

Variable invariables - dimensional instability  
with time and temperature

S.F. Jacobs

Optical Sciences Center, University of Arizona  
Tucson, Arizona 85721

**ABSTRACT**

How stable are structures made of fused silica, Zerodur, ULE, Invar or Superinvar? We review what is known about dimensional changes with time or temperature for these important materials, including some recent findings.

What are the variations in commercially available materials? How does one go about *obtaining* the best Invar and Superinvar?

**1. INTRODUCTION**

Recent advances in astrometry and ultrastable lasers are imposing very stringent demands for dimensional stability of precision structures and science instrument components. As a result, it has become necessary to critically reexamine much of our old reliable data to see whether it truly applies to real-world conditions. We describe here some of the variations that exist in what we may have considered invariable expectations. The discussion is restricted to temperature and time. Other parameters, such as refractive index, may require consideration as well.

When it comes to real-world performance, there are many parameters to consider. For example, fused silica is a very important and well refined material, excellent both for its structural and its optical properties. Most manufacturers provide detailed information concerning its spectral transmittance, but how much variation is there in the instantaneous<sup>1</sup> linear coefficient of thermal expansion,  $\alpha'$ , vs temperature for **different** fused silicas, including behavior at cryogenic temperatures? What about **hysteresis** (return to original length after thermal cycling)? What about Invar's thermal expansivity **vs. temperature**? How can one reliably *obtain* Invar with the lowest thermal expansivity? What can be meaningfully said about thermal expansivity vs. temperature of composite materials? What about **temporal instability** (changes in length at constant temperature)? For example, Invar generally elongates as it ages at room temperature. What can we expect it if is used at an **elevated** temperature? What is known about **temporal** instability of other low thermal expansivity materials? We are finding that any synthetic material whose dimensions **can** change, **will** change. And that we can observe this change, given enough time or measurement sensitivity.

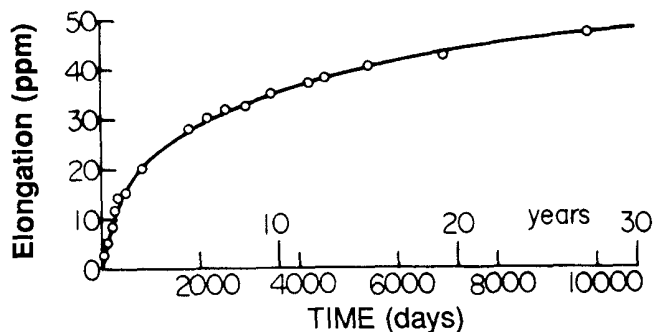


Fig. 1 Elongation of Invar at room temperature.<sup>2</sup>

In the late 1920's, Guillaume described Invar's temporal instability, which he measured at constant temperature, by mechanical means, over a period of 30 years! (See Fig. 1.) In the early 1970's, Justice<sup>3</sup> studied temporal instability of fused silica and ULE over a period of three years, using optical interferometry. More recently, lasers have made possible the technique of optical heterodyning, which faithfully compares a stable laser's frequency with that of another laser, which may be locked to the resonant frequency of an optical cavity with mirrors spaced by a material whose length change is being measured. Initially, HeNe lasers were used, stabilized with respect to neon atoms ( $\Delta\nu/\nu \sim 10^{-9}$ ), or molecules such as Iodine ( $\Delta\nu/\nu \sim 10^{-11}$ ). Later Hall et al. showed<sup>4</sup> that even better stability can be achieved by stabilizing a laser with respect to the length of an empty cavity which is superbly temperature controlled. For example, if the cavity spacer material's thermal expansivity is  $.01 \text{ ppm K}^{-1}$ , then  $\Delta\nu/\nu = \Delta L/L = \alpha\Delta T = 10^{-14}$ .

Renewed interest in highly stable lasers has been motivated by such challenges as gravity wave detection and the availability of trapped and frozen atoms. Laser linewidths approaching a few milliHertz have been demonstrated, which makes them comparable in stability to the best hydrogen masers. Thus the search for dimensionally stable materials has come full circle: stable lasers helping to evaluate stable materials which in turn will be used to make stabler lasers.

## 2. THERMAL EXPANSIVITY

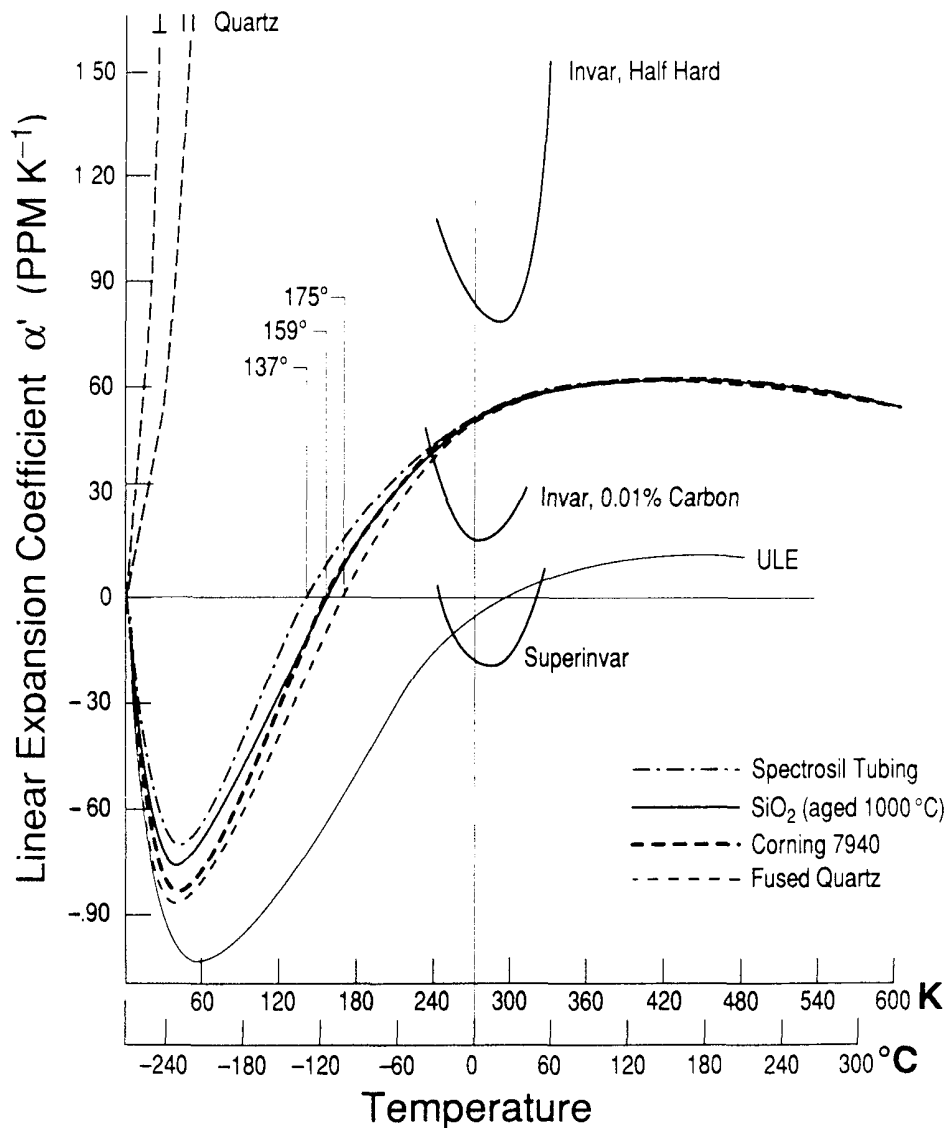
### 2.1 Fused silica

The term "quartz" is used here to mean the crystalline form of  $\text{SiO}_2$ . It occurs in nature, but can be made synthetically. Vitreous silica is  $\text{SiO}_2$  in the glassy state, which can be made, starting either from quartz (fused quartz) or from compounds such as  $\text{SiCl}_4$ , e.g. by flame hydrolysis (fused silica).

