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Full-Range Interpolations for Long-Stem Standard Platinum Resistance Thermometers Down to the Triple Point of Argon

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Abstract. This paper offers a possible solution to the present and potential future difficulties with the International Temperature Scale of 1990, ITS-90, regarding the triple point of mercury, TP Hg. This is discrepant within the ITS-90 and also may become unavailable for regulatory reasons on account of its toxicity. The suggestion is that for long-stem Standard Platinum Resistance Thermometers (L-SPRTs) requiring calibration below the triple point of water, TPW, the ITS-90 subranges above the TPW (ITS-90 Section 3.3.2) could simply be extended down to the triple point of argon, TP Ar, with no replacement for the TP Hg, but with an extra term in the interpolation equations. Such interpolations based on the TP Ar, the TPW, and the freezing points of Sn, Zn and Al, as far as is required, are found to be well-behaved and consistent with each other and with the ITS-90 above TPW, within about 0.5 mK. Below TPW the agreement with the ITS-90 is less good (~1 mK at TP Hg), mainly due to the problem with the mercury point. These new interpolations have been tested for internal consistency and for consistency with calibration data for L-SPRTs, and we suggest that they should be considered for inclusion in any amendment or revision of the ITS-90. The paper discusses some complications arising from this suggestion.

INTRODUCTION

The International Temperature Scale of 1990, ITS-90 [1], was formulated in two independent parts, for temperatures above and below the triple-point of water (TPW). This was done to avoid propagation of errors from high temperatures to low temperatures, such as had been encountered in the previous scale, the IPTS-68, where the ‘alpha’ coefficient (essentially the steam point) was used to define the first derivative dW/dT_{68} for an SPRT at the ice point¹, 273.15 K. In the ITS-90 the steam point was removed and replaced by a point between the TP Ar and the TPW, for which the TP Hg (at $T_{90} = 234.3156$ K) was chosen, because although it is quite close to the TPW it is a fixed point of the highest quality. However, it soon became apparent that the corresponding reference resistance ratio, $W_r(\text{Hg})$, was not well chosen, with the result that the discontinuity in the first derivative of the ITS-90 at the TPW was after all significant. The implied inconsistency of the TP Hg amounts to approximately +1 mK, which propagates to ~2 mK in the ITS-90 subrange from the TP Ar to the TPW [1, Section 3.3.1.3].

While this has not been a practical issue outside NMIs, a more serious problem may be the growing concerns over the use of mercury, even in well-controlled scientific laboratories, because of its toxicity [2]. If, as may happen, the use of mercury is banned, it will be necessary to amend the ITS-90 to implement the ban. Various possible alternative fixed points are being investigated for this purpose [3], though none is of the same quality as the TP Hg. The point favored by workers in cryogenic thermometry is the TP Xe, $T_{90} \sim 160$ K, because it is approximately mid-way between the TP Ar ($T_{90} = 83.8058$ K) and the TPW. However, it is below the temperature at which liquid baths can be operated, thereby presenting a barrier to using xenon cells for the calibration of long-stem Standard Platinum Resistance Thermometers (L-SPRTs).

¹ In the ITS-90 $W(T_{90})$ is the SPRT resistance ratio at the triple-point of water, $R(T_{90})/R(273.16 \text{ K})$.

To overcome this difficulty, we suggest in this paper that ‘full-range’ interpolations could be used, from TP Ar up to the maximum temperature desired, with no replacement for the TP Hg. Simple polynomials in $(W - 1)$ are proposed, effectively extending the subranges above the TPW (Section 3.3.2 of the ITS-90) down to the TP Ar, with an extra term in the interpolations. Specifically, the equation we propose for TP Ar to FP Al is a modification of the ITS-90 Equation 14,

$$(W - W_r) = a(W - 1) + b(W - 1)^2 + c(W - 1)^3 + d(W - 1)^4.$$

For the subrange TP Ar to FP Zn, $d = 0$, and for TP Ar to FP Sn, $c = d = 0$.

The fixed points TP Ar (83.8058 K), TPW (273.16 K), FP Sn (505.078 K), FP Zn (692.677 K) and FP Al (933.473 K), are spaced at intervals of about 200 K, which is close enough to the nodes of the Chebyshev functions [4] over these intervals that quadratic, cubic or quartic interpolations from TP Ar to progressively higher temperatures are well-behaved, with good consistency between them. They are also consistent with the existing ITS-90 above TPW (which would continue to be used if the low temperature extension is not needed), apart from subranges in which the ITS-90 includes FP In (429.7485 K).

