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Germanium thermometer calibration

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The advisability of calibrating only carefully selected thermometers is emphasized. The relation between calibration point spacing and the weighting method used in curve fitting the calibration is discussed and then illustrated by various fits to different data sets for a particular germanium thermometer. Apart from different end effects, which could be minimized by a higher density of points at each end of the range, there is little significant difference between the results of the various methods tried.

INTRODUCTION

The average germanium thermometer is not completely stable, presumably because the contacts are made with gold, which has a total thermal contraction between room temperature and liquid helium temperatures which is four times greater than that of germanium.¹ Apart from the possible partial or complete breakage of the contact area, germanium also shows a high piezoresistance effect.² Thus reliable stability of the type seen in the platinum resistance thermometer is scarcely to be expected. Many germanium thermometers are stable to ± 1 mK at liquid helium temperatures, but larger shifts are often seen at higher temperatures where the thermometer resistance and sensitivity are much lower. Careful selection is necessary to obtain a thermometer stable to ± 1 mK over a wide temperature range. Great care is necessary in handling these thermometers. It is especially important to avoid any significant heating of the element (e.g., while soldering leads) which will cause a calibration shift.

PRELIMINARY SELECTION

Before proceeding with a calibration, thermometers should therefore be checked for obvious instabilities caused by thermal cycling. Apart from the normal four-terminal resistance measurements, it is also advisable to make two-terminal measurements on the current leads and potential leads, respectively, to check the contact resistances directly. These measurements should be made at room temperature as well as at liquid nitrogen and liquid helium temperatures because a small constant shift of resistance is more likely to be measurable when the total resistance is low. Furthermore, some thermometers show either one of two resistances at a given low temperature,³ and therefore a complete set of measurements should be made during every cycling, otherwise instabilities may escape detection. By measuring several thermometers at one time the effect of temperature changes of the liquid bath may be eliminated.⁴

The need for this selection procedure is illustrated by the author's recent experience with two batches of Ge thermometers received in 1973 and 1974. The first batch consisted of five low sensitivity thermometers ($\sim 50 \Omega$ at 4.2 K) intended for use from 0.3 K up to about 4 K. One of this

batch showed shifts of up to 1.4Ω and another a shift of 0.15Ω , both in four-terminal resistance at 4.2 K. On the basis of the calibration of a stable thermometer from this batch, the corresponding temperature instabilities are about 0.3 and 0.03 K at 4.2 K. A third thermometer showed an increase of 0.01Ω in the two-terminal current lead resistance at room temperature. The second batch contained six higher sensitivity thermometers ($\sim 500 \Omega$ at 4.2 K) intended for use up to 30 K. One of these showed a shift of about 8Ω in the four-terminal resistance at 4.2 K (~ 0.04 K) and another an increase of more than 20Ω in the two-terminal current lead resistance at the same temperature. The three best of the second batch were then calibrated in the 2–30 K region, but only two of these were stable to ± 1 mK over the whole range during three successive coolings.⁵ Even so, there remains a strong possibility that these two thermometers will not remain stable indefinitely. For example, three of the five thermometers used in the development of the National Bureau of Standards superconductive fixed point device proved to be unstable.⁶ Similarly, in international temperature scale comparisons in the 2–30 K range, 5 out of 13 thermometers showed some degree of instability,⁷ and Cetas and Swenson⁸ concluded that only an exceptional germanium thermometer is stable to 0.01% over a period of years. It must, of course, be remembered that these high stability requirements are necessary only for certain applications (e.g., temperature standards work and calorimetry). However, the possibility of calibration shifts should be considered whenever germanium thermometers are used, and it is advisable to make routine calibration checks (e.g., by comparison with a second germanium thermometer). The test data in this paper and in the cited references will give some idea of the magnitude and frequency of the shifts which may occur at the present state of the art. Working group four of the Comité Consultatif de Thermométrie (of the Comité International des Poids et Mesures) is currently concerned with problems of germanium thermometer stability.⁹

ACCURACY OF MEASUREMENTS

Apart from the problems of thermometer stability, the accurate measurement of thermometer resistance (within the current limit set by significant self-heating) does not

normally present a problem with modern equipment. The difference between ac and dc resistance, ascribed to the Peltier effect,¹⁰ is probably negligibly small within the normal range of use of germanium thermometers.^{11,12} If the temperature scale has been set up using a primary thermometer of the gas or acoustic type, then there is a random error in temperature which is independent of the temperature being measured (i.e., the temperature is based on a length measurement). Hopefully there are no systematic errors in the temperature scale, and there are no temperature gradients between thermometers during calibration.