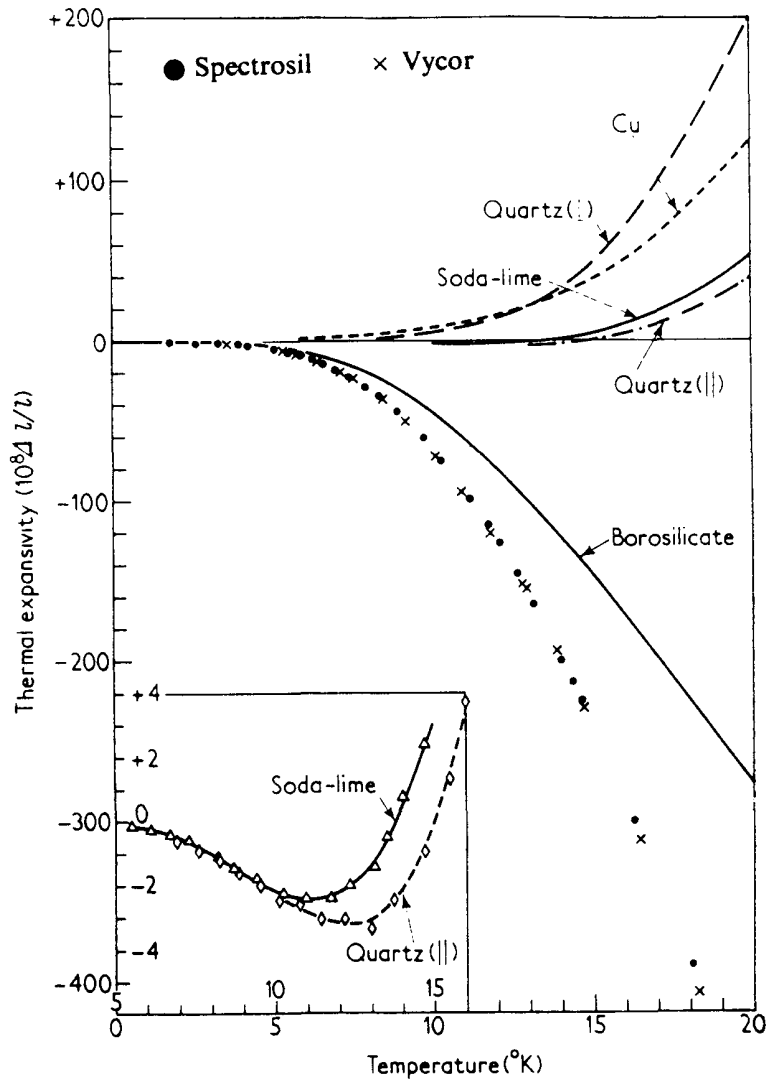
Manufacturers' data today contains little information about the instantaneous thermal expansivity  $\alpha'$ . Often  $\alpha'$  is stated, but the temperature intervals are not small, and just as often a single  $\alpha$  is quoted without mention of any temperature at all. To clarify the situation, we present Fig. 2, which includes G.K. White's low temperature measurements and ours at higher temperatures. I was surprised to see how little

variation there is in commercially available fused silicas, despite the variations possible by varying heat treatments.<sup>6</sup> One thing that **does** vary a little is the  $\alpha'$  zero-crossing temperature for fused silicas: from 137K (for specially annealed fused silica tubing<sup>7</sup>) to 175K (for fused quartz<sup>8</sup>). It is interesting to note that although crystalline quartz has very large thermal expansivity at room temperature, its expansivity becomes smaller in magnitude than that of fused silica at temperatures below 20K<sup>5</sup> (See Fig. 3; Table I).

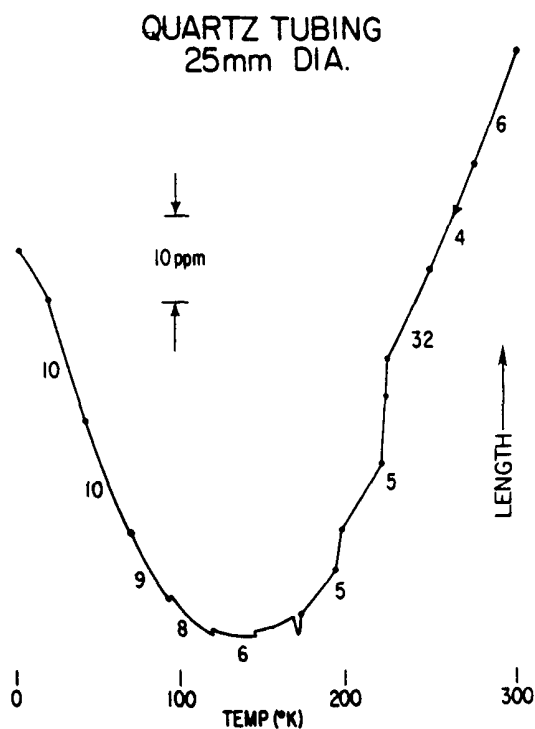
**Fig. 2 Thermal expansivity vs. temperature of quartz, fused silica, Invar, Superinvar, and ULE.**



**Fig. 3 Thermal expansivity of glasses and quartz; curve for copper is included for comparison. (Reproduced by permission of G.K. White and the publishers, Butterworth Heinemann Ltd. ©)**



Again in the cryogenic temperature region, around 235K, we have often encountered hysteresis-like effects in well annealed fused silica (see Fig. 4), Zerodur, and Solgel. These effects need further investigation, and may be avoidable, as Schott Glaswerke has shown with their development of Zerodur M (see next section).



**Fig. 4** Thermal expansion of Spectrosil grade tubing annealed 1050 to 850°C at 15°/hour. Numbers show waiting times in hours. (Similar behavior was observed for 18 and 14mm tubing).

## 2.2 Zerodur

Zerodur is a glass-ceramic made by Schott which achieves near-zero thermal expansivity over a wide temperature range by balancing a positive expanding glassy phase component with a negative expanding crystalline phase component. Fig. 5 shows  $\alpha'$  vs temperature of Zerodur.<sup>8,9,10</sup> What is not shown in this curve is the hysteresis behavior<sup>11,12</sup> shown in Fig. 6. Here the sample is thermally cycled at 60 K/hr, waiting every 25° for the sample length to stop changing. We see that after reaching thermal equilibrium, the sample sometimes undergoes (often very time-consuming) relaxation effects. To avoid this problem, Schott developed Zerodur M.<sup>13</sup> Note that the general shape of the curve  $\alpha'$  vs temperature is greatly changed from that of standard Zerodur. A comparison is shown in Fig. 5.

