for silicon, germanium, and indium antimonide.

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[8] R. F. Potter, Phys. Rev. **103**, 47 (1956).

[9] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939).

[10] T. H. K. Barron, Phil. Mag. **46**, 720 (1955).

and all directions, with temperature. Barron[10,11] has recently explained the variation of γ with temperature by a detailed analysis of the frequency spectrum of cubic lattices, in a manner similar to that used by Blackman[12] for the Debye characteristic temperature θ. By assuming various force laws between atoms, Barron has been able to show (a) that one can expect high- and low-temperature limits for γ, namely, γ_∞ and γ_0; (b) that the main variation in γ should be expected in the region $T/\theta_\infty \sim 0.3$ where θ_∞ is the high-temperature limit of the Debye θ; and (c) that it is possible to have a negative value of γ associated with certain transverse modes. Thus, since the experimentally determined γ is the weighted average of $\sum\gamma_j$, if the transverse modes dominate, γ may be negative for particular cases.[13] A physical interpretation of a negative γ can be seen from Eq. (1), namely, that the frequency of vibration increases with increasing volume. Barron[11] has suggested a mechanical analog for such behavior.

In the case of silicon and germanium it is possible to evaluate γ, as defined by Eq. (3), from existing experimental data without involving any empirical relationships. It is believed that this is the first case where this has been possible in the critical temperature range, i.e., below $T/\theta_\infty = 0.3$. For silicon, γ was calculated using the following data: C_v from the values for C_p of Pearlman and Keesom[14] and Anderson[15] using the thermodynamic relation $C_p - C_v = 9V\alpha^2/\chi$, χ from the results of the author,[16] and a value of V_{25° of 12.08 cm^3/gram atom. For germanium γ was calculated using the following data: C_v from the values for C_p of Esterman and Wertman[17] and Hill and Parkinson,[18] χ from values of Fine[19] and McSkimin,[20] and a value for V_{25° of 13.63 cm^3/gram atom. The variation of γ with the reduced temperature T/θ_∞ is shown in Fig. 2.

In the case of germanium it can be seen that γ varies rapidly in the region $T/\theta_\infty \simeq 0.3$ and is beginning to approach a limiting value below $T/\theta_\infty \simeq 0.1$. These results provide an excellent confirmation of Barron's general arguments. Silicon again shows a rapid variation of γ in the region $T/\theta_\infty \simeq 0.3$; however, the low-temperature region is obscured by the minimum at $T/\theta_\infty \simeq 0.13$ which is a consequence of the point of inflection in the expansivity near 80°K. Unfortunately, it is not possible to evaluate γ below $T/\theta_\infty \simeq 0.08$ as the interferometric technique for measuring α is not sufficiently sensitive, even though values for C_p are available. In order experimentally to determine the low-temperature limit γ_0, a technique which is at least an order of magnitude more sensitive than the interferometric method will have to be found.

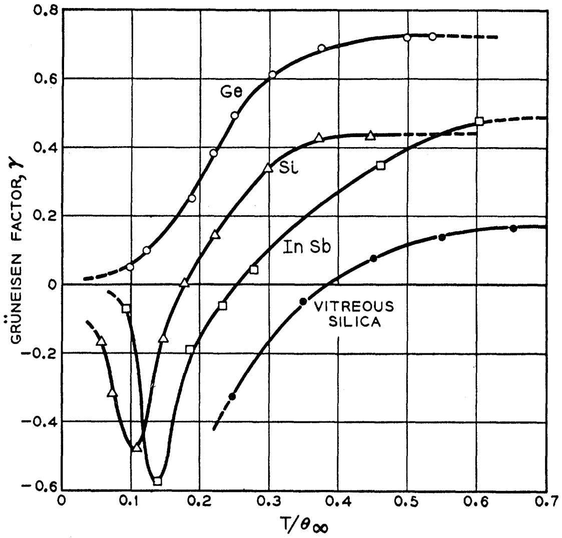

FIG. 2. Variation of Grüneisen factor γ with reduced temperature T/θ_∞ for germanium ($\theta_\infty = 400$°K), silicon ($\theta_\infty = 674$°K), vitreous silica ($\theta_\infty = 495$°K), and indium antimonide ($\theta_\infty = 214$°K). [The specific heat data used for indium antimonide was obtained from P. H. Keesom and N. Pearlman (private communication); the compressibility from R. F. Potter.[7]]

Although reliable measured values are not available below 120°K, it is interesting to note the similarity in the variation of γ with temperature in vitreous silica and those of germanium and silicon. The γ for vitreous silica is plotted in Fig. 2 using the following data: C_p from Westrum[21]; χ from Fine,[22] McSkimin,[20] and Spinner[23]; α from the data of Beattie *et al.*,[24] and a value of V_{25° of 0.454 cm^3/gram atom.