CALIBRATION POINT SPACING AND CURVE FITTING

There appear to be two schools of thought on the optimum spacing of calibration points. If the calibration points are at roughly equal intervals in temperature, then interpolation errors should be roughly the same over the range of the scale. The NBS Acoustic scale¹³ is of this type with calibration points at approximately 1 K intervals from 2 to 20 K. Another approach is to consider the equation used most often^{14,15} to fit Ge thermometer calibrations,

$$\log R = \sum_{n=0}^{n=m} a_n (\log T)^n, \quad (1)$$

where R is the resistance at temperature T . An argument can obviously be advanced to space the calibration points at equal intervals in $\log T$. This was done by Osborne, Flotow, and Schreiner¹⁶ who used a weighting factor $(d \log T / d \log R)^2$ so that the sum of squares of fractional deviations in temperature was minimized. In terms of absolute temperature this will ensure a better fit at low temperatures than at high temperatures which, as discussed above, is not usually justified by the accuracy of the primary temperature determinations. (If the fitted data include both gas thermometer and vapor pressure data, then the latter would probably require a higher weight since they are generally more accurate.) Powell, Hall, and Hust¹⁷ have also recommended that calibration data be spaced at equal intervals in $\log T$. Their weighting factor T^2 approximately minimizes the sum of squares of absolute rather than fractional temperature deviations and therefore appears

more correct than that of Osborne *et al.*,¹⁶ discussed above. It is derived from the observation that the calibration data for Ge thermometers are approximately represented in the 2–20 K range by

$$\log R = A - B \log T, \quad (2)$$

where A and B are constants. Then

$$\Delta(\log R) = -B \Delta(\log T) = -B \Delta T / T = C / T, \quad (3)$$

where ΔT is assumed constant and C is a constant. If the recommendations of Powell *et al.*¹⁷ are followed, then the density of calibration points will be an order of magnitude higher at 2 K than at 20 K, whereas the weighting factor is two orders of magnitude higher at 20 K than at 2 K. This is mathematically equivalent to using no weighting with a density of points an order of magnitude higher at 20 K than at 2 K. Thus the optimum weighting factor depends on the spacing of calibration points.

The above investigation of weighting recommendations followed the observation that, for a particular thermometer, calibrations on our local temperature scale¹⁸ were slightly better (25% in rms temperature deviation) represented by an unweighted fit than by the T^2 weighting recommended by Powell *et al.*,¹⁷ whereas for another thermometer the difference was 10% in the opposite direction. This is probably because the data are roughly linearly spaced in temperature with a few extra points at each end of the range. The T^2 weighting marginally improves the high temperature end of the fit, but the low temperature end is significantly worse.

Several workers (e.g., Refs. 14 and 18) have in fact fitted calibration data taken at roughly equal intervals in temperature to Eq. (1) without any weighting. The above arguments show that this method is close to the optimum. Indeed, since the germanium thermometer sensitivity is decreasing at higher temperatures, the more significant effect of random errors in resistance determination here will be minimized by taking more points (rather than relying on a large weighting factor with very few points). Another argument for roughly linear spacing of calibration temperatures arises if "spot" temperatures are to be determined (e.g., a transition temperature). The effect of any deviation of the fitted function from true temperature is reduced by keeping the interpolation intervals short. Residual differences between the fit obtained using Eq. (1) and true temperature may be minimized by using a difference table.¹⁸

The above conclusions have been investigated by using the smoothed calibration of a particular Ge thermometer (which had been calibrated by comparison at 61 temperatures with another Ge thermometer which had in turn been calibrated by comparison with vapor pressure, gas, and platinum resistance thermometers¹⁸). The smoothed calibration was in terms of Eq. (1) with a nine term series, together with cubic interpolation in a difference table covering the 2–31 K range at 1 K intervals. The deviation of calibration points from the smoothed fit are shown in Fig. 1. It will be seen that the fit is very good except for pronounced "wiggles" in the first and last 2 K regions.

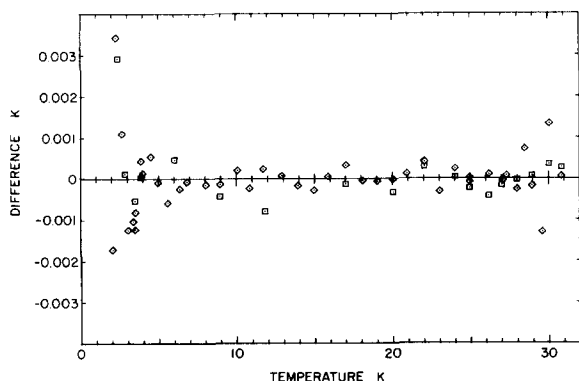


Fig. 1. Illustrating the smoothed fit to the 61-point calibration of the secondary germanium thermometer. Two different symbols refer to two calibration runs and give an indication of reproducibility after intermediate warming to room temperature.