We have investigated these interpolations and present figures showing firstly that errors or uncertainties propagate with no amplification except above FP Zn. We then investigate the sensitivity of the Subrange Inconsistency (SRI, Type 1 non-uniqueness) to errors in the data, the consistency of these interpolations with each other, using experimental data, and finally we compare the interpolations with those of the ITS-90.

INTERPOLATION SENSITIVITY TO ERROR AND INTERNAL CONSISTENCY

Figure 1 shows the propagation of unit ($e = 1$ mK) errors or uncertainties in the quartic interpolation from TP Ar to FP Al. The errors for the end points are well localized, and the main propagations occur for FP Sn and FP Zn. There is no amplification beyond 1 mK except above the Zn point, where the interval to FP Al is larger, at ~ 240 K, but in practice the peak effect, at $W \sim 3$, will be smoothed out by the expected larger uncertainty in FP Al. Elsewhere, the largest propagated effect is due to the FP Sn below TPW. Propagation of errors in the quadratic Ar-Sn and cubic Ar-Zn interpolations are similar to, but somewhat smaller than, those in the relevant parts of Figure 1.

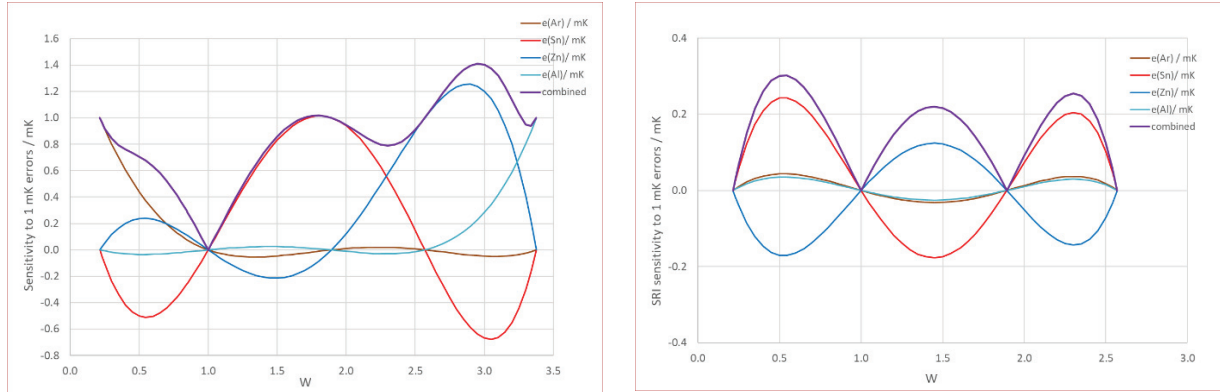


FIGURE 1 (left): sensitivity to 1 mK fixed-point errors (or uncertainties) in the quartic interpolation from TP Ar to FP Al, and **FIGURE 2** (right): the sensitivity of the SRI[Ar-Zn:Ar-Al] to 1 mK errors in the fixed points.

Figure 2 shows that errors in the Ar-Zn and Ar-Al interpolations are well-compensated, such that the sensitivity to error of the Subrange inconsistency, designated SRI[Ar-Zn:Ar-Al], is quite small, comparable with those of the ITS-90 [5]. These figures show the contributions of each fixed point, which are then combined in quadrature, assuming for convenience that they are independent.

Figure 3 shows that the sensitivity to 1 mK errors for SRI[Ar-Sn:Ar-Zn] is of similar magnitude to Figure 2, but in Figure 4 the sensitivity of SRI[Ar-Sn:Ar-Al] is somewhat larger.