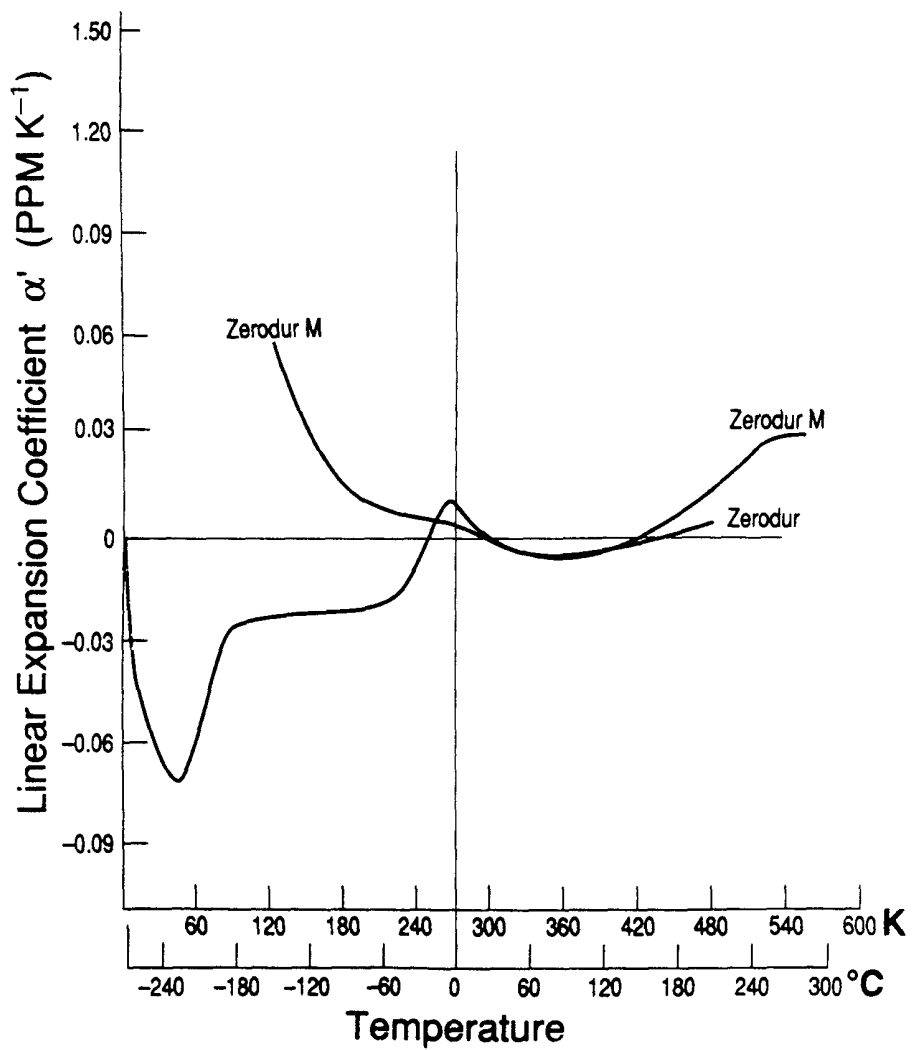
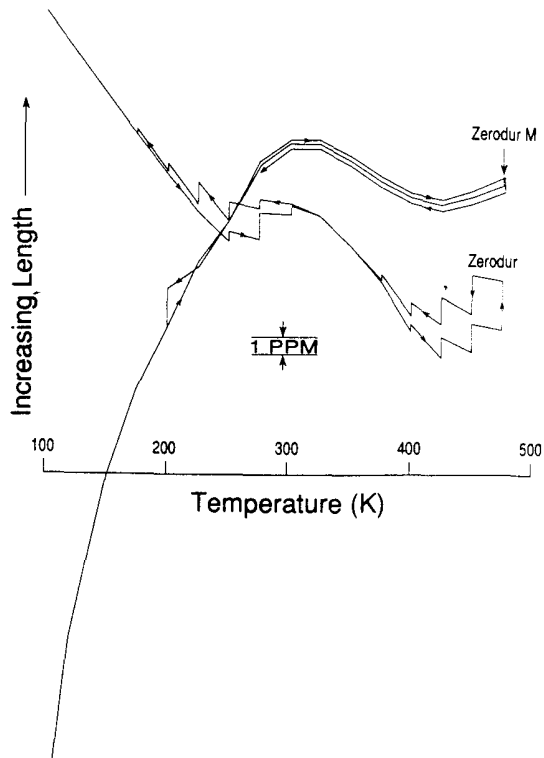


Fig. 5  $\alpha'$  vs temperature for Zerodur and Zerodur M.

$T^{\circ}K$	<i>Spectro-sil</i>	<i>Vycor</i>	<i>Boro-silicate</i>	<i>Soda</i>	<i>Quartz</i> (I)	<i>Quartz</i> (II)	<i>Quartz</i> <i>Average</i>
283	(50)	(75)	(300)	(900)	1370	750	1160
85	—	—	—	—	640	260	510
75	—	—	—	—	570	225	455
30	-72*	-68	—	+62	160	49	123
25	-66	-64	-20	+37	103	30.5	79
20	-59	-58	-27	+17	53	13.3	40
15	-45	-45	-24	+4.0	17.5	3.0	13
12	-33	-33	-19	+0.5	6.9	0.0	4.6
10	-23.5	-24	-15	-0.5	2.7	-0.6	1.6
8	-14.3	-14.5	-9.5	-0.7	1.0	-0.5	0.5
6	-6.8	-6.4	-4.5	-0.2	0.4	-0.25	0.2
4	-2.0	-1.8	-1.3	—	—	—	—

**Table I. Linear thermal Expansion Coefficients ( $\times 10^8 \text{ deg. K}^{-1}$ ). Value marked \* is extrapolated. Those in brackets have been quoted in commercial literature of tables for glasses of similar composition.<sup>5</sup> (Reproduced by permission of the publishers, Butterworth Heinemann Ltd. ©)**



**Fig. 6 Thermal expansion  $\Delta L/L$  vs temperature of Zerodur and Zerodur M.**

### 2.3 ULE

ULE (Corning Code 7971) is a vitreous mixture of  $\text{SiO}_2$  + nominal 7.4 wt% of  $\text{TiO}_2$ .  $\alpha'$  vs temperature is shown in Fig. 2.<sup>14,15</sup> Note the similarity between the shapes of  $\alpha'$  vs temperature curves for ULE and fused silica. This is because  $\text{TiO}_2$  has a negative expansivity near room temperature. Of special interest is the fact that ULE does not exhibit the hysteresis problem that can occur in glass ceramics. Fig. 7 shows the results of repeated thermal cycling of ULE.

