

Accurate measurement of thermal expansion of solids between 77 K and 350 K by 3-terminal capacitance method

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Abstract. The construction of a three-terminal capacitance cell and a bath type cryostat to measure thermal expansion of solids in the temperature range 77 K to 350 K is described. Calculation of the thermal expansion coefficients by using spline approximation is discussed along with the various errors involved in the measurement. The capacitance cell is calibrated by using aluminium and germanium as standard reference materials. The cell has an accuracy of 4% in the measurement of thermal expansion coefficient and a resolution of 1 Å change in length of sample of length 1 cm.

Keywords. Thermal expansion; low temperature; three-terminal capacitance method.

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1. Introduction

Thermal expansion of solids gives useful information about their electronic and lattice properties. A large number of techniques have been developed for accurate measurement of thermal expansion over a wide range of temperatures (Barron *et al* 1980; Krishnan *et al* 1979). Some of the important techniques are based on x-ray diffractometer, optical interferometer, linear variable differential transformer and three-terminal capacitor. Among these, the three-terminal capacitance technique (White 1961) is very sensitive and accurate. In this method, a change in the length of the sample produces the displacement of one capacitor plate, relative to the other and hence a change of electrical capacitance. This change is detected by a ratio transformer bridge (Thompson 1958) with a ppm resolution.

Depending on the nature, shape and dimensions of the sample, capacitance cells of different geometries have been used by earlier workers (White 1961; Tilford and Swenson 1972; Browder and Ballard 1969; Schefer *et al* 1975; Pott and Schefzyk 1983; Villar *et al* 1980 and Heberlein 1974). The capacitance cell we have designed has several unique features. It has an adjustable gap so that samples of different dimensions can be used. It has provision for adjusting the parallelism of the capacitor plates. Further, it has an open structure so that one has an easy access to the sample.

2. Capacitance cell

The capacitance cell is shown in figure 1. Except for the mica insulators and the stainless steel springs, all parts of the cell are made of high conductivity copper. The copper parts

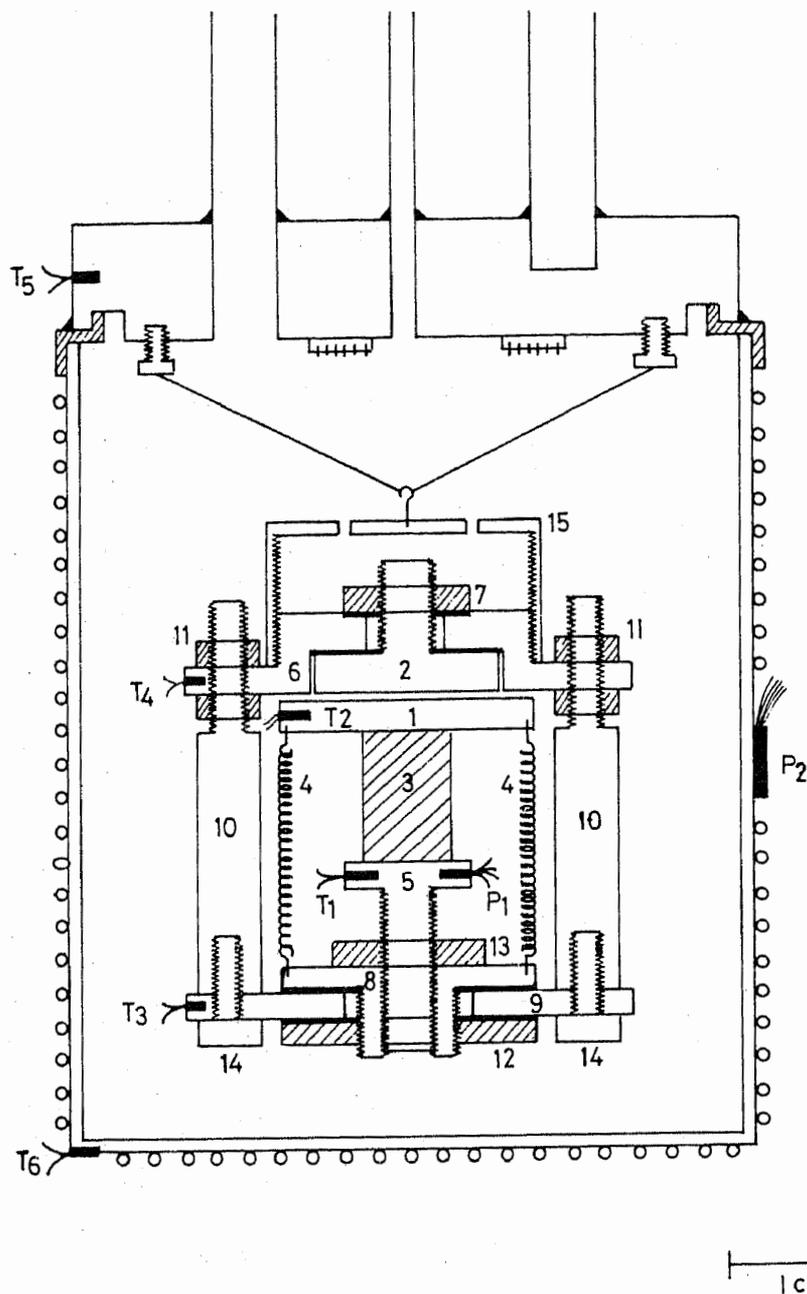


Figure 1. Capacitance cell.