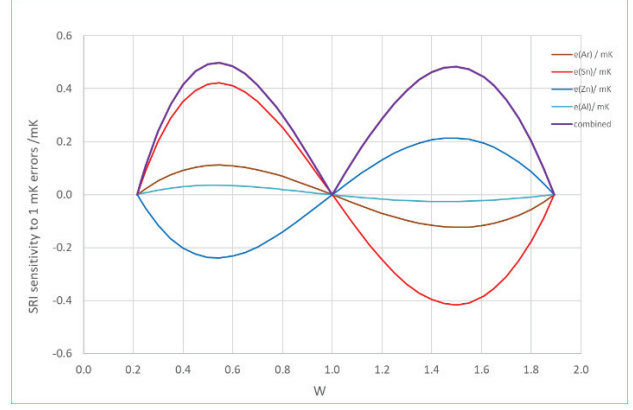
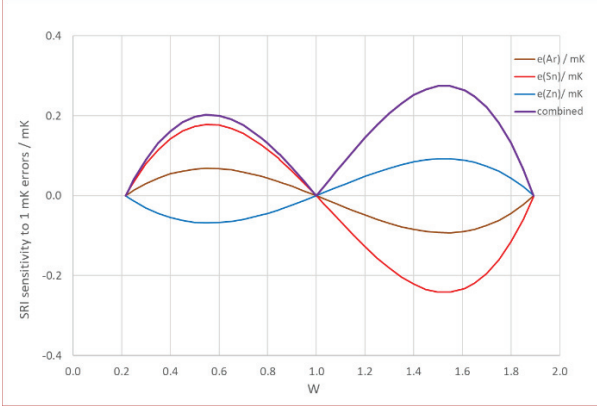


FIGURE 3 (left): the sensitivity of the SRI[Ar-Sn:Ar:Zn] to 1 mK errors in the fixed points, and **FIGURE 4** (right): the same for SRI[Ar-Sn:Ar:Al]. (Note that the contributions in Figure 4 are the sum of those in Figures 2 and 3, up to FP Sn.)

CONSISTENCY OF L-SPRT INTERPOLATIONS

(For ease of reading, from here on we refer to fixed points and subranges just by the chemical symbols of the elements concerned.)

We now examine the internal consistency (Subrange Inconsistency) of the full-range interpolations in practice, by comparing them using real calibration data, which are of course subject to experimental uncertainties. To do this we have taken data from CCT Key Comparison K9 [6], but as CCT-K9 did not extend to FP Al, we have also used calibrations from NRC (National Research Council of Canada) and PTB (Physikalisch-Technische Bundesanstalt), as reported recently in Table 1 of [7].

Comparing quadratic interpolations from Ar to Sn with cubic interpolations from Ar to Zn, Figure 5 shows that the 11 SPRTs from CCT-K9 are bunched within $\pm \sim 0.3$ mK, with a mean systematic undulation also of about $\pm \sim 0.3$ mK. Figure 6 shows the same for the 17 SPRTs in [7], with similar results, but with two discrepant SPRTs, Nos 13 and 77 in Table 1 of [7], which also provide the envelope of the results in Figures 7 and 8.

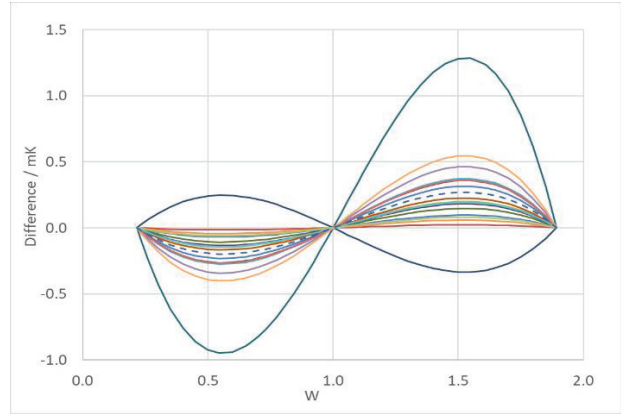
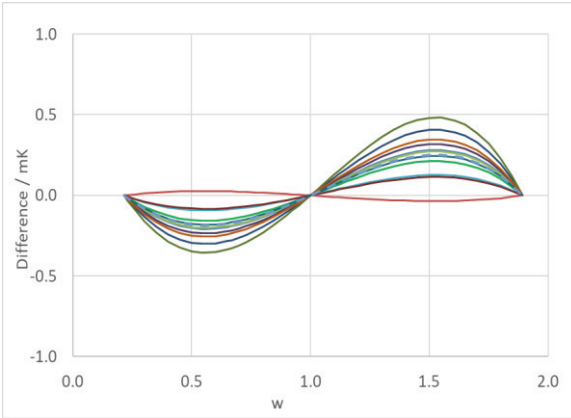


FIGURE 5 (left): the differences between quadratic interpolations from Ar to Sn and cubic interpolations from Ar to Zn, for 11 SPRTs used in CCT-K9 [6]. **FIGURE 6** (right): the result using the 17 SPRTs from [7].