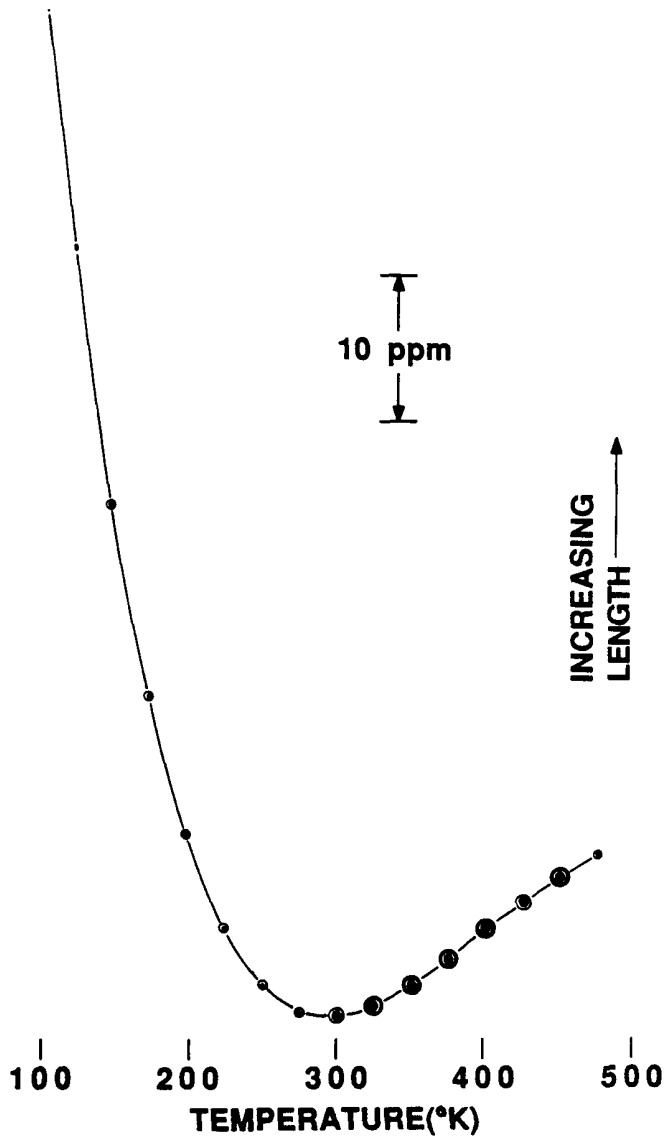


Fig. 7 Repeated thermal cycling of ULE.



## 2.4 Invar

When a low thermal expansivity **metal** is required, usually for reasons of strength, there is little alternative but to use some form of Invar, an iron-nickel alloy containing about 36% nickel. Discovered by Guillaume in 1886,<sup>16</sup> Invar has a low thermal expansivity near room temperature which arises from the interplay of two phenomena. Although Invar is face-centered cubic at room temperature, it is ferromagnetic, with a Curie temperature of 260°C. On heating, at temperatures below the Curie temperature, the magnetic order decreases, with a corresponding decrease in volume. The normal lattice expansion occurs simultaneously, however, and for a temperature interval below the magnetic transition, there is a temperature at which the net expansion can be very close to zero, and in some instances<sup>17</sup> even less than zero. Referring to Fig. 2, the lower Invar curve describes the lowest expansivity Invar we have measured. In general, we find U-shaped curves with various magnitudes, such as that shown for half-hard<sup>18</sup> Invar. G. Girard at the Bureau International des Poids & Mesures has done excellent work on treating Invar **tapes** and **wires**, by a combination of thermal and mechanical working. Expansivities  $< 1 \text{ ppm K}^{-1}$  are reported, along with temporal stability  $< 1 \text{ ppm/yr}$ .<sup>19</sup>

For certain applications, the smallest expansivity possible is not desired, but rather an expansivity *match* with vitreous silica. Fig. 2 shows the temperature range over which this match is possible.

Lement and Averbach showed<sup>17</sup> that Invar's low expansivity is adversely affected by the presence of carbon, manganese, silicon, sulfur, phosphorus, and virtually any other impurity. We describe in Appendix I how Jet Propulsion Laboratory obtained the Invar shown in the lower curve of Fig. 2.

## 2.5 Superinvar

Several variations on the Invar theme have been produced. These include Superinvar (Fe, Ni, Co) and Stainless Invar (Fe, Co, Cr).<sup>16</sup> It has been possible to obtain thermal expansivity zero crossings with such materials (see Fig. 2), as well as good temporal stability. (See Section II.) Appendix II shows the composition of the Superinvar sample shown in Fig. 2, as well as its heat treatment. Unfortunately, with Superinvar there appears to be a delicate balance not only in the fabrication (composition and heat treatment) but in post-fabrication thermal, magnetic and mechanical treatment. E.g., Don't heat it, magnetize it, or drop it! In addition, with Superinvar (but not Stainless Invar!) there is an irreversible phase transition (from face-centered cubic to body-centered cubic) which occurs at temperatures ranging from about 270K to 100K, depending on composition.<sup>16</sup> We deliberately cycled Superinvar through this phase transition by immersing a sample in liquid nitrogen. The material promptly elongated by 3/4 of one percent, and its temporal stability worsened. This will be discussed further in Part 3.

### 3. TEMPORAL INSTABILITY - LENGTH CHANGE AT CONSTANT TEMPERATURE

#### 3.1 Fused silica

We have always considered vitreous silica to be dimensionally stable with time. In the early 1970's, we measured the temporal stability of different fused silicas, Heraeus-Amersil's Homosil and Corning Code 7940, ULE, Zerodur, Invar and Superinvar using an iodine-stabilized HeNe laser.<sup>20</sup> Since that time, we have included the same optically contacted Homosil sample (cavity) in all our temporal stability measurements to serve as a secondary standard; the primary standard was a Zeeman stabilized HeNe laser.<sup>21</sup> Recently, Ben Dolgin, noting the excellent agreement between our early measurements of Homosil and those of Ben Justice, urged us to examine our subsequent data obtained with the same sample, over various time periods ranging from two to four months. Fig. 8 shows this. The large error bars are due chiefly to temperature fluctuations. For fused silica near room temperature,  $\Delta T = .04^\circ\text{C}$  corresponds to  $\Delta L/L = .02\text{ppm}$ . These results suggest that perhaps fused silica shrinks with time, with a time constant of about 10 years. Because of the importance of this material, further work, with better temperature control, seems indicated.