are first machined to dimensions slightly higher than required, stress-relieved by heat-treating in vacuum at 300 C and then the final machining performed. The cell is of cylindrical shape with dimensions of about 4 cm length and 3.5 cm in diameter. 1 and 2 in the figure are the two capacitor plates. The lower plate 1, which is a high potential electrode is a circular copper disc of about 2 cm diameter and 0.25 cm thickness. This plate rests firmly on the top of the sample 3 by virtue of three stainless steel springs 4. The upper plate 2 which is a low potential electrode is of diameter 1.5 cm and is firmly mounted inside the guard ring 6 by means of the nut 7. The plate 2 is insulated from the guard ring and the nut by using mica sheets of thickness 0.05 mm. A similar mechanical

fastening with mica insulation is used at the bottom of the cell to fix the sample platform base 8 to the cell base 9 by means of the nut 12. The guard ring 6 is firmly fixed at the top of the three posts 10 by means of three pairs of nuts 11. The three posts, each of dimension 3 cm in length and 0.5 cm in diameter, are firmly fixed to the base 9 by means of three copper screws 14. The sample platform 5 can be raised or lowered and fixed to the base 9 by means of the checknut 13. This arrangement allows one to get any desired gap between the electrodes 1 and 2. The sample geometry is unimportant except that it should have two flat and parallel surfaces defining the length of the sample. The length of the sample can be anywhere between 0.5 cm and 1.5 cm. By using the nuts at the top of the posts, the guard ring with the plate 2 can be tilted a little to get a parallel gap between the electrodes. A parallel gap is an important consideration in securing linearity between the gap and the reciprocal of capacitance (Brown and Bulleid 1978; Khan *et al* 1980). Both faces of the electrode 1 are polished and made parallel to each other to better than 1' of arc. The electrode 2 along with the guard ring is also ground and lapped, a tolerance of a few millionths of an inch being placed on flatness. This ensures a uniform gap between the capacitor plates. A copper cup 15 serves to shield the electrode 2 completely from surroundings. The cell is suspended inside a metal chamber by a teflon thread by means of a hook attached to copper cup. To realize the three-terminal geometry, this cup is earthed along with the guard ring.

3. Cryostat

A schematic diagram of the cryostat used for low temperature measurement is shown in figure 2. The capacitance cell described earlier is suspended inside the chamber 1. This chamber can be sealed to the top flange 2 by means of Wood's metal. A thin-walled narrow stainless steel tube 3 of diameter 0.35 cm and a wide tube 4 of diameter 0.9 cm open into this chamber. The narrow tube 3 is used to inject dry helium gas into the chamber 1 from a helium balloon. This tube is also connected to the vacuum system through the valve 6. By operating the valves 5 and 6, the chamber 1 can be flushed with helium gas initially and then maintained at a pressure of 1 torr. The wider tube is used to bring the capacitor leads, platinum resistance thermometer leads and the thermocouple leads into the chamber.

Chamber 1 is surrounded by two more coaxial cylindrical chambers 8 and 9. Chamber 8 can be screwed into the flange 10 while the chamber 9 can be sealed to the flange 11 by using Wood's metal. The space between the chambers 1 and 9 is evacuated and maintained at a pressure of about 10^{-2} torr. Two stainless steel tubes open into this space and serve for evacuation and bringing in the leads. The chamber 9 is completely immersed in a liquid nitrogen dewar.

4. Thermometry and temperature control

A digital cryogenic thermometer/controller (Model DRC-84C, Lakeshore Cryotronics Inc) is used for both measuring and controlling temperature to a resolution of 0.1 K. The platinum resistance thermometer P_1 mounted just below the sample platform measures the sample temperature while the other thermometer P_2 mounted on chamber 1 serves as a sensor. The thermometers with a layer of Apiezon grease are