Figure 7 illustrates the differences between the full-range quadratic (Ar to Sn) and quartic (Ar to Al) for the data in [7], and Figure 8 shows the same for the cubic interpolation for the Ar to Zn subrange. Note that the differences in Figures 5-8 are qualitatively comparable up to FP Sn. Also, Figure 8 should be the difference between Figure 7 and Figure 6, but in fact it is not quite so because more SPRTs are included in Figure 6. Between (Ar to Sn) and (Ar to Al) the maximum mean peaks are -0.37 mK and $+0.39$ mK. These averages are larger than in Fig 5, only partly because of the two prominent discrepant SPRTs.

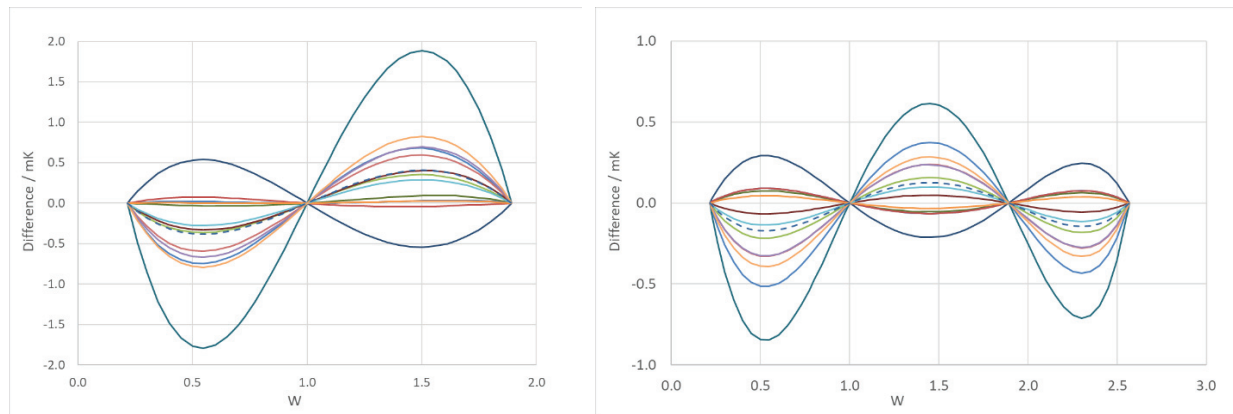


FIGURE 7 (left): differences between the full-range quadratic (Ar to Sn) and the quartic (Ar-Al), for L-SPRT data from [7]. **FIGURE 8** (right): differences between the full-range cubic (Ar to Zn) and quartic (Ar to Al).

COMPARISON WITH THE ITS-90

We now present four graphs showing the differences between full-range interpolations and the ITS-90 interpolations over the same ranges, using the same calibration data as in the previous section.

Figures 9 and 10 show the CCT-K9 data for the differences between full range interpolations and the ITS-90, from Ar to Sn and Ar to Zn, respectively. Both figures show discontinuities in the ITS-90 at TPW and substantial dispersion between the SPRTs below this, which are mainly associated with the offset at TP Hg and differences of more than ± 0.5 mK in its realization. Above TPW, Figure 9 (left) shows that the data are much more closely bunched (within ± 0.3 mK), but that there is a systematic offset, which is potentially caused by an inconsistency of ~ 1 mK in the ITS-90 at FP In at ~ 429 K, compared with FP Sn, at ~ 505 K [6]. Neither the TP Hg nor the FP In is used in the full-range interpolations.

Figure 10, for interpolations from Ar to Zn, shows similar discrepancy below TPW, but much better agreement above TPW, where there is a modest undulation, of mean amplitude ± 0.25 mK at $W = \sim 1.4$.