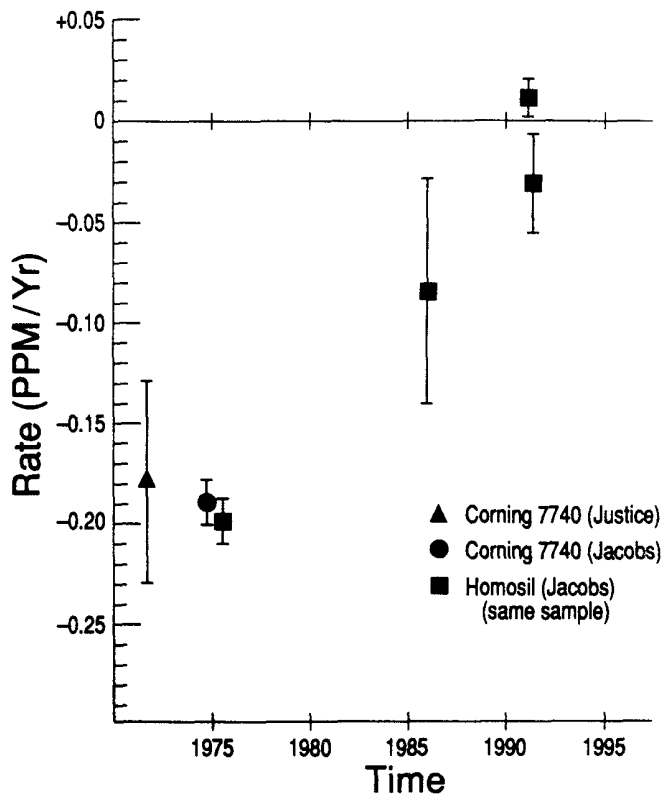
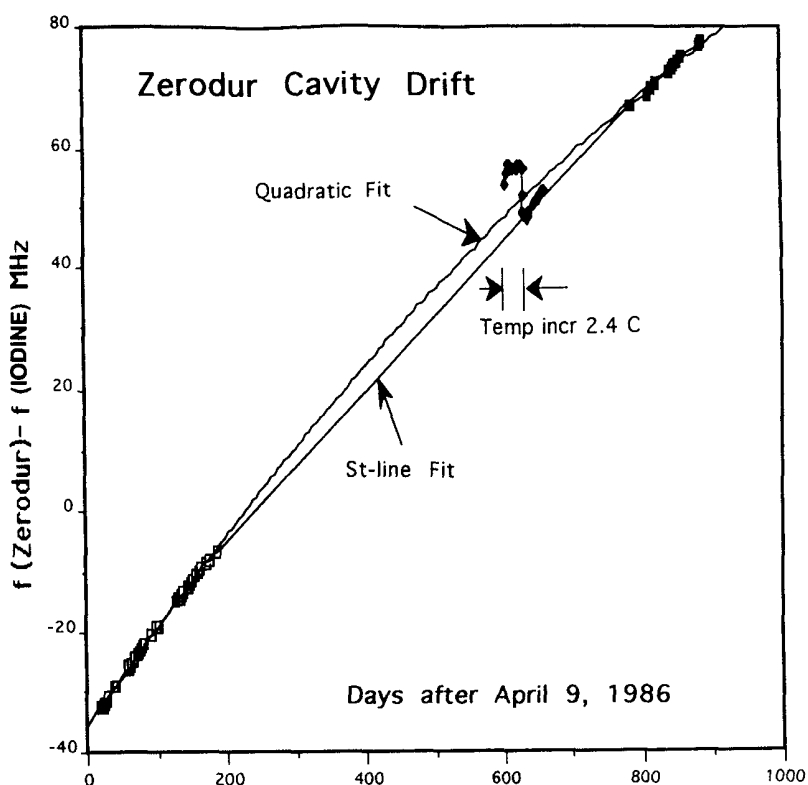


Fig. 8 Fused silica shrinkage with time.

### 3.2 Zerodur

In 1975 we reported measurements of temporal stability of Zerodur<sup>20</sup>. Over a six-month period, we found less than .01 ppm change. However, Schott only claims <0.1 ppm/yr stability. Recently, John Hall evaluated Zerodur for use as an ultrastable cavity for stabilizing lasers. Fig. 9 shows his unpublished results, which were obtained using an iodine-stabilized laser and (several) microdegree temperature control. These results imply a shrinking of 0.1 ppm/yr. This stability is more than adequate for most purposes, however for the ultimate in stability there remains some concern about the so-called "thermal memory" of glass ceramics.

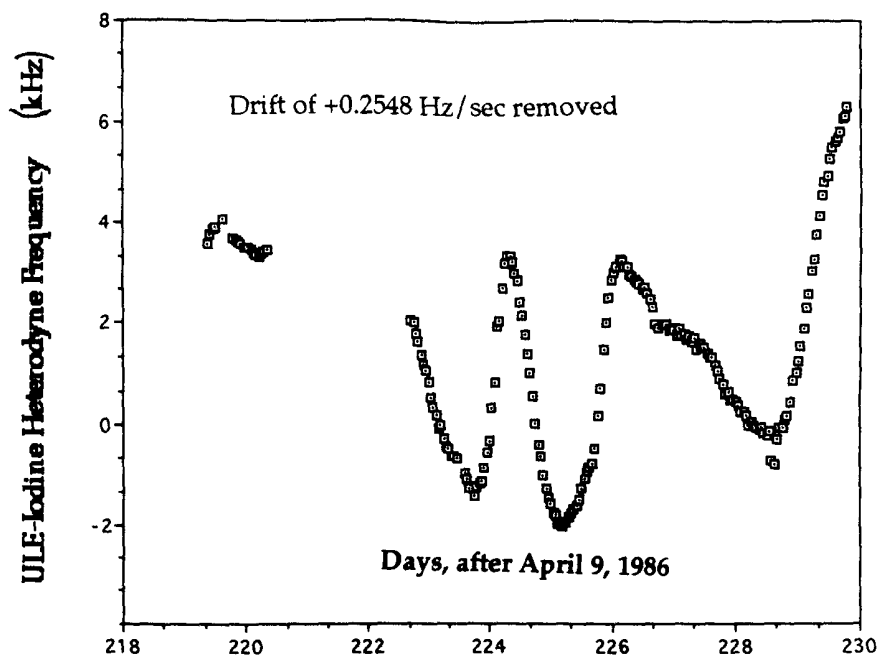


**Fig. 9** Heterodyne beat of Zerodur cavity stabilized laser vs iodine stabilized laser. (Adapted from J.L. Hall unpublished figure.)

### 3.3 ULE

Our 1975 results<sup>20</sup> showed ULE shrinking .06 ppm/yr. John Hall's recent results with ULE show shrinkage of .025 ppm/yr., (drift of .2548 Hz/sec.). Fig. 10 shows the laser stability he achieved by locking to a cavity made of this material, with the material's length drift removed.<sup>22</sup>