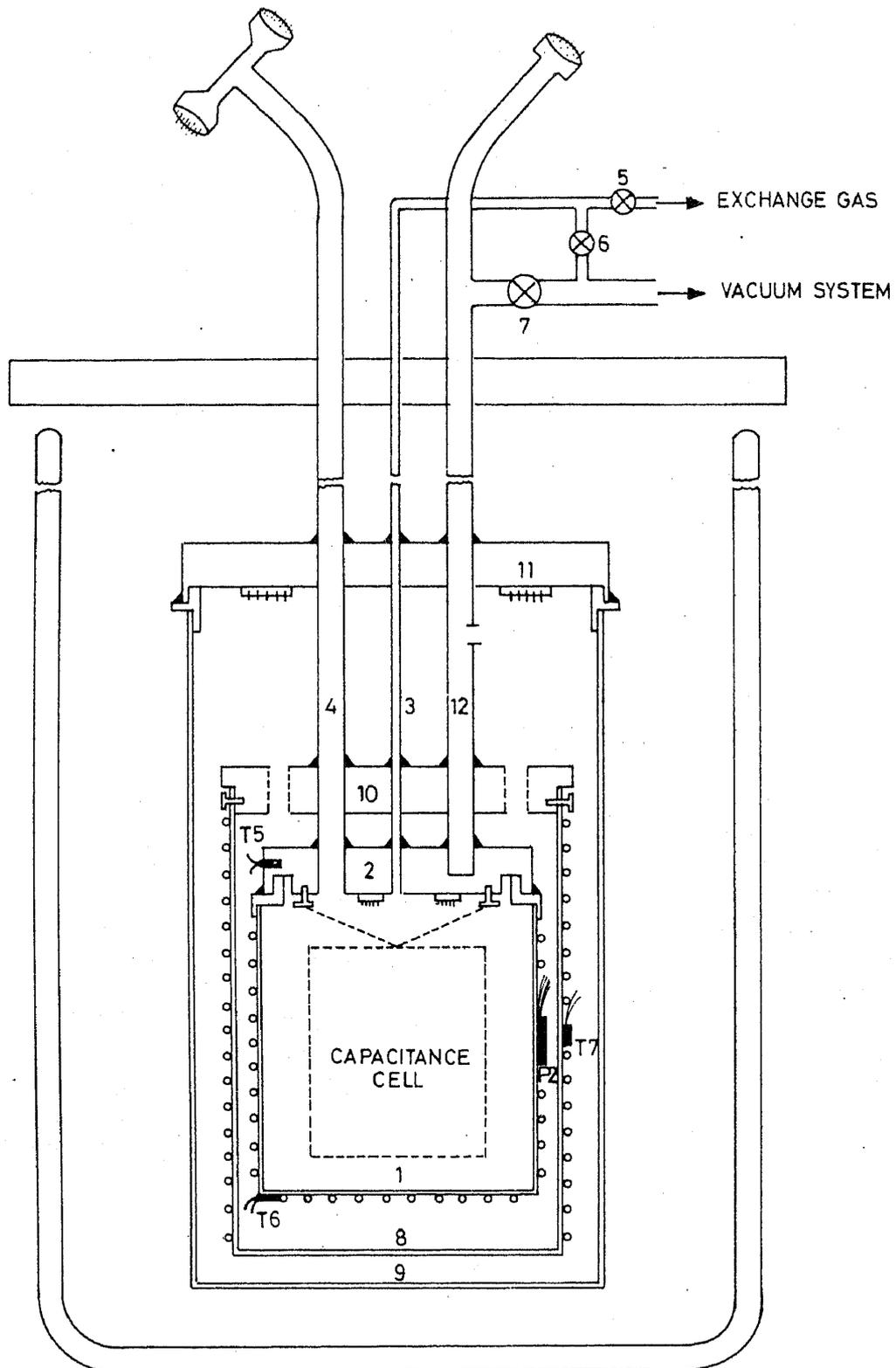


Figure 2. Schematic diagram of cryostat assembly.

inserted into thin-walled close fitting copper tubes which are then soldered for good thermal contact. A 25 ohm heater element is wrapped around chamber 1. The sample and the capacitance cell are indirectly heated by a controlled heating of the chamber 1. Helium exchange gas filled at a pressure of about 1 torr in the chamber helps the cell and the sample to quickly attain the temperature of chamber 1. The exchange gas also helps in maintaining a uniform temperature all over the cell and the sample. Any thermal gradient across the sample or the cell is checked by four copper-constantan differential thermocouples T_1 to T_4 with their common terminal at the sample platform. To reduce any thermal gradient across the chamber 1, the temperature of the chamber 8 is manually controlled by winding a heater over it and feeding by a continuously variable power supply. Three more copper-constantan thermocouples T_5 , T_6 and T_7 , one each at the top and bottom of the chamber and another at the chamber 8, with their common junction at the sensor are used to measure the gradient across the chamber 1 and the gradient between the chambers 1 and 8. Power to the heater on the chamber 8 is manually varied so as to achieve minimum temperature gradient across chamber 1.

5. Capacitance measurement

The capacitance is measured by using a six-decade ratio transformer bridge, constructed in our laboratory and whose details are given elsewhere (Krishnapur 1983). The null detector of the bridge is a lock-in amplifier (Brookdeal model 9503). It has a sensitivity of $1 \mu\text{V}$ and incorporates an oscillator which provides a sinusoidal signal of 10 V rms and 5 kHz to excite the bridge. A 10 pF standard capacitor with 0.1% accuracy in its value and 1 ppm stability, supplied by M/s. Gen Rad Co., USA has been used as a reference capacitor. The connection between the capacitance cell and the bridge is performed via stainless steel coaxial cables. The upper electrode is connected to the 'low' side of the bridge and the lower plate to the 'high' side.

The functional block diagram of the experimental assembly is shown in figure 3.

6. Calculation of results

Let L_c and L_s represent the length of the cell and the sample contributing to the variation of the capacitor gap g with temperature. Since only that length of the cell which is equal to the length of the sample plus the capacitor gap contributes to the differential expansion, we have

$$L_s = L_c - g. \quad (1)$$

Hence

$$\alpha_s = \left(\frac{L_c}{L_s}\right) \alpha_c - \left(\frac{1}{L_s}\right) \frac{d}{dT}(g), \quad (2)$$

where α_s and α_c represent the linear expansion coefficients of the sample and the cell material respectively.

For an ideal parallel plate capacitor having plates each of area $A \text{ cm}^2$ and separated by a gap $g \text{ cm}$ in a medium of dielectric constant ϵ , we have