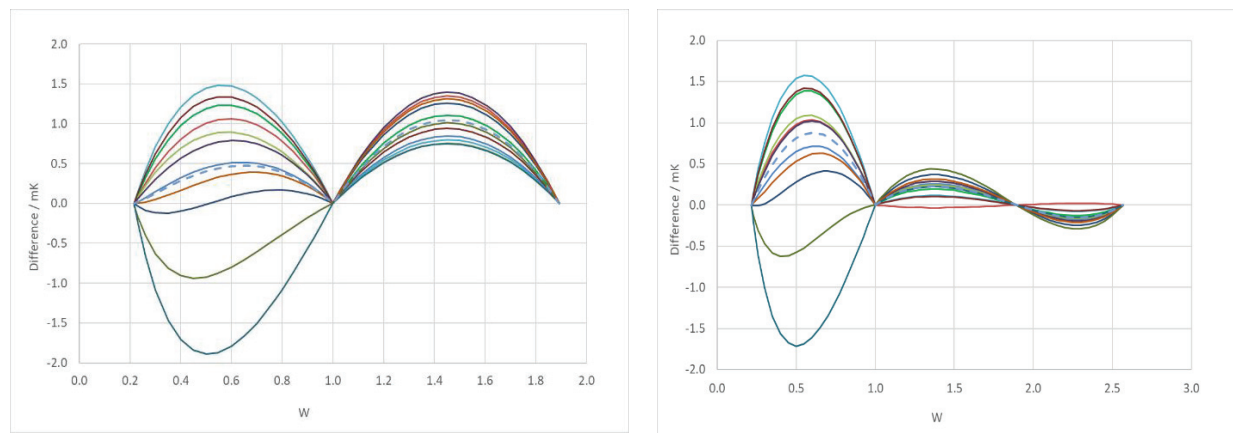


FIGURE 9 (left): differences between quadratic full-range interpolations with respect to the ITS-90, from Ar to Sn, using data for 11 SPRTs in CCT-K9. **FIGURE 10** (right) shows the same, for cubic full-range interpolations from Ar to Zn.

Figures 11 and 12 plot the differences from the ITS-90 for full-range interpolations for Ar to Zn and Ar to Al, using the data from [7]. Below TPW there are again two discrepant SPRTs in these figures (now Nos 17 and 77 from [7]). We note that these SPRTs also showed big changes in the S parameter, $(W-1)/(W_r-1)$ [8], of $+6 \cdot 10^{-5}$ and $-5 \cdot 10^{-5}$, respectively, between the Ar and Hg points, which suggests that the TP Hg data are anomalous, and we discount

them². In Figure 11, below TPW the remaining 13 SPRTs are more closely bunched than in Figures 9 and 10, with a mean peak value of ~ 1 mK. From TPW to FP Zn, Figure 11 shows similar bunching as in Figures 9 and 10, but with stray results for Nos 17 and 77. The comparisons from TP Ar to FP Al in Figure 12 shows rather more dispersion than Figure 11 below TPW, and also above TPW, though there the distribution is more nearly normal. The envelopes above TPW are again provided by SPRTs 13 and 77.

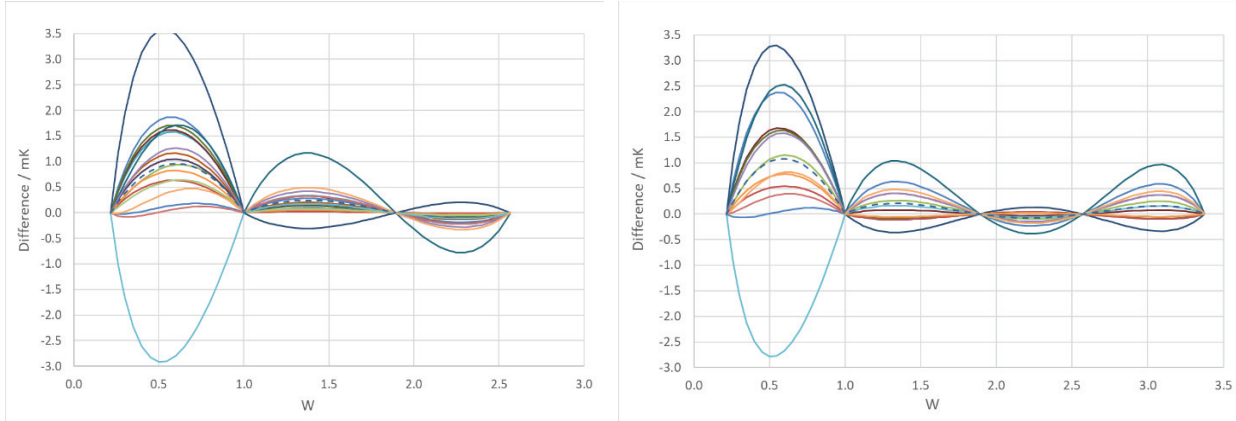


FIGURE 11 (left): differences between cubic full-range interpolations with respect to the ITS-90, from Ar to Zn, using data for 17 SPRTs from [7] (cf Figure 10). **FIGURE 12** (right) shows the differences between full-range interpolations with respect to the ITS-90, from Ar to Al for 13 SPRTs from [7].