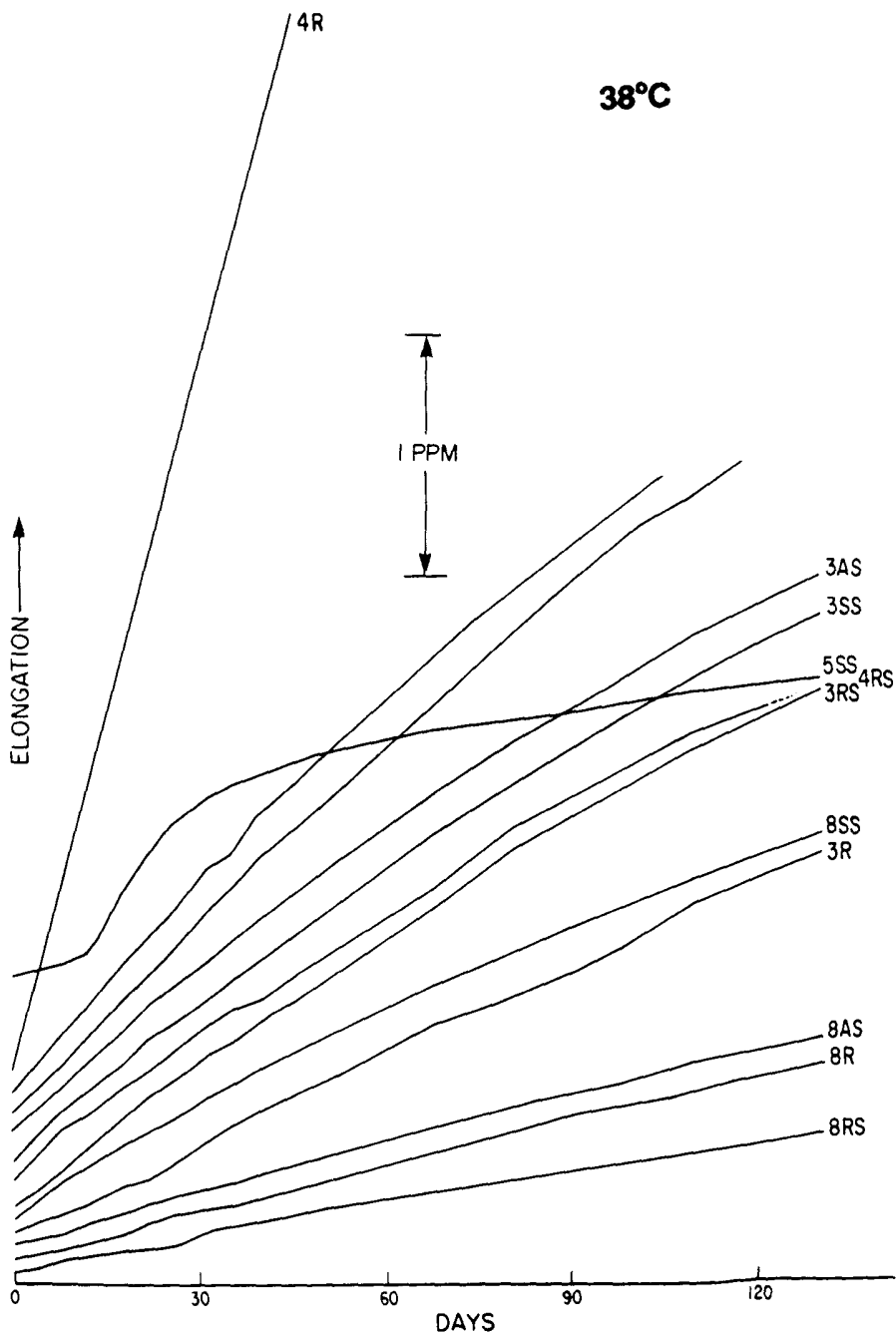
**Fig. 10** Relative beat frequency between ULE cavity stabilized laser and iodine stabilized laser. (Adapted from J.L. Hall unpublished figure.)



### 3.4 Invar

The temporal instability of Invar has long been recognized, yet its desirability as a low thermal expansivity metal often makes Invar the material of choice for applications near room temperature. One approach to the temporal instability problem has been to stockpile and age the material. Another has been to try various heat treatments in order to accelerate the aging process.

In 1983 a study was designed by David Schwab<sup>23</sup> to investigate the aging effectiveness of four different heat treatments. Fig. 11 shows the results at 38°C. It was found that the simplest of the treatments tried<sup>24</sup> proved the most effective.



**Fig. 11** Elongation with time of Invar samples with various heat treatments.  
**R** = untreated; **RS** = (see reference 23).

Recently, an unusual problem came up: How to predict accurately the future length change with time for well characterized Invar, to be used at an elevated temperature. The literature contained almost no information, and so an experiment was performed<sup>25</sup> to compare temporal stability, first at 25°C, then at 35°C, then back at 25°C for variously treated Invars. In addition to obtaining excellent time constant measurements for this material, it was concluded that most of the material variables (see Table II) made little difference to the aging curves (Fig. 12), but low carbon content notably improved the temporal stability. This is consistent with the findings of Lement et al.<sup>17</sup>

### Typical Sample Growth at 35°C

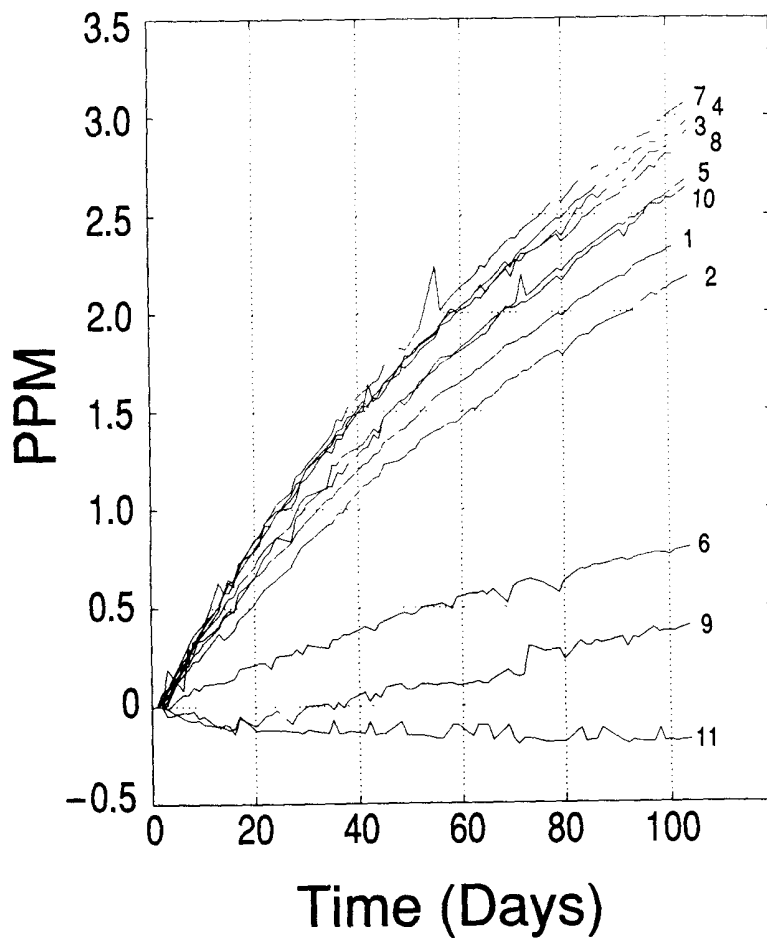


Fig. 12 Invar temporal length change with time. Numbers refer to sample variables shown in Table II.

Despite the many studies of temporal instability of Invar, today's user is faced with a problem: What can I expect of material I obtain *now*? We are currently measuring the temporal stability of the material described in the lower Invar curve of Fig. 2. This appears to be exceptionally stable material, but unfortunately it has not yet proven cost effective for a steel manufacturer to produce, characterize and make available for sale a large batch of material. As a result, every special job remains a special project for a metallurgical specialist.

### 3.5 Superinvar

We discussed earlier what happened when Superinvar underwent the infamous phase transition. After we deliberately immersed two of three samples of Superinvar in liquid nitrogen, their subsequent temporal instability, compared with that of the pristine third sample, was considerably worsened, as shown in Fig. 13.

