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CRYOGENIC TEMPERATURE MEASUREMENT
WITH PLATINUM RESISTANCE THERMOMETERS
IS FIXED-POINT CALIBRATION ADEQUATE?

BY   ROBERT J. CORRUCCINI

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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NATIONAL BUREAU OF STANDARDS

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147

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Cryogenic Temperature Measurement with Platinum Resistance

Thermometers-Is Fixed-Point Calibration Adequate?

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Cryogenic Temperature Measurement with Platinum

Resistance Thermometers-Is Fixed-Point Calibration Adequate?[*]

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ABSTRACT

An analysis of extensive calibration data for strain-free "capsule"-type platinum resistance thermometers indicates that the above question can be answered affirmatively for temperatures down to 14°K. For such thermometers, interpolation can be performed by a numerical procedure that makes use of similarities in the form of the departures of various thermometers from Matthiessen's rule. Where thermometers of more rugged construction or lower purity are concerned, the data needed to answer the question are not available. However it is suggested that the answer may still be "yes" provided the thermometers are sufficiently uniform in their characteristics.

INTRODUCTION

When an instrument is to be calibrated for use over a wide range of conditions, it is generally thought to be advantageous on grounds of convenience to represent its behavior by some simple mathematical formula. Then, the number of calibration points to be measured need not exceed the number of constants in the formula, whereas, lacking such a formula, many closely-spaced calibration points may have to be measured.

Thus in platinum resistance thermometry, the Callendar-van Dusen equation is used in the range, 90.18° to 273.15°K. This equation is as follows:

$$w = 1 + a\left[t - \delta\left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right) - \beta\left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right)^3\right] \qquad (1)$$

Here w is the reduced resistance R_t/R_0, t is Celsius temperature, and a, δ and β are constants. Attempts to find a similar analytical representation covering the entire useful range down to 10°K have been unsuccessful, due to the w - t relation becoming increasingly sensitive to impurities and lattice defects with decreasing temperature. Consequently it is customary to calibrate between 10° and 90.18°K at intervals of a few degrees. The Heat Division, of the National Bureau of Standards, Washington, D. C., in making such calibrations takes sixteen points in this interval.

INTERPOLATION METHODS

1 <u>Cragoe's Z function.</u> In recent years a number of attempts have been made to overcome the above difficulty, starting with a proposal by Cragoe[1] based on the assumption that the function Z, defined as $(R - R_1)/(R_2 - R_1)$, is practically the same for all

thermometers. Here, R is the resistance at temperature, $T°K$, while R_1 and R_2 are the resistances at calibration points T_1 and T_2. If R_1 and R_2 are determined for a given thermometer, then its resistance-temperature relationship can be constructed if a reference table of Z vs. T is available. However, errors up to several hundredths of a degree commonly result from this procedure using strain-free laboratory thermometers and taking T_1 as the boiling point of hydrogen (about 20°K) and T_2 as the boiling point of oxygen (about 90°K). This has not been regarded as acceptable, inasmuch as such thermometers can have stability and precision of the order of a millidegree. The worst errors occurred below 50°K.

Now, it is easy to show that applicability of Cragoe's function would be consistent with the empirical rule of Matthiessen,

$$\rho = \rho_i + \rho_o \tag{2}$$

in which ρ is the resistivity of a particular sample, ρ_i is the "ideal" resistivity, a temperature-dependent function which is the same for all platinums, and ρ_o is the "residual" resistivity, a temperature-independent component. The residual resistivity tends toward zero as the crystalline perfection of platinum is increased by purification and annealing. In general this rule is a useful approximation, but it must be modified in order to obtain a more accurate representation.

2. <u>Kohler's deviation term.</u> A general treatment of deviation from Matthiessen's rule has been given by Kohler[2], who has shown that the deviations must be positive. By introducing certain assumptions about the electron distribution function, he obtained for the additional resistivity the term,

$$\rho_\Delta = pq\rho_o\rho_i / (p\rho_o + q\rho_i).$$

This term is an approximation, and the parameters, p and q, may be functions of temperature and cannot be readily calculated at present from theory. In Fig. 1 is shown schematically the forms of the three components of the resistivity on this model. Inspection of resistance-temperature data for various metals including platinum indicates that the deviation term of Kohler is qualitatively of the right form to represent the departures from Matthiessen's rule.

