DONNAY, J. D. H. & NOWACKI, W. (1954). Memoir No. 60, The Geological Society of America.
HAVIGHURST, R. J., MACK, E. & BLAKE, F. C. (1924). *J. Amer. Chem. Soc.* **46**, 2368.
NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc., Lond.* **57**, 477.
TAYLOR, A. & FLOYD, R. W. (1950). *Acta Cryst.* **3**, 285.
SETTERBERG, C. (1882). *Öfvers. Vetensk. Akad. Förh., Stockh.* **6**, p. 23.
SHARMA, S. S. (1950). *Proc. Indian Acad. Sci.* A, **31**, 339.
VISVAMITRA, M. A. (1959). *Proc. Indian. Acad. Sci.* **49**, 326.

Acta Cryst. (1961). **14**, 355

Thermal Expansion of Tetragonal Tin

BY V. T. DESHPANDE AND D. B. SIRDESHMUKH
Physics Department, College of Science, Osmania University, Hyderabad – 7, India

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Accurate values of the lattice parameters of tetragonal tin have been determined at various temperatures up to 151 °C., using a back-reflection camera and Cohen's analytical procedure. These data have been used to evaluate the two principal coefficients of thermal expansion and their variation with temperature. The room-temperature results agree with those reported in the literature but the rates of increase of the coefficients with temperature are found to be higher.

Values of the mean Grüneisen's constant are found to increase with temperature.

Introduction

Childs & Weintroub (1950) have made the first extensive study of the coefficients of thermal expansion of tetragonal tin, giving their variations from room temperature to the melting point. They found that both $\alpha_{\perp}$ and $\alpha_{\parallel}$ increase with temperature. They also observed that large discrepancies existed between their results and the single X-ray values of mean coefficients given by Shinoda (1933) and Kossolapow & Trapesnikow (1936). Lee & Raynor (1954) report a linear variation of the lattice parameter with temperature, (cf. Pearson, 1958), over the range of temperature studied. The present paper reports the results of a similar X-ray study.

Experimental

Tin metal obtained from Johnsons of Hendon was melted and fine filings were taken from the cooled block. These were annealed at 150 °C. for 16 hrs. The experimental set-up used to obtain X-ray diffraction pictures was the same as described by Deshpande & Mudholker (1960). Three or four $\alpha_1\alpha_2$ doublets, all with $\sin^2\theta > 0{\cdot}90$, were used to evaluate the lattice parameters. Cohen's (1935) least-squares method was used, in combination with the error function $f(\varphi) = \cos\varphi - \cos^2\varphi$. The accuracy of the results was checked by (i) comparing the room-temperature values of the parameters obtained by the back-reflection camera with those obtained with the help of Debye–Scherrer photographs, (ii) imposing a deliberate systematic error in the camera radius to test the efficacy of the error function and (iii) taking two photographs at the same temperature and comparing the results. Invariably these checks gave satisfactory results and it is estimated that the uncertainty in both the parameters is not more than 0·0003 Å.

Results and discussion

The lattice parameters at various temperatures are given in Table 1. Their values at 25 °C., obtained by graphical extrapolation, are

$$a = 5{\cdot}8318 \pm 0{\cdot}0003,\quad c = 3{\cdot}1819 \pm 0{\cdot}0003 \text{ Å}.$$

These are in fair agreement with the values,

$$a = 5{\cdot}8312,\quad c = 3{\cdot}1814 \text{ Å}$$

(converted from kX.), given by Jette & Foote (1935). From the cell dimensions the two coefficients of expansion defined by

$$\alpha_{\perp} = \frac{1}{a_{25}}\cdot\frac{\Delta a}{\Delta t} \quad\text{and}\quad \alpha_{\parallel} = \frac{1}{c_{25}}\cdot\frac{\Delta c}{\Delta t},$$

have been evaluated, at different temperatures. Usual methods of curve fitting give for the two coefficients the following equations.

$$\alpha_{\perp} = 14{\cdot}64 \times 10^{-6} + 6{\cdot}00 \times 10^{-8}t - 0{\cdot}576 \times 10^{-10}t^2$$
$$\alpha_{\parallel} = 28{\cdot}14 \times 10^{-6} + 9{\cdot}36 \times 10^{-8}t + 0{\cdot}029 \times 10^{-10}t^2 .$$

Table 1. *Lattice parameters of tin at various temperatures*

Temperature (°C.)	a	c
35	5·8327 Å	3·1825 Å
60	5·8357	3·1854
82	5·8383	3·1882
98	5·8396	3·1897
112	5·8412	3·1921
137	5·8451	3·1954
151·5	5·8461	3·1971

The values of the coefficients calculated from these equations (A) are given in Table 2, along with corresponding values from Childs & Wintroub (CW). The last column of this table contains the values of the coefficient of volume expansion, $\beta=2\alpha_{\perp}+\alpha_{\parallel}$. Results from other workers are summarized in Table 3.