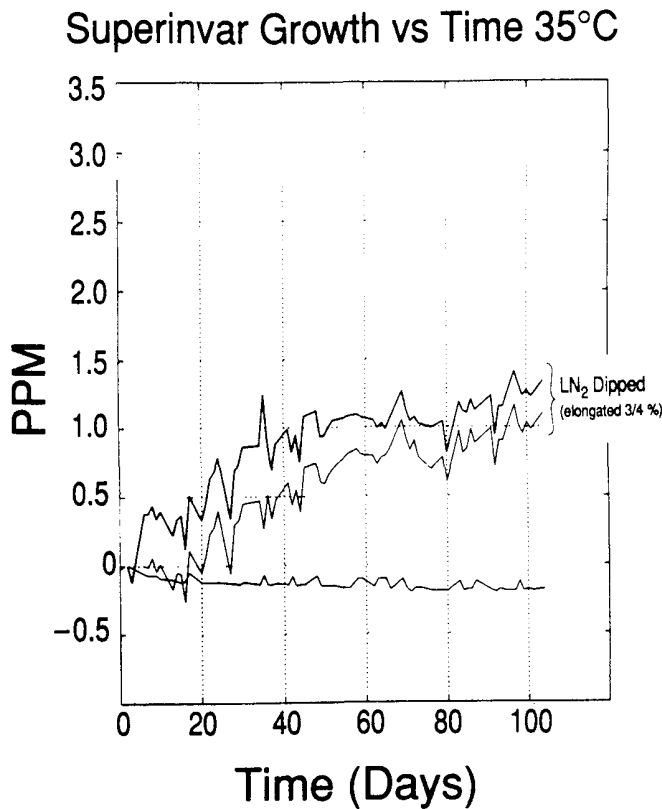


Fig. 13 Effect of phase transition on temporal stability of Superinvar.

The best Superinvar we have encountered is that whose expansivity is shown in Fig. 2. Its composition has been verified several times, and is shown in Appendix II along with its heat treatment. Because of its low thermal expansivity, we have studied the temporal stability of this sample frequently over the past 20 years, with varying results (see Table III). We find that the superb temporal stability, initially obtained through the heat treatment described, is easily degraded by rather small changes in temperature. It is undoubtedly because of this that Averbach recommends<sup>26</sup> that the most reliable route to development of a very stable Invar is ultrahigh purity Invar, rather than through the delicate balances involved in Superinvar.

#### 4. MEASUREMENT METHOD

The most prevalent expansivity measurement method in use today is the dilatometer,<sup>27,28</sup> employing for example a linear differential voltage transformer to sense differential length changes with respect of a known, calibrated sample. These instruments are very useful for general studies of expansivity, providing high sensitivity often exceeding 0.1 ppm. The  $\Delta T$  part of the problem is often the weak link, especially when expansivity is not small. Reaching thermal equilibrium takes time, and time costs money. As a result, most measurements are made without waiting for true thermal equilibrium, but rather with a slow temperature scan. What is lost by this omission, in addition to precision, is information about the waiting time, which gives us a clue concerning what is going on inside the material. For example, Zerodur in some temperature ranges can take over 24 hours to equilibrate to a criterion of  $\Delta L/L \leq .01$  ppm over an hour's time.<sup>29</sup>

The laser/interferometric method we use was described by A.D. White,<sup>30</sup> who frequency locked a tunable HeNe laser to a Cervit cavity of length  $L$  and then compared the tunable laser's frequency  $\nu$  with that of a HeNe laser stabilized with respect to a Neon atom. He then varied the temperature of the Cervit cavity and deduced the change in cavity length  $\Delta L$  in the locked tunable laser's frequency, using the relationship  $\Delta L/L = \Delta \nu/\nu$ . The precision of this method is essentially that of the stable laser's stability, excluding temperature errors. Thus, for low expansivity materials, where temperature errors are generally unimportant, laser stability  $\Delta \nu/\nu = 10^{-9}$  allows  $\Delta L/L$  precision of .001 ppm. Parks recently noted<sup>31</sup> that the Japanese have written a National Industrial Standard based on this technique.

Figs. 14 and 15 show how we utilize the above principle for thermal expansivity and temporal stability measurements respectively. Fig. 15 also shows our typical sample configuration. For very high precision work, we optically contact the mirrors to the sample ends, however it is more convenient to use a vertical optical axis, with gravity holding the cavity together.



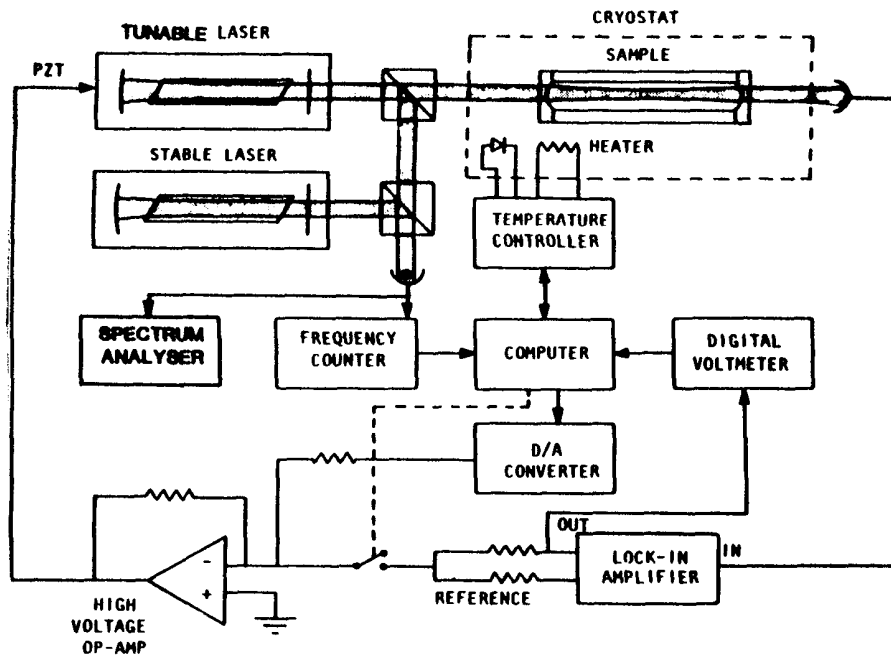
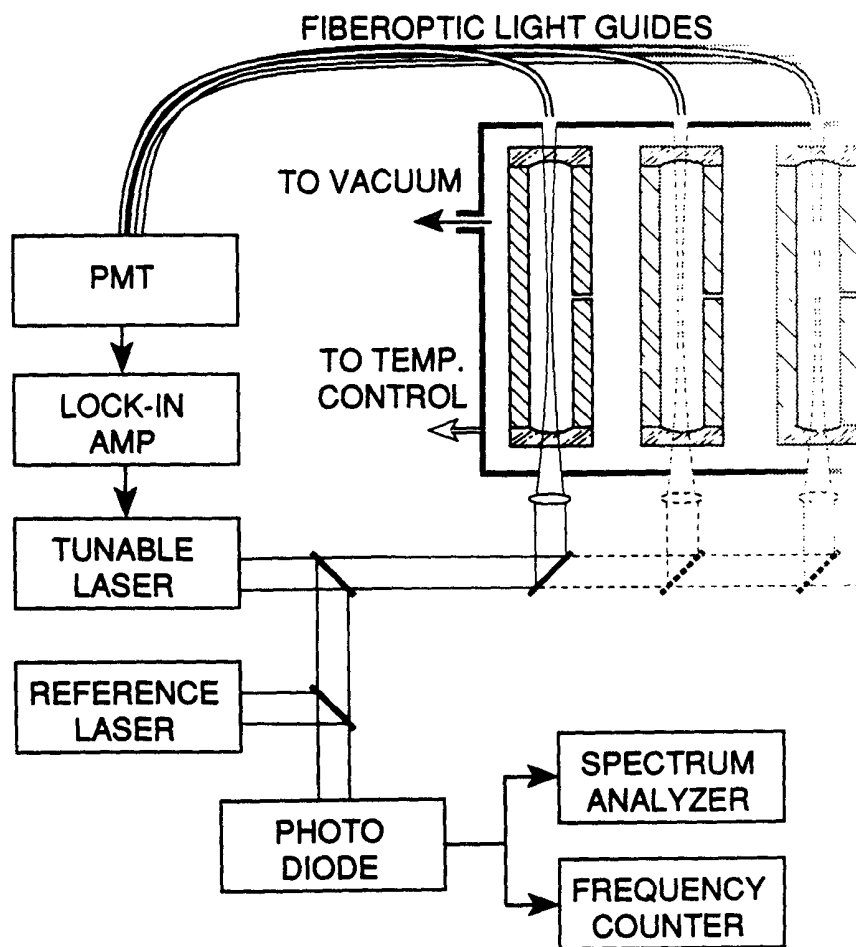