In order to apply this deviation term to resistance thermometer data in a simple way, it is necessary to assume that p and q are constants and to transform the modified Matthiessen rule into an expression for the reduced resistance. This was done by Schultz[3] with the result,

$$w = w_i + w_o (1 - w_i) (1 + \Delta) \tag{3}$$

in which $w_i = \rho_{i, T}/\rho_{i, 273.15}$, $w_o = \rho_o/\rho_{273.15}$ and $\Delta = aw_i/(1+cw_i)$. The constants, a and c, can be evaluated for each thermometer by calibration at two temperatures, T_1 and T_2, °K. Then

$$c = (\Delta_1 - \Delta_2 \, w_{i1}/w_{i2})/w_{i1} (\Delta_2 - \Delta_1) \tag{4}$$

$$a = \Delta_2 (1 + cw_{i2})/w_{i2} \tag{5}$$

The subscripts, 1 and 2, indicate values at the temperatures, T_1 and T_2.

Because of the theoretical basis of formula (3) it is reasonable to expect that it should be applicable over the whole range of temperatures. Thus we might hope to obtain a good fit over all temperatures up to ambient by taking T_1 and T_2 as before at about 20° and 90°K, respectively. The reduced residual resistance, w_o,

can be obtained by a measurement at the boiling point of helium,
4.2°K, since w_i is negligible there. Inasmuch as the resistance
at the ice point, 273.15°K, is also required, application of eq. (3)
involves measuring four fixed points.

An unfortunate aspect of this method is the fact that there is
no unambiguous way of establishing the function, w_i vs. T, the
reduced resistance of hypothetical pure and perfect crystalline
platinum. Customarily this function is calculated from the w - T
relation of the most pure sample for which one has data, using the
assumption that Δ for this sample is zero. When applied in this way,
eq. (3) is found to provide a good fit to strain-free laboratory
thermometers down to about 50°K. Between this temperature and
20°K the errors are as large as several hundredths of a degree.
Thus, while eq. (3) is applicable with fair accuracy over a much
wider range than Cragoe's function, it also fails to represent
thermometers in the region below 50°K within the accuracy of which
they are capable.

Obviously a better result could be obtained by narrowing the
temperature range. For example, the reduced resistance could be
taken relative to the oxygen point rather than the ice point, which
would permit locating T_2 between 20 and 90°K. Then a better fit
would surely be obtained below 90°K. However, this would amount
to using Kohler's deviation term as if it were an empirical function.
If empirical methods are to be employed, then another one may be
mentioned which possesses greater flexibility and requires fewer
calibration points than does eq. (3).

3. <u>Three-point empirical method.</u>[4, 5] This method makes
use of the fact that deviations of various thermometers from a Z
function are similar in form. This is illustrated in Fig. 2 which

shows resistance deviations of a group of thermometers from the Z function of one of the group. That is, we have plotted for any thermometer, "X", the quantity, $R'_X - R_X$, where

$$R'_X = R_{1X} + \left(\frac{R_{2X} - R_{1X}}{R_{2A} - R_{1A}} \right) (R_A - R_{1A}) = R_{1X} + (R_{2X} - R_{1X}) Z_A \quad (6)$$

Here, the subscript "A" denotes the thermometer from whose calibration the reference function Z was derived. T_1 and T_2 were taken as 20° and 90°K, respectively. If one of the error curves of representative shape is adopted as a reference standard, then it can be scaled up or down to provide an approximation to the error curve of any other thermometer. Let us designate the thermometer used to provide the error function as "B". Then the scaling factor is derived from a comparison of the errors of X and B at some third calibration point, T_3. The value of resistance calculated in this way, R''_X, is given by

$$R''_X = R'_X - \left(\frac{R'_{3X} - R_{3X}}{R'_{3B} - R_{3B}} \right) (R'_B - R_B) \quad (7)$$

From the appearance of figure 2 it might be thought that in order to obtain the best results between 20 and 90°K, T_3 should be taken midway between, or at about the triple point of oxygen, 54°K. Indeed a very satisfactory result is obtained in this way. However, nearly as good a result is obtained by using the ice point as T_3. The latter is much to be preferred on grounds of experimental ease. The worst temperature errors between 20° and 90°K occur just above 20°K and, consequently, a result far superior to either of the above is obtained by locating T_3 at about 30°K.