$$c = (\epsilon A / (4\pi g)) \text{ e.s.u.} \quad (3)$$

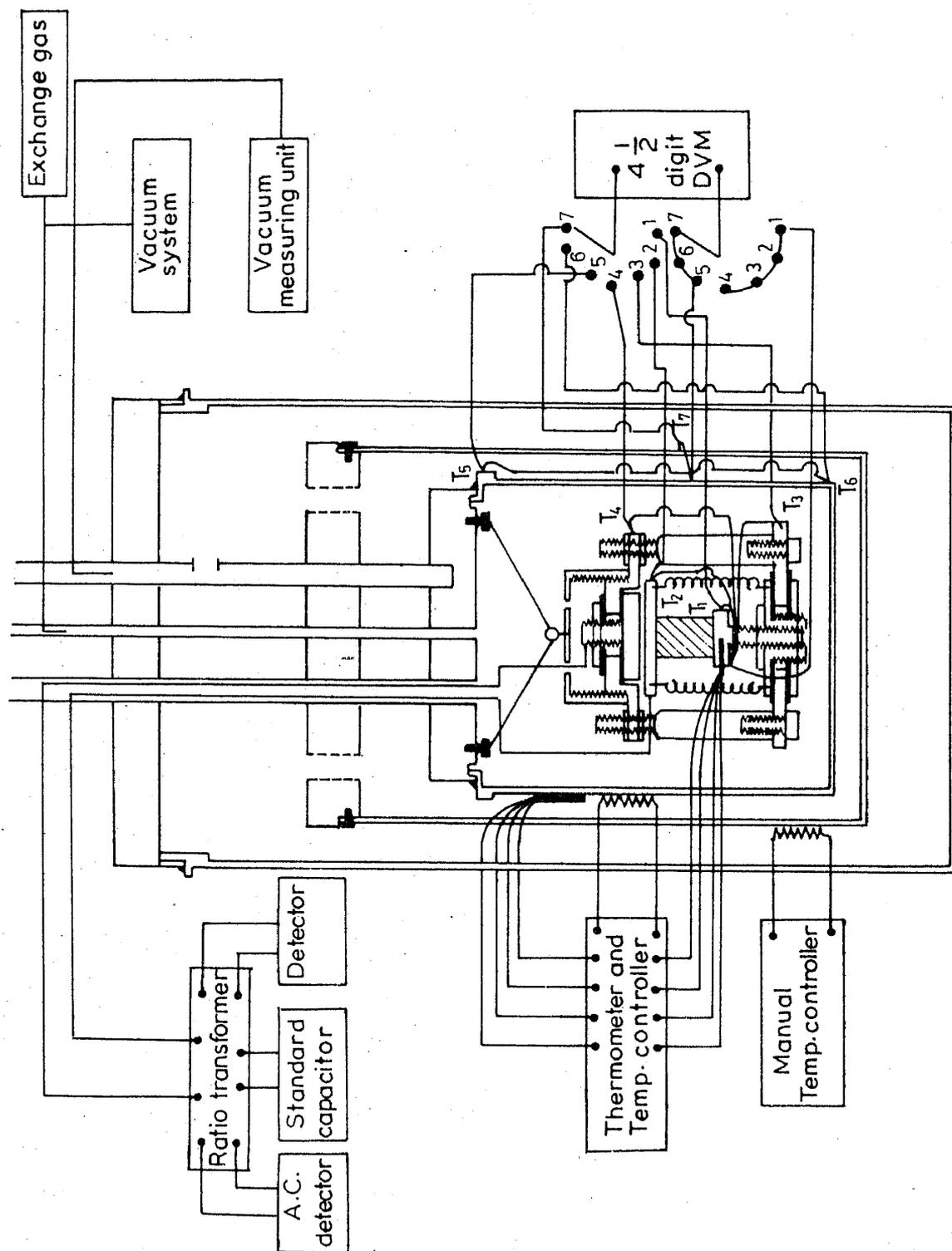


Figure 3. Functional block diagram of the experimental assembly.

The medium in the cell volume being dry helium gas at a pressure of about 1 torr, its dielectric constant is very near to unity. The capacitor plates being circular of radius r cm, we have

$$c = (r^2/4g) \text{ e.s.u.} \quad (4)$$

For our cell $r = 0.75$ cm and 1 esu of capacitance = $(10/9) \times 10^{-12}$ Farads. Hence

$$c = (0.15625/g) \text{ pF.} \quad (5)$$

In all the experiments the gap is normally adjusted to be about 0.02 cm. For this $c = 7.8$ pF. Further, since $g = 0.15625/c$ and $\Delta g = (0.15625/c^2) \Delta c$. The resolution in the capacitance measurement being 10^{-6} pF, we have $\Delta g = 0.25 \text{ \AA}$. Substituting (5) in (1) we get

$$\alpha_s = \left(\frac{L_c}{L_s} \right) \alpha_c - \frac{0.15625}{L_s} \frac{d}{dT} \left(\frac{1}{c} \right). \quad (6)$$

The ratio transformer bridge is set to read $1/c$ directly. By measuring $1/c$ as a function of temperature T , $(d/dT)(1/c)$ can be calculated at different temperatures either by numerical differentiation or by a graphical method or by a computer fit. α_c is the thermal expansion coefficient of the cell material i.e. copper which contributes to the differential expansion. Since the overall contribution of the cell including the mica insulation has to be included in this term, α_c is referred to as the cell constant. To calculate α_s , the cell constant should be first determined, as a function of temperature. This is done by making measurements on some standard samples of known thermal expansion behaviour. Equation (6) can then be rearranged to calculate α_c as

$$\alpha_c = \left(\frac{L_s}{L_c} \right) \alpha_s + \frac{0.15625}{L_c} \frac{d}{dT} \left(\frac{1}{c} \right). \quad (7)$$

7. Sources of error

The above equations hold good only for an ideal parallel plate capacitor. The departure from ideality introduces errors in the calculations, a few of which are discussed below.

7.1 Non-uniformity of the electric field

The capacitance of an ideal parallel plate capacitor for which the electric field between the capacitor plates is strictly uniform is given by

$$c = \epsilon_0 \pi r^2 / g, \quad (8)$$

where $\epsilon_0 = 8.85 \times 10^{-12} \text{ fm}^{-1}$. But in practice, the electric field is never uniform near the edges, the lines of force fringing near the edges. The condition of no fringing near the edges of the capacitor may be largely produced by surrounding the electrode by a guard ring at the same electric potential. Even with the guard ring, there is still a distortion of the electric field near the edges. Consequently a correction has to be applied which roughly approximates to increasing the effective area of the central

electrode from A to $A + \Delta A$, where ΔA is the area of the additional strip extending over half the width w between the central electrode and the guard ring. This correction is given by (Pott and Schefzyk 1983)

$$c = \frac{\epsilon_0 \pi r^2}{g} + \frac{\epsilon_0 \pi r w}{g + 0.22 w} \left(1 + \frac{w}{2r}\right). \quad (9)$$

For our cell, $w = 0.01$ cm and $r = 0.75$ cm, therefore $w/r = \frac{1}{75}$. Neglecting the term containing $(w/r)^2$, (9) can be rewritten as

$$c = c_0 \left(1 + \frac{\Delta c}{c_0}\right), \quad (10)$$

where $c_0 = \epsilon_0 \pi r^2 / g$ (11)

and $\frac{\Delta c}{c_0} = \frac{w}{r} \cdot \frac{g}{g + 0.22 w}$. (12)

Substituting $w = 0.01$ cm, $g = 0.02$ cm and $r = 0.75$ cm, we have $\Delta c/c_0 = 0.012$. Hence an error of about 1.2% is possible due to the non-uniformity in the electric field.