Table 2. *Coefficients of expansion of tin at different temperatures*

Temp. (°C.)	$\alpha_{\perp}\times 10^6$ A*	$\alpha_{\perp}\times 10^6$ CW	$\alpha_{\parallel}\times 10^6$ A*	$\alpha_{\parallel}\times 10^6$ CW	$\beta\times 10^6$ A*
30	16·4	16·2	30·9	32·0	63·7
50	17·5	16·6	32·8	32·9	67·8
70	18·5	17·2	34·7	34·1	71·7
90	19·6	17·7	36·6	35·1	75·8
110	20·5	18·2	38·5	36·4	79·5
130	21·5	18·7	40·4	37·4	83·4
150	22·3	19·2	42·2	38·4	86·8

* Present authors.

A comparison of these values indicates that the present values are much lower than those given by Kossolpow & Trapesnikow and by Shinoda. They agree reasonably with those of Ieviņš & Straumanis and also, at low temperatures, with those given by Childs & Weintroub. As regards the temperature variation of the coefficients, Lee & Raynor report constant values over the whole range, while Childs & Weintroub find that the coefficients increase with temperature. Our results support the finding of the latter, but the increase with temperature of both the coefficients is more rapid in our results than in those of Childs & Weintroub. This difference in temperature variation is probably linked with the effects of lattice defects discussed by Deshpande & Mudholker (1960) and Deshpande (1960).

Table 3. *Coefficients of expansion of tin as given by various authors*

Authors	Range of temp. or mean temp.	$\alpha_{\perp}\times 10^6$	$\alpha_{\parallel}\times 10^6$
Shinoda (1933)	114 °C.	25·7	45·8
Kossolpow & Trapesnikow (1936)	72 °C.	22·4	46·4
Ieviņš & Straumanis (1938)	14–48 °C.	16·77	32·24
Lee & Raynor (1954)	up to 170 °C.	16·7	36·4

Calculation of Grüneisen's constant

We have calculated Grüneisen's constant for tin at different temperatures, using the relation $\gamma=\beta V/\psi C_v$ and the present data on the coefficient of volume expansion. The specific heat C_v was calculated from the Nernst–Lindemann formula, $C_p-C_v=AC_p^2T$, using for C_p the data given by Kelley (1934). Room temperature values of the volume V and the compressibility ψ were utilized. Table 4 gives the results of these calculations. Grüneisen (1926) gives 2·14 as the value of this constant. Our value is also of the same order. However, γ is found to increase with temperature. Sharma (1950, 1951) has calculated Grüneisen's constants for many cubic substances and has observed similar increase in their values. Wilson (1941) and Wilson & Stokes (1941) have arrived at similar conclusions after comparing the ratio β/C_p for aluminium and lead respectively, at different temperatures.

Table 4. *Values of the Grüneisen's constant of tin at different temperatures*

$V = 16{\cdot}33$ cm.^{3} $\quad \psi = 1{\cdot}91\times 10^{-12}$ cm.^{2}/dyne
$C_p = 5{\cdot}05+0{\cdot}0048T$ (°K) $\quad A = 2{\cdot}08\times 10^{-5}$

t (°C.)	$\beta\times 10^6$	C_p	C_v	$\gamma=\beta V/\psi C_v$
30	63·7	6·50	6·23	2·01
50	67·8	6·60	6·31	2·12
70	71·7	6·70	6·38	2·22
90	75·8	6·79	6·44	2·32
110	79·5	6·89	6·51	2·44
130	83·4	6·98	6·57	2·50
150	86·8	7·08	6·64	2·58

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References

Childs, B. G. & Weintroub, S. (1950). *Proc. Phys. Soc., Lond.* B, **63**, 267.
Cohen, M. U. (1935). *Rev. Sci. Instrum.* **6**, 68.
Deshpande, V. T. & Mudholker, V. M. (1960). *Acta Cryst.* **13**, 483.
Deshpande, V. T. (1960). Paper read at the Symposium on Solid State, Bangalore.
Grüneisen, E. (1926). *Handbuch der Physik*, Band X. p. 32. Berlin: Springer.
Ieviņš, A. & Straumanis, M. (1938). *Z. anorg. Chem.* **238**, 175.
Jette, E. R. & Foote, F. (1935). *J. Chem. Phys.* **3**, 605.
Kelley (1934). *Bur. Min. Bull.* p. 371.
Kossolapow, G. F. & Trapesnikow, A. K. (1936). *F. Exp. Theor. Phys. U.S.S.R.* **6**, 577.
Lee, J. A. & Raynor, G. V. (1954). *Proc. Phys. Soc., Lond.* B, **67**, 737.
Pearson, W. B. (1958). *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, p. 860. London: Pergamon Press.
Sharma, S. S. (1950). *Proc. Indian. Acad. Sci.* A, **31**, 83.
Sharma, S. S. (1951). *Proc. Indian. Acad. Sci.* A, **32**, 268.
Shinoda, G. (1933). *Kyoto Imp. Univ. Proc.* A, **16**, 193.
Wilson, A. J. C. (1941). *Proc. Phys. Soc., Lond.* **53**, 235.
Wilson, A. J. C. & Stokes, A. R. (1941). *Proc. Phys. Soc.. Lond.* **53**, 658.