The results of some calculations along these lines are summarized in table I. These were performed on a group of thirty-five closely similar strain-free laboratory thermometers that had been calibrated on the NBS provisional temperature scale. Their a values all exceeded 0.003924, and their w_o values lay between 0.0004 and 0.0007. It will be noted that the region, 20 to 90°K, could be fitted within a few millidegrees. It would seem pointless to wish for better accuracy than this inasmuch as the uncertainty of the relationship of the NBS provisional scale to the absolute thermodynamic scale of temperature is of the order of 0.01 degree. For comparison, the errors using Cragoe's function or eq. (3) with the same thermometers approached 0.02 degree.

The calculations of table I have been described more fully elsewhere[5]. It is important to emphasize the close similarity of the thermometers used in this evaluation. A few tests of eq. (7) that have been made using thermometers of lower purity ($a < 0.003920$ and $w_o > 0.002$) not only show a great deterioration in accuracy below 90°K but also suggest that eq. (7) has less advantage over Cragoe's function when applied to thermometers that differ so greatly. On the other hand the region above 90°K is much less sensitive to variations in quality of the platinum. Here eq. (7) is fully adequate and can perform the same function as the Callendar-van Dusen equation with one less calibration point.

CONCLUSIONS

We can now attempt to answer the question posed in the title. Our conclusions will rest on the foregoing analyses of strain-free laboratory thermometers. Unfortunately, many users are concerned with a different class of platinum resistance thermometers in which the necessity for achieving ruggedness or speed of response

has dictated a mode of construction in which the platinum is more constrained. Also, the platinum in such thermometers is often somewhat less pure. Sufficient calibration data on such thermometers are not available to permit giving a definite answer regarding them. However, the following inferences about them can be drawn from the studies of strain-free laboratory thermometers.

1.) The answer to the question in the title is "yes", with the qualification that some restriction of the thermometer characteristics may be necessary, and that this restriction must be made more stringent the greater the desired interpolation accuracy.

2.) For interpolation accuracy of a few millidegrees from 20°K upwards, the three-point empirical method can be used. Apparently, the range of α values of the thermometers should not exceed about 2×10^{-6} and the range of w_o values should not exceed about 2×10^{-4}.

3.) If the desired accuracy is only a few hundredths of a degree, then perhaps a tenfold greater range of values of α and w_o can be permitted. As the thermometers are allowed to become more diverse, the advantage of the three-point method over Cragoe's function will probably become less marked, and particularly so if T_3 lies outside the range of use of the thermometers. Eq. (3) may be useful where it is necessary to cover both a wide range of thermometer characteristics and a wide range of temperatures.

4.) Whatever interpolation method is chosen, optimum results will be obtained only if the reference functions to be used - R_A, R_B, Z, and possibly even w_i - have been derived from thermometers having characteristics similar to those being fitted.

TABLE I

Summary of Interpolation Errors

Equation Used	T_1	T_2	T_3	Interval Examined	Max. error in interval	Average of max. errors of 35 thermometers
	°K	°K	°K	°K	deg	deg
6	20	90		20 to 90	0.016	0.005
7	20	90	273.15	20 to 90	.006	.003
				90 to 273.15	.009	.002
7	20	90	50	20 to 90	.005	.002
6	30	90		30 to 90	.010	.003
7	30	90	273.15	20 to 30	.024	.007
				30 to 90	.004	.0013
				90 to 273.15	.009	.002
7	20	90	30	20 to 30	.003	.0012
				30 to 90	.003	.0012
7	20	50	30	20 to 30	.002	.0008
				30 to 50	.002	.0003
7	30	90	50	20 to 30	.015	.005
				30 to 50	.002	.0002
				50 to 90	.001	.0002
7	14	20	90	14 to 20	.005	.003
7	10	20	90	10 to 20	.023	.009
7	90	200	273.15	90 to 273.15	.0006	

REFERENCES

1. Procès-Verbaux Comité Intern. Poids et Mesures, Vol. 21, T84 (1948).

2. "General Theory of Deviations from Matthiessen's Rule", Kohler, M., Z. Physik, Vol. 126, 495 (1949). (In German). Or see "The Theory of Metals", Wilson, A. H., Cambridge University Press, 2nd ed., 1953, pp. 310-313.

3. "Deviations of Platinum Resistance Thermometers from Matthiessen's Rule in the Temperature Region from 20° to 90°K", Schultz, H., Z. angew. Physik, Vol. 9, 465 (1957). (In German).