The smoothed fit coefficients and difference table were used to generate two calibration sets: (i) 28 points (T, R) at equal intervals in temperature from 3 to 30 K and (ii) 28 points (T, R) at equal intervals in log (temperature) from 3 to 30 K, together with a reference set (T, R) covering the 3–30 K range in 0.2 K steps. The two calibration sets were separately least squares fitted (by an orthogonal polynomial method) first with no weighting and then with T^2 weighting. The best fits obtained are shown in Fig. 2 (as differences from the reference set), noting that in the case of set (i) with T^2 weighting the least squares program halted with an arithmetical error for the next higher polynomial to that shown in Fig. 2 (presumably because the arithmetical software had insufficient precision for this particular case). Thus the fit in Fig. 2 may not be the best for this case. It will be observed that there is little to choose between the fits. Next, a difference table was constructed (at 1 K intervals) for each fit using only the observed deviations at the original calibration points. (This is rather a subjective process.) Figure 3 shows the differences from the reference set for this “final” calibration using both the fitted polynomial (1) and cubic interpolation in the difference table. From Fig. 3 it will be clear that T^2 weighting has had little effect on the calibration from set (i) (equally spaced in T) but has improved the results from (ii), i.e., it has compensated for the low density of points at the high temperature end of the range. Calibrations from set (ii) are much better at the low temperature end, partly because the higher density of points here has enabled a more accurate difference table to be constructed. On the other hand the high tempera-

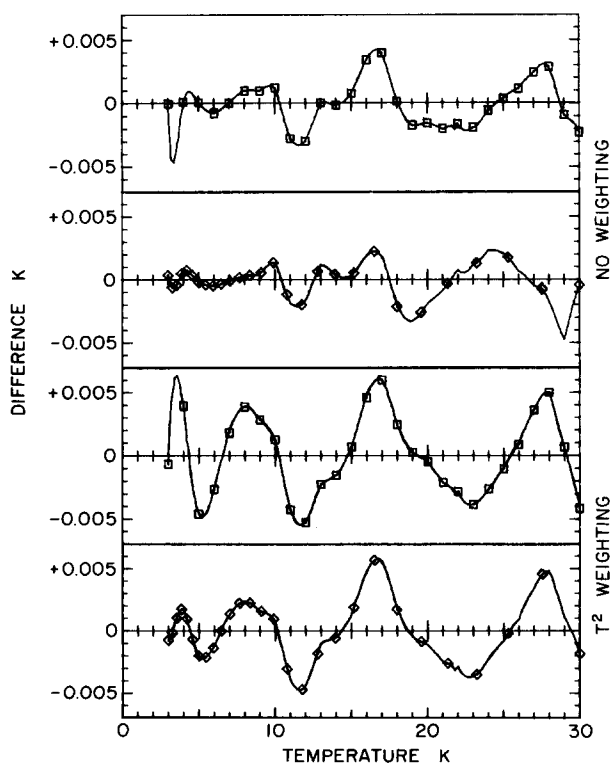


FIG. 2. Differences between temperatures obtained from the original smoothed fit of the secondary thermometer (Fig. 1) and from the best least squares fits of Eq. (1) to the 28-point calibration sets for the same thermometer. The corresponding values of m in Eq. (1) are 8, 9, 7, and 8, respectively.

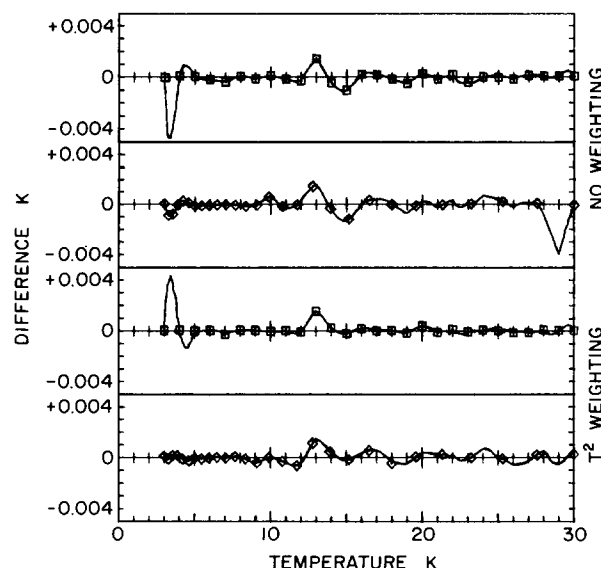


FIG. 3. As Fig. 2 but using in addition a difference table to represent the fits to the 28-point calibration sets.

ture end is better represented by set (i). It was mentioned above that the first and last 2 K of the 61-point calibration showed “wiggles” (Fig. 1), and this behavior tends to be repeated in the case of the 28-point calibrations (Fig. 3). It is clear, as pointed out by Powell *et al.*,¹⁷ that a higher density of points at each end of the range is desirable. Otherwise there seems little to choose between the two data spacings and two weighting methods investigated. This may be a general conclusion or may relate only to the characteristics of the particular germanium thermometer studied and the defects of the temperature scale¹⁸ used. That the spacing of calibration points in the middle of the range is not crucial is shown by the work of van Rijn *et al.*,¹⁹ who found that good calibration accuracy was obtained with a very low density of calibration points here, provided there was adequate density towards each end of the range.

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