7.2 Non-parallel capacitor plates

If the capacitor plates are not flat or not parallel to one another, the gap g between the plates will be a function of position. Then the expression for the capacitance given by (8) gets modified in a complicated way. When the plate separation is very much larger than the surface undulations, the surface roughness of the plate has negligible effect on the linear relationship between c and $1/g$ (Brown and Bulleid 1978). The effect of non-flatness can be removed by lapping the surfaces of the capacitor plates facing each other to optical finish. For gaps g comparable to w , the effect of non-parallelism becomes significant and should be considered (Khan *et al* 1980; Gladwin and Joseph 1975). For a tilted plate capacitor with gap g at the centre and varying from a minimum value of $(g - a)$ at one end to a maximum value of $(g + a)$ at the other end, the capacitance is given by (Pott and Schefzyk 1983)

$$c = \frac{\epsilon_0 \pi r^2}{g} \cdot \frac{2g^2}{a^2} \{1 - [1 - (a/g)^2]^{\frac{1}{2}}\}. \quad (13)$$

The tilting a can be determined experimentally. The capacitance reaches a maximum value c_{\max} for $a = g$. Hence

$$c_{\max} = 2\epsilon_0 \pi r^2 / g. \quad (14)$$

From (13) and (14), we get

$$g = \frac{\epsilon_0 \pi r^2}{c} \left\{1 + \left(\frac{c}{c_{\max}}\right)^2\right\}, \quad (15)$$

or $c = \frac{\epsilon_0 \pi r^2}{g} \left\{1 + \left(\frac{c}{c_{\max}}\right)^2\right\}. \quad (16)$

By careful adjustment, parallelism can be achieved easily to better than 10% of the gap. If $c = 7.8$ pF, $c_{\max} = 78$ pF. Hence $(c/c_{\max})^2 = 0.01$. Then the error due to non-parallelism can at best be of the order of 1% and easily be made less by better adjustment for parallelism.

7.3 Thermal expansion of capacitor plates

As the temperature increases, the area of the capacitor plates also increases, causing a change in capacitance. For a change in temperature from 80 K to 340 K, the increase in area is approximately given by $\Delta A = 2\alpha_{\text{Cu}} A \Delta T$. Hence the relative change in area is given by $\Delta A/A = 2\alpha_{\text{Cu}} \Delta T \approx 2 \times 12 \times 10^{-6} \times 250 = 0.006$. Thus the expansion of the capacitor plates introduce an error of about 0.6%.

8. Calibration of capacitance cell

The capacitance cell being differential one, the sample expands relative to the cell material i.e. copper. To calculate the thermal expansion coefficient of a sample, the expansion of the cell must be first determined. The cell is calibrated by measurements on standard reference materials of known thermal expansion behaviour. We have chosen high purity aluminium and germanium as reference materials. The use of two standard reference materials helps in comparing the cell constants as determined by two independent measurements. Further the choice is such that one material has expansivity larger than that of copper and the other lower.

8.1 Experimental details

The aluminium and germanium samples are cut in the form of cylinders of diameter 1 cm and height 1 cm. The two circular faces are ground to optical flatness and parallelism. The sample with the plate 1 on its top is placed symmetrically on the platform 5. The platform is slowly raised so that there is no gap between the plates 1 and 2. The three stainless steel springs are now fixed between the hooks in the plate 1 and the base 8. The platform is now slightly lowered to get a small gap between the plates 1 and 2 and normally adjusted to be about 0.02 cm. This is checked by measuring the capacitance using equation (5). The checknut 13 is tightened to fix the platform in this position.

Parallelism of the gap is checked in the following way. In the beginning a rough adjustment is done by seeing that the gap is visibly parallel. The gap is illuminated with bright light and viewed from two perpendicular directions with a white background. The three pairs of nuts 11 are then slowly adjusted to get a gap which is visibly parallel. Parallelism is further checked (Villar *et al* 1980) by introducing a thin plastic sheet over a definite area between the two plates. The capacitance increases accordingly due to high dielectric constant of plastic. The amount of increase depends on the distance between the two plates at the zone covered by the plastic. If the sheet is introduced at some other region and the plates are not parallel, the amount of increase would be accordingly different. The three pairs of nuts are then adjusted until the parallelism is better than 10% of the capacitor gap.

The experiment is carried out during a heating run as the sample is heated from 77 K to 340 K. The temperature of the sample is increased in steps of 5 to 6 K by using the

temperature controller. When the sample attains a steady temperature with no thermal gradients across the sample and the cell as read by the differential thermocouples T_1 to T_4 , the ratio transformer reading $1/c$ is taken. Since the resolution of capacitance measurement is larger than the resolution of temperature measurement, the cell capacitance is used to judge when a stable uniform temperature is obtained in the cell. The bridge balance is checked once in every ten minutes until a stable balance is obtained. At this stage, the sample temperature as shown by the thermometer P_1 , is recorded along with the ratio transformer reading for balance.