SUMMARY AND CONCLUSIONS

This paper has presented three alternative interpolations which could usefully extend the ITS-90 subranges from the TPW to the Sn, Zn and Al points, respectively, down to the TP Ar. The objectives are to avoid the split in the ITS-90 subranges at TPW, which has led to discontinuities in the first derivative dW/dT_{90} , and to remove the need to use the TP Hg, which may in any case be banned because of its toxicity. The paper does not address the requirements for realizations of the ITS-90 using capsule-type SPRTs in subranges below TP Ar: this is a separate issue, though it is important that arrangements for capsule SPRTs and L-SPRTs are compatible where they overlap, and that in removing the TP Hg, the opportunity is taken to remove the inconsistencies for which it is responsible.

The three proposed interpolations use quadratic, cubic and quartic equations from TP Ar and TPW to FP Sn, Zn or Al, as far as required, making use of the fortuitously even temperature intervals between these five points. The spacing is not ideal, as dictated by the nodes of Chebyshev functions [4], but errors or uncertainties propagate without amplification except above the FP Zn, and the sensitivities to errors are in general less than those of the ITS-90 above TPW (see Figures 1 to 4 and [9]).

In Figures 5 to 8 the mutual compatibility of the interpolations is tested using calibration data taken from CCT-K9 [6] up to FP Zn and [7] up to FP Al. They are further tested by comparing them with the ITS-90 interpolations in Figures 9 to 12. In these figures we encounter effects due to errors in the data and the difficulties in the ITS-90 at the TP Hg and also at the FP In, as is discussed above, but we believe that, overall, the high quality of the interpolations is not only to be expected but is borne out in practice.

There are, however, some complications and concerns which may be raised. The first is that if the TP Hg is simply removed from the ITS-90, an NMI without TP Ar would be unable to realize the scale anywhere below TPW. A replacement for TP Hg, such as TP SF₆ or TP CO₂ [3] would at least allow realizations down to 223 K and 216 K, respectively. The TP Xe has not yet been successfully realized using L-SPRTs, and otherwise only TP Ar would enable realizations using L-SPRTs to cover the whole range of comparisons baths used for secondary calibrations, currently down to ~ 175 K.

² We are not able to investigate these data further, and cannot rule out that they are valid results, rather than erroneous data or unstable SPRTs. We can only say that it would surprise us if these changes in the S -values genuinely represent the behavior of the resistivities of compliant samples of platinum. If they do, then it calls into question the ability of reference and deviation functions to interpolate satisfactorily with the limited data in this subrange, and hence of the ITS-90 itself. (Such difficulties do occur at lower temperatures, where the density of fixed points in the ITS-90 was increased in order to achieve acceptable interpolations.)

Secondly, the conclusions are not definitive, in the sense that we have only been able to test the interpolations by reference to each other or the ITS-90, by comparing consistency and error sensitivity. The experimental data, as used in Figures 5 to 12, are not ideal, and we have had to make judgements about whether particular results are genuine or not.

Thirdly, we have briefly referred to the FP In, but not the melting point of gallium. These points were introduced in the ITS-90 to provide precise short-range interpolations, but we have found evidence that FP In may be discrepant relative to the FP Sn, by up to ~ 1 mK. This clearly needs to be investigated, by further consistency checks and by thermodynamic means. We have not tried including FP In in full-range interpolations, because it would upset the spacing of the points. In least squares interpolations, as in [10], it would certainly reduce the sensitivity to error in the mid-range, but we suspect that it may have adverse consequences elsewhere. We believe that including the MP Ga would not have much impact in least-squares interpolations especially if, as is desirable, they are forced to pass through the TPW.

ACKNOWLEDGMENTS

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