Fig. 14 Arrangement used for laser/interferometric measurement of length changes with temperature.



**Fig. 15** Arrangement used to study changes of length at constant temperature.  
Present chamber capacity: 37 samples.

## 5. CONCLUSIONS

We have shown that

1. Regarding thermal expansivity of different fused silicas, the few differences there are, lie at **cryogenic** temperatures.
2. Regarding Zerodur and Zerodur M, both have extremely low thermal expansivity over a wide temperature range. One should be aware of the hysteresis problem and the different shapes of the curve of  $\alpha'$  vs temperature.
3. ULE has no hysteresis problem.
4. Regarding Invar, indications are that  $\alpha' = 0$  can be obtained from Invar made extremely free from impurities. Especially carbon. It is then reasonable to expect temporal stability better than 1 ppm/yr. (See acknowledgements.)
5. Regarding Superinvar, detailed information is presented describing the best Superinvar we have seen. While the thermal expansivity is superb, the temporal stability is shown to vary with temperature.

Work is in progress in our laboratory to characterize graphite/epoxy, PEEK, and carbon/carbon with respect to thermal expansivity and temporal stability. These materials can be tailored to meet various requirements, however their technology has not yet matured to the point where detailed characterization is useful. Graphite/epoxy is especially attractive for its shape flexibility as an optics mounting material. Unfortunately, unlike carbon/carbon, graphite/epoxy has a water absorption problem which hampers characterization. A current approach is to seal graphite/epoxy and hope to prevent water absorption in this way. Two ways of evaluating this are:

1. Test different sealants.
2. Correlate weight change with temporal instability.

## 6. ACKNOWLEDGEMENTS

We gratefully acknowledge the encouragement and assistance of JPL personnel Tim O'Donnell, Cheng Hsieh, Mark Lane and Witold Sokolowski, who have succeeded in obtaining the strong, low expansivity Invar described in Appendix I and are willing to advise others. Many thanks to John Hall for useful discussions and permission to use his unpublished data. Also thanks to Henry Hagy for background concerning ULE and fused silica, and to Guy White for permission to use his excellent low temperature expansivity data. Finally, thanks to Dan Bass, who made most of our measurements.

## 7. APPENDICES

### Appendix I. Preparation of the Invar shown in Fig. 2, lower curve.

This material was produced through powder metallurgy by Spang Specialty Metals in July, 1990, with the request for very high purity material. Essentially, Fe 64%, Ni 36%, and nothing else. The material tests showed

Al	<	.001%
C		.002
Ni		36.0
Mn	<	.001
P	<	.01
S		.001
Fe		(balance)

Spang produced a 500 lb. sintered billet, 4 x 8 x 54". To increase the material's strength, the billet was then sent to Scientific Alloys, Inc. for hot forming (hammering to increase density), and finally extrusion into rods and other shapes.

**Appendix II.** The Superinvar sample shown in Fig. 2 was manufactured by Simond Steel Division of Wallace-Murray Corporation in the mid-1960's. It was Heat J-3058, purchased by Charles Freed of MIT. Its composition and heat treatment is as follows:

Al	.01%
C	.03
Co	5.10
Cr	.05
Cu	.04
Fe	(balance)
Mn	.46
Mo	.024
Ni	31.2
P	.005
Si	.06
S	.013
Ti	.01
V	.01
Zr	.001

Lement, et al.<sup>17</sup> developed a heat treatment that is often referred to as the *MIT triple treat*. The first step is an 830°C soak and then water quench, typically followed by rough machining. The second step is soak at 315° for one hour and then air cool, followed by a third soak at 93° for 48 hours and air cool or furnace cool. The Superinvar part is then finish-machined as required. A 780 - 830° soak with air cooled or controlled oven cool heat treatment can be substituted for Step 1. This results in higher expansivity, but greater temporal stability compared with the water quenched material.

## 8. REFERENCES

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Coefficient of linear thermal expansion (or thermal expansivity)

$$\alpha \equiv \frac{1}{L} \frac{\Delta L}{\Delta T}$$

*Instantaneous* coefficient of linear thermal expansion

$$\alpha' \equiv \lim_{\Delta T \rightarrow 0} \left( \frac{1}{L} \frac{\Delta L}{\Delta T} \right)$$

*Mean* coefficient of linear thermal expansion

$$\bar{\alpha} \equiv \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} \alpha' dT, \text{ stating } T_1 \text{ and } T_2$$

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Table II.

Invar variables tried in elevated temperature stability tests.

	INVAR	SUPERINVAR
<b>SHEET</b>		
040 thick	x x x x x x x x	x
.060 thick	x x x x x x x x	x
Bent	x x x x x x x x	x
e-beam Welded	x x x x x x x x	x
48 hrs Stabilization	x x x x x x x x	x
96 hrs Stabilization	x x x x x x x x	x
Soln Anneal-Slow Cool	x x x x x x x x	x
Decarburized-Quenched	x x x x x x x x	x
Decarburized-Slow Cool	x x x x x x x x	x
I rolling direction	x x x x x x x x	x
II rolling direction	x x x x x x x x	x
<b>PLATE</b>		
24 hr Stabilization	x x x x x x x x	x
48 hr Stabilization	x x x x x x x x	x
Thermal Cycled	x x x x x x x x	x
<b>NO. SAMPLES</b>	3 3 3 3 3 3 3 3 3 3	3
<b>GROUP NO.</b> (see Figure)	I 2 3 4 5 6 7 8 9 10	11

Table III.

Temperature history and temporal instability of the Superinvar sample described in Fig. 2. (Sample was stored at room temperature between measurement periods.)

Date	Temperature ( C )	Instability (ppm/yr)
1975 (6 months)	27	< .01
1983 (4 months)	60	+ 1.2
1991 (3 months)	25.8	+ 1.0
1991 (3 months)	37.8	- 0.5
1991 (3 weeks)	25.8	+ 1.2