8.2 Analysis of data

The plot of experimental data of $1/c$ versus T for two experimental runs with aluminium and two experimental runs with germanium are given in figure 4. The cell constant is determined from (7). α_s is the thermal expansion coefficient of the reference sample. The data for aluminium and germanium samples are taken from TPRC Data Series Handbook (Touloukian *et al* 1975). For convenience of handling, these data are fitted into polynomials of degree seven, over the entire range of temperature 80 to 340 K. For aluminium

$$\begin{aligned} \alpha_s \times 10^6 = & 0.831865 + (0.373814 \times 10^{-1}) T + (0.186450 \times 10^{-2}) T^2 \\ & - (0.186214 \times 10^{-3}) T^3 + (0.918849 \times 10^{-7}) T^4 - (0.253571 \times 10^{-9}) T^5 \\ & + (0.357722 \times 10^{-12}) T^6 - (0.193396 \times 10^{-15}) T^7. \end{aligned}$$

For germanium

$$\begin{aligned} \alpha_s \times 10^6 = & -0.367793 \times 10^2 + (0.122934 \times 10^1) T - (0.164886 \times 10^{-1}) T^2 \\ & + (0.122112 \times 10^{-3}) T^3 - (0.532999 \times 10^{-6}) T^4 + (0.136510 \times 10^{-8}) T^5 \\ & - (0.190523 \times 10^{-11}) T^6 + (0.112151 \times 10^{-14}) T^7. \end{aligned}$$

This helps in calculating α values for the reference sample at any desired temperature and also in feeding the data to the computer for further calculations.

From a series of data points of $1/c$ versus T , calculation of $(d/dT)(1/c)$ at different temperatures can be done in several ways. Numerical differentiation and graphical methods of finding $(d/dT)(1/c)$ generate lot of scatter. An accurate method is to fit the raw data into a polynomial of suitable degree and differentiate it to get the derivative. As cubic spline fitting has distinct advantages over the polynomial fitting (Pott and Schefzyk 1983) we have used the spline approximation. A cubic spline consists of a number of cubic polynomial segments joined end to end with continuity in first and second derivatives at the joints or knots. The number of knots for a good fit is determined by trial and error. By using NAGLIB subroutines EO2BAF, EO2BBF and EO2BCF, given in 'NAG Fortran Library Manual', Mark 9, Vol. 2, Numerical Algorithm Group (1982), the data of $1/c$ versus T is fitted into least-square cubic splines and the derivative $(d/dT)(1/c)$ is determined at the experimental temperatures. The above subroutines are included in a general program which is written to calculate the cell constant directly in accordance with (7). Along with $1/c$ versus T data, the length of the sample, the value of $1/c$ at room temperature, the value of polynomial coefficients giving of reference sample are also fed to the computer. The program calculates the cell