4. "Interpolation of Platinum Resistance Thermometers, 20° to 273.15°K", Corruccini, R. J., Rev. Sci. Instr., Vol. 31, 637 (1960). (Equations [2] in this reference are put down incorrectly.)

5. "Interpolation of Platinum Resistance Thermometers, 10° to 273.15°K", Corruccini, R. J., in "Temperature, Its Measurement and Control in Science and Industry", Reinhold Publ. Corp., New York. In press. (Papers presented at the Fourth Symposium on Temperature, Columbus, Ohio, March 27-31, 1961.)
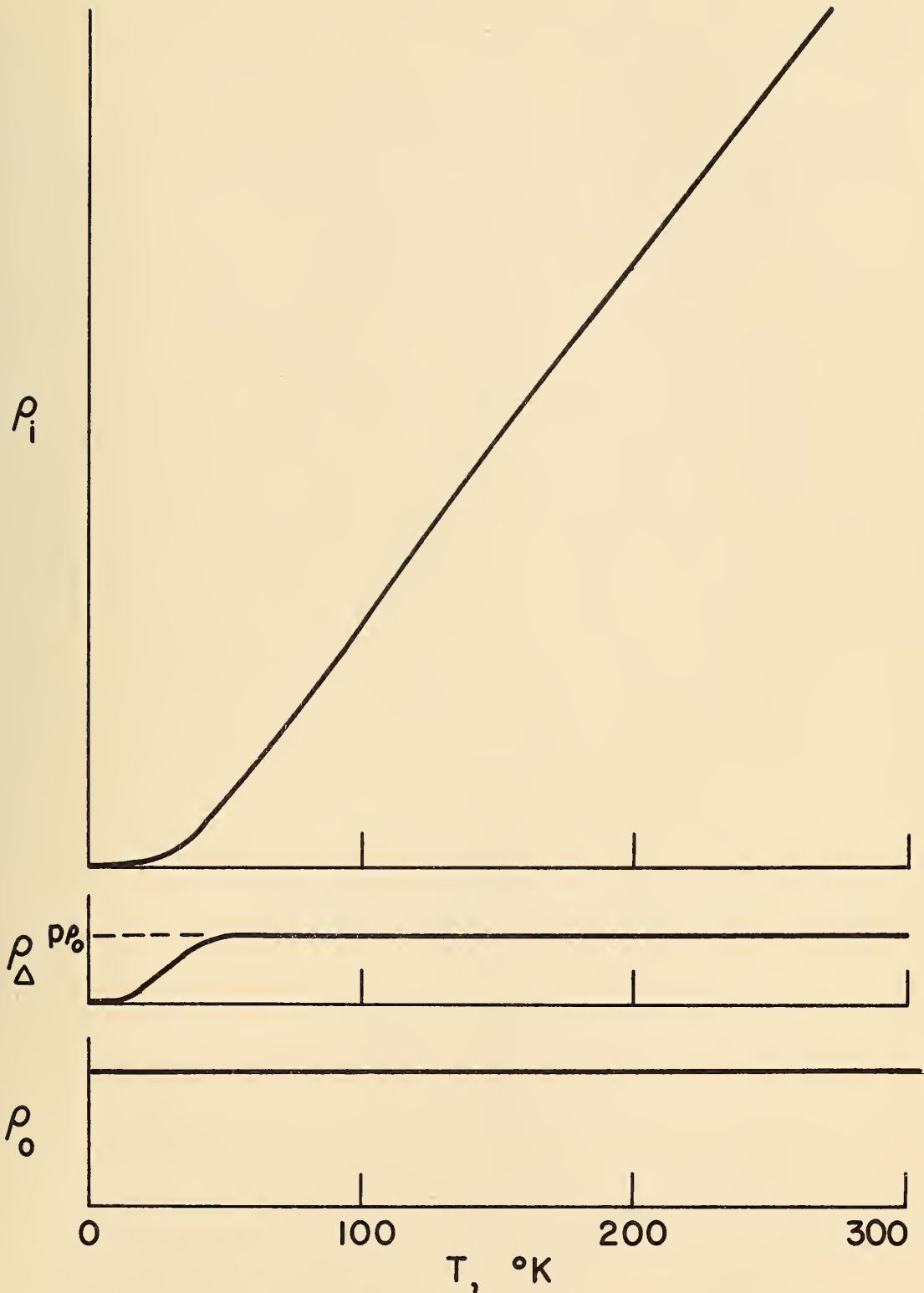
Fig. 1-Schematic representation of the "ideal" or lattice resistivity
(ρ_i), the residual resistivity (ρ_o), and Kohler's deviation
term (ρ_Δ) for a metal. The magnitudes of ρ_o and ρ_Δ have
been exaggerated relative to ρ_i.
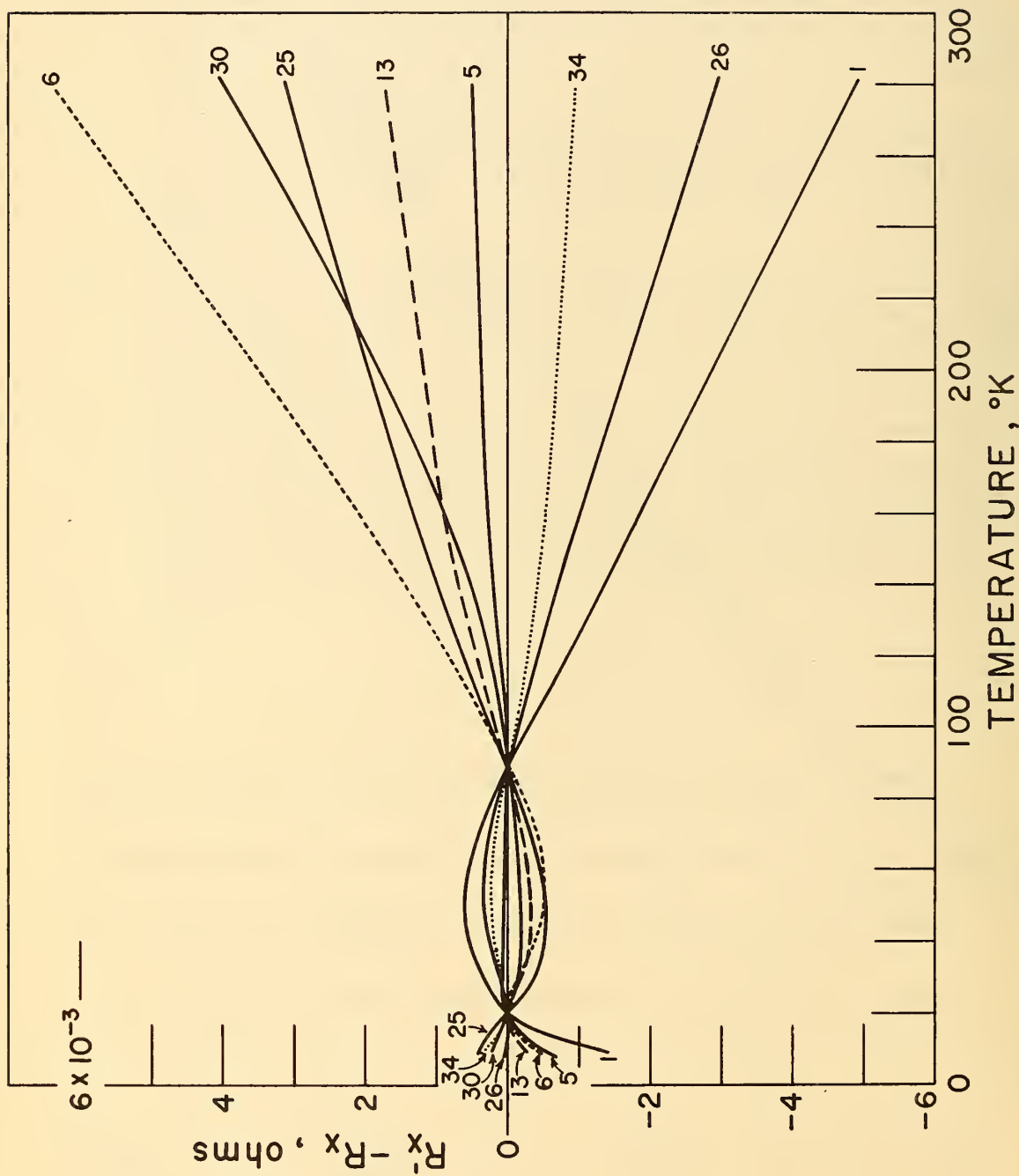
Fig. 2-Resistance errors for some representative thermometers using eq. (6) with $T_1 = 20°$, $T_2 = 90°K$.

THE NATIONAL BUREAU OF STANDARDS

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