Grüneisen's factor γ for silicon becomes negative below 120°K, which can be interpreted as $\sum\gamma_j$ for the transverse modes being negative and dominating the longitudinal contributions. The only other established cases for such behavior are vitreous silica,[25] zinc blende,[26] and indium antimonide reported in this paper. It is of interest to note that in each of these cases the atoms have a fourfold coordination, they are loosely packed structures, and the interatomic covalent bonding is strong. Because of the loose packing, the restoring force for transverse modes of the bonds may be weak, and this characteristic may be the factor responsible for the transverse modes, which have associated with them negative γ_j's, dominating at temperatures small compared with θ_D.

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[12] M. Blackman, Proc. Roy. Soc. (London) A148, 365 (1934).

[13] M. Blackman (private communication) has recently determined theoretically a negative γ_0 for the zinc blende structure.

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[19] M. E. Fine, J. Appl. Phys. 26, 862 (1955).

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[25] R. B. Sosman, *Properties of Silica* (Chemical Catalogue Company, New York, 1927), p. 384.

[26] H. Adenstedt, Ann. Physik 26, 69 (1936).

Polycrystalline α-uranium has been reported[27] to exhibit a negative volume coefficient of thermal expansion near 50°K. The α-uranium structure is an "open" structure and consists of corrugated layers of atoms parallel to (010) planes in which the atoms have fourfold coordination. Furthermore, it has been suggested[28] that the bonding in these layers is at least partially covalent in nature. In view of the foregoing discussion, it is not surprising that the volume coefficient of thermal expansion could become negative at low temperatures.

Using similar arguments, Anderson[29] has recently made an analysis of the conflicting values for θ_D from elastic and thermal measurements. He showed that for vitreous silica the low-temperature vibrational behavior was dominated by transverse vibrations. If these transverse modes have associated with them negative γ_j's, it is not surprising that vitreous silica has a low-temperature negative expansivity.

According to the arguments of Barron, therefore, the magnitude of the expansivity depends upon the competition between negative γ_j's arising from some transverse modes and positive γ_j's arising from all longitudinal modes and some transverse modes. To determine *a priori* whether the integrated γ would be positive or negative at any particular temperature involves a very exact knowledge of the lattice spectrum, and in particular the details of the force constants. One can conceive the possibility that the weighted average $\sum\gamma_j$ would remain positive at all temperatures for germanium, while with slightly different force constants the weighted average $\sum\gamma_j$ would be negative at low temperatures for silicon. It is obvious that there is a need for determining the precise details of the force constants in diamond-like structures.

ACKNOWLEDGMENTS

I would like to thank Mr. V. G. Chirba for his invaluable help in making many of the measurements and Dr. O. L. Anderson for many stimulating discussions.

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Asymptotic Solution of the Thomas-Fermi Equation for Large Atom Radius

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The general form of the solution ϕ of the Thomas-Fermi equation in the limit of large atom radius x_b is determined as an asymptotic series valid for points x near the atom boundary, by a perturbation on the Sommerfeld inverse-cube form. This generalization of the Coulson-March solution yields the complete form of that part of the asymptotic solution which depends on disposable constants of integration (two in number). The general terms of the series are determined explicitly, and coefficients of leading terms are given numerically as ratios in terms of the disposable constants. The two constants of integration are fixed simultaneously, in general, by the requirement of continuity in value and slope of ϕ with the result of a series solution for small x, and by the boundary condition. The general method of obtaining the two constants of integration for a compressed atom as power series in an inverse power $x_b^{-\lambda_2}$ of x_b is outlined, where $\lambda_2=\frac{1}{2}(73^{\frac{1}{2}}-7)$; coefficients of leading terms are calculated by making use of numerical results of Kobayashi *et al.* The products $x_b^3\phi_b$, where ϕ_b is the boundary value of ϕ, and $x_b^7(\phi_i'-\phi_{i,\infty}')$, where $\phi_i'-\phi_{i,\infty}'$ is the difference of the initial slope of ϕ from its value for an isolated atom, are each represented as an asymptotic power series in $x_b^{-\lambda_2}$ for x_b large. The two leading coefficients in the former series and the leading coefficient in the latter are determined numerically to relatively high accuracy and compared with values obtained by Gilvarry from the approximate solution of Sauvenier. The results are used to construct a fitted function for ϕ_b in which only one of five terms appearing is evaluated empirically, and which reproduces accurate numerical values of ϕ_b from solutions of the Thomas-Fermi equation within 0.1%, in general. This accuracy exceeds by a factor of about ten that obtained previously by March and by Gilvarry with fitted functions containing three and two theoretical terms, respectively. The connection between the general asymptotic solution and previous approximate results is discussed.

I. INTRODUCTION

CONSIDERABLE attention has been focused in the past few years on the calculation of equations of state and thermodynamic functions for materials under pressure, and a practicable, if oversimplified, approach to this problem is provided by the Thomas-Fermi approximation, as first emphasized by Slater and Krutter.[1] All the thermodynamic functions on this model for zero temperature can be obtained conveniently from functions of the pertinent parameters, as proposed originally by Gilvarry,[2] which are based on a fit to the numerical data but are of a form which tends

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[2] J. J. Gilvarry, Phys. Rev. **96**, 934 (1954).