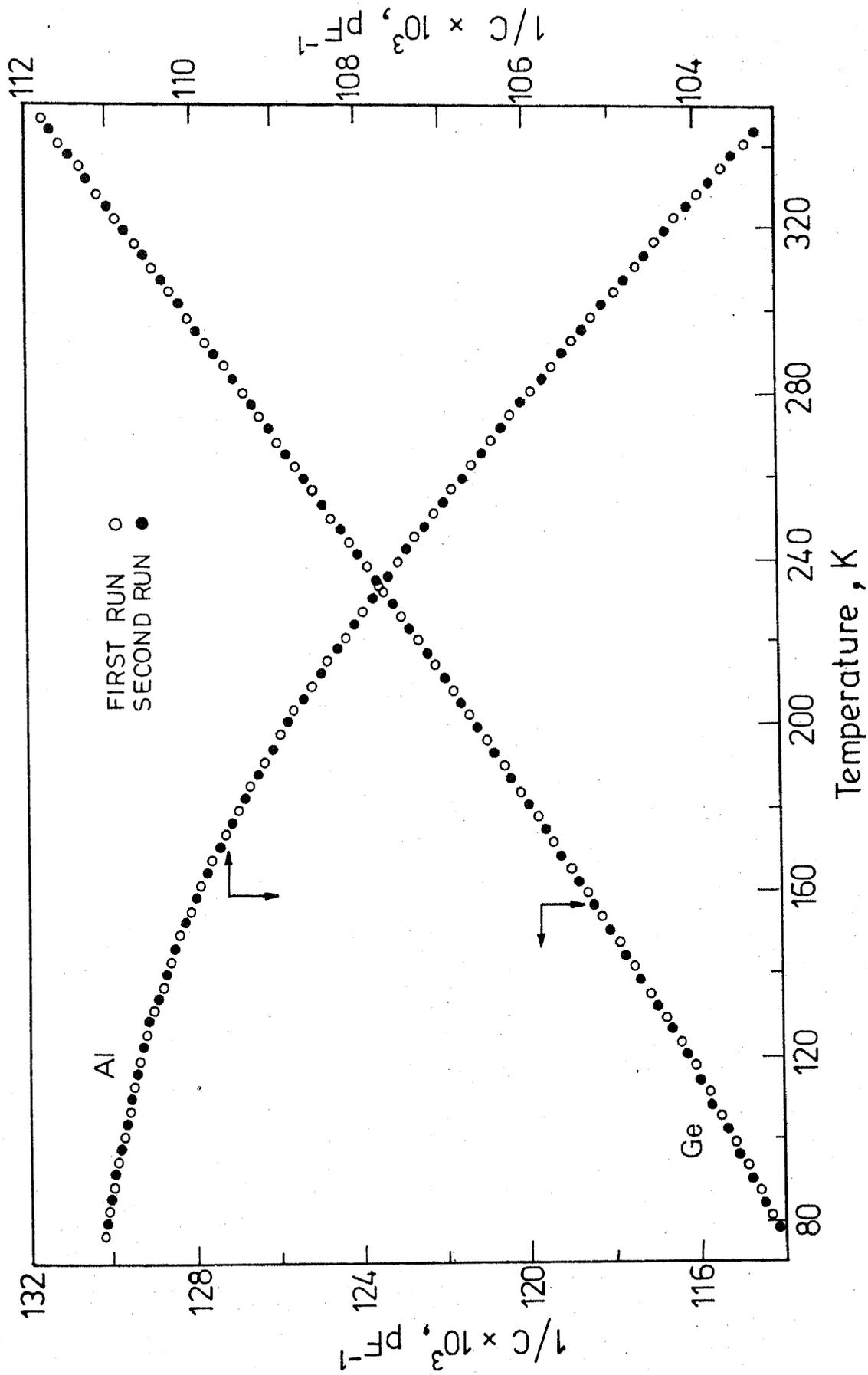


Figure 4. Variation of $1/c$ with temperature for aluminium and germanium.

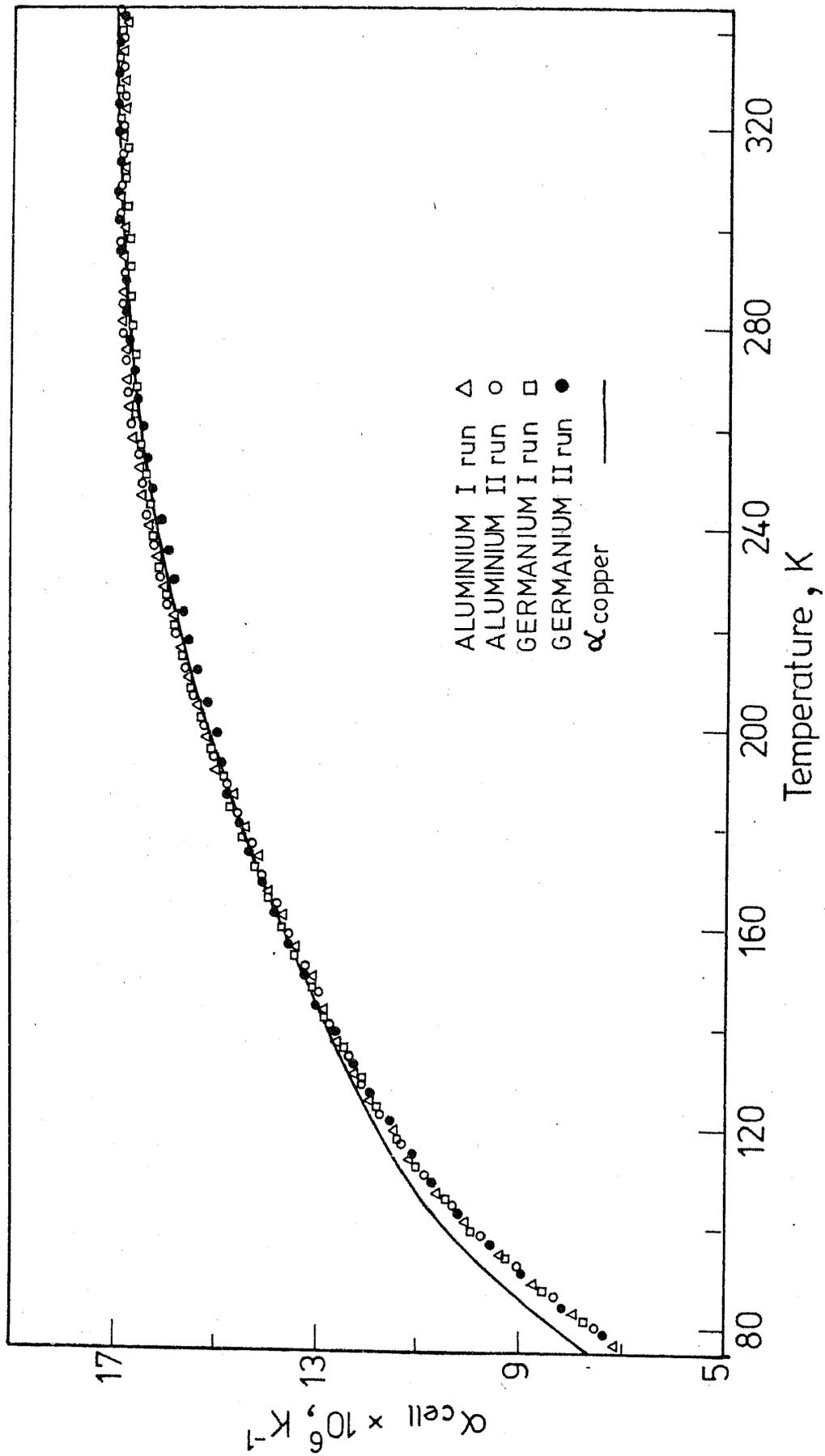


Figure 5. Variation of cell constant with temperature.

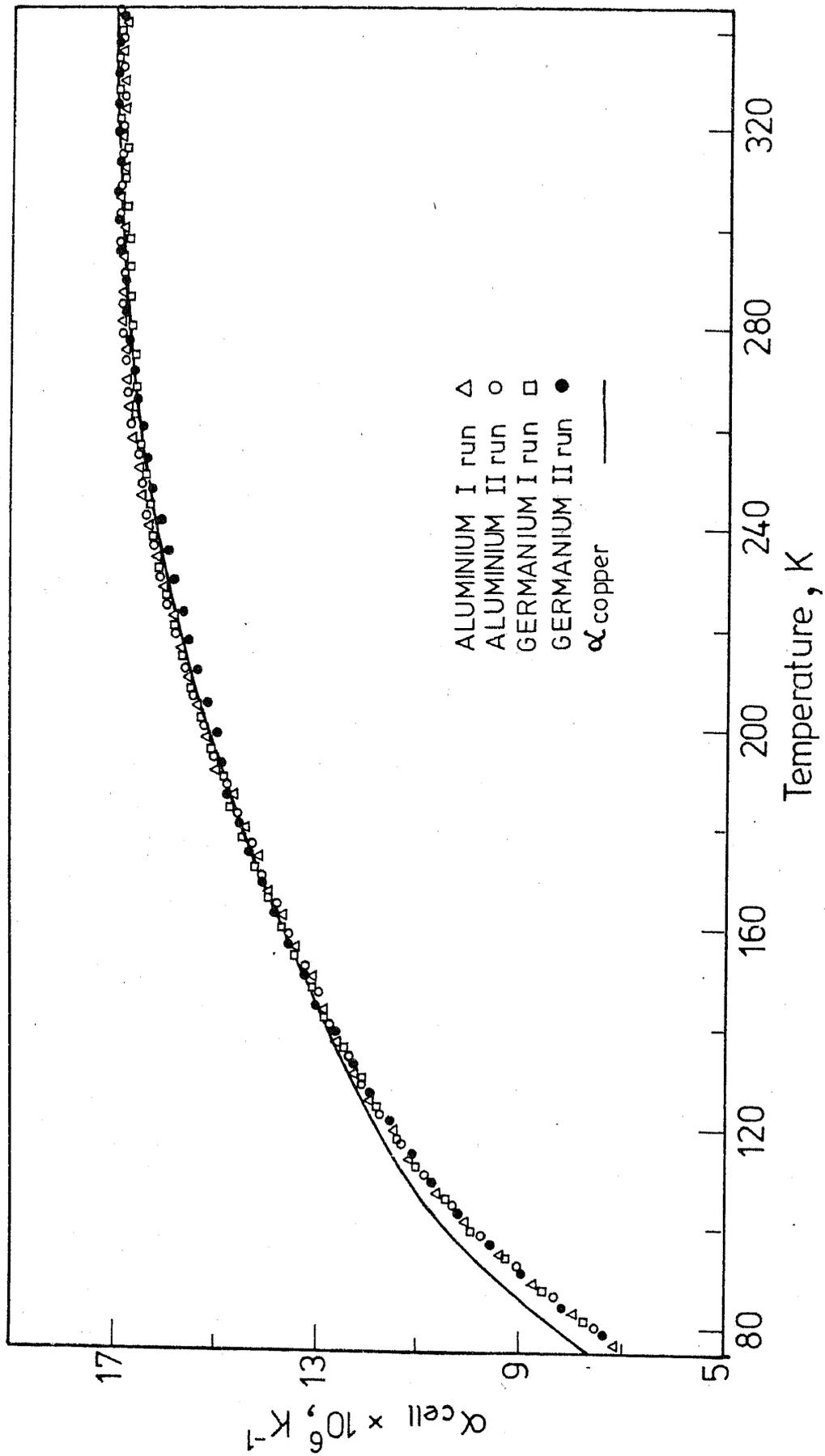


Figure 5. Variation of cell constant with temperature.

constant at different measured temperatures in accordance with (7). The cell constant so obtained from two different runs of aluminium and two different runs of germanium at about 180 different temperatures are plotted in figure 5.

9 Results and discussion

From figure 5, it can be seen that the cell constants as found by two different runs for two reference samples agree very well at low temperatures. At high temperatures, there is a spread in the data of about 2%. This is not surprising since the accuracy of the thermal expansion data of germanium and aluminium standard samples itself is about 3% (Touloukian *et al* 1975). The thermal expansion coefficient of OFHC copper taken from the TPRC data series is also plotted in figure 7 for comparison. The variation of α_c with temperature is very much similar to that of copper. This is to be expected since the cell is mostly made of copper. In the temperature range 130 to 340 K the agreement between α_c and the expansivity of OFHC copper is better than 2%. Below 130 K, the discrepancy between the two is very large, reaching about 10 to 11% at 80 K. This is, however, not disturbing since the cell is only made of commercial copper and not OFHC copper. Even in α values of OFHC copper as found by different workers, there is a discrepancy of about 3 to 4%. The mica sheets used for insulation in the cell can also contribute to deviation. As the cell is not made of a monolith copper block, but made of different pieces mechanically joined together, the imperfectness at joints can also contribute to the observed discrepancy. These contributions being small, show up only at low temperatures where the expansion coefficient of copper itself is very small.

9.1 Accuracy of measurement

The accuracy of measurement in α_c depends on the accuracy of various other factors involved in determining it, as given in (7). The accuracy of the thermal expansion data of the reference sample is only 3%. The accuracy in the sample length measurement is about 0.13%. It is difficult to estimate precisely the accuracy in the measurement of $(d/dT)(1/c)$. Considering the numerical derivative, instead, this can be approximately calculated. The resolution in the temperature measurement being 0.1 K and the temperature increments being about 6 K, the accuracy in the measurement of ΔT is about 3%. The resolution in $1/c$ measurement is 10^{-6} pF. The change in $1/c$ for a temperature increment of 6 K being a function of temperature, varies from 50×10^{-6} to 250×10^{-6} pF $^{-1}$ for aluminium and 250×10^{-6} to 400×10^{-6} pF $^{-1}$ for germanium. Hence the accuracy in the measurement of $\Delta(1/c)$ is also a function of temperature and is 1% or less in a larger portion of the temperature interval. Hence the overall accuracy in the measurement of α_c is about 4%. This is roughly the same as the accuracy in the expansion data of the reference samples.

This set up has been used for the measurement of thermal expansion of gamma irradiated polymers (polymethyl methacrylate, polystyrene, polytetrafluoroethylene and polyoxymethylene) and these results will be published separately.

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