Chapter 4

Operational Stability

A major question for the future development of ionic conducting thermoelectrics, particularly Cu_2Se and $Cu_{1.97}Ag_{0.03}Se$, is whether these materials will be stable under device conditions of sustained temperature gradients and currents. Both copper and silver show fast interdiffusion in many materials [52, 89]. Therefore there is strong concern about the decomposition of these materials when operated under the device condition of steady state current operation. Indeed, $Cu_{1.97}Ag_{0.03}Se$, Cu_2Se, and Cu_2Se are empirically known to be unstable under current density of $10\,\mathrm{A/cm^2}$ at elevated temperatures in their super-ionic phase [24, 48]. However, while these issues may occur at elevated temperatures, my empirical testing shows no evidence of electrochemical degradation at the phase transition temperature.

In section 4.1 I will discuss the publication [24] I wrote summarizing the DOE/NASA studies of $Cu_{1.97}Ag_{0.03}Se$ in the 1970s. In this publication I also repeated and re-demonstrated the electrochemical effects in Cu_2Se. In section 4.2 I show the work I did repeating this experiment in the low temperature phase. I will also discuss the possible reasons for the difference in degradation behavior between the high temperature and low temperature phase, with particular reference to the extensive studies on Cu_2Se performed by Mikhail Korzhuev of the Baikov Metallurgical Institute.

4.1 $Cu_{1.97}Ag_{0.03}Se$ at NASA

In the late 1960s the 3M corporation designed and patented a set of highly efficient selenide thermoelectric materials to be used for the next generation of radioisotope thermal generators (RTGs) and for other DOE applications [72, 73, 74, 40].The n-type material developed was based on Gd_2Se_{3-x}. The p-type material was $Cu_{1.97}Ag_{.03}Se_{1+y}$, $y < 0.01$ [75]. This proprietary material was referred to as TPM-217. 3Ms reports indicated good thermoelectric properties that were stable over 4000 hours, though typically the material would take several hundred hours to become stable [72]. Further material studies were done by the General Atomics Corporation [58, 59, 57, 55, 56, 60] and NASA Jet Propulsion Laboratory [183, 182, 181]. Device and generator development was done by 3M and Teledyne Energy Systems [149].

The technical reports cited in this thesis are merely a representative sample of the dozens of quarterly and annual reports available from the DOE OSTI database and easily searched for with the key word "TPM-217." There is signifcant overlap between many of these reports; the set referenced above is representative of the program as a whole. General Atomics images of the material as synthesized by 3M showed clear Cu and Ag rich regions, which could be eliminated by further hot-pressing and annealing of the material [71]. The 3M reports also indicate that there was a small problem of Cu extrusion at the interface between the $Cu_{1.97}Ag_{0.03}Se_{1+y}$ and the cold side endcap [72]. Though this issue was identified at the beginning of the program, it was not addressed until it began to cause systematic issues, such as increasing device contact resistances under extended operation [80]. The failure of the TPM-217 program was as much or more a failure of program management as it was of the materials' properties themselves.

Data from 3M indicates that $Cu_{1.97}Ag_{0.03}Se_{1+y}$ has a peak zT of 1.2 at 1000 K,[9] see Figure 4.1. 3M typically synthesized 0.1% excess selenium samples. Data from JPL indicated a peak zT of 0.8 at 800 K. JPL bonded their samples to copper at the cold end. Therefore the equilibrium Se excess in their samples varied from 0.02% to 0.08% depending on the temperature as the copper in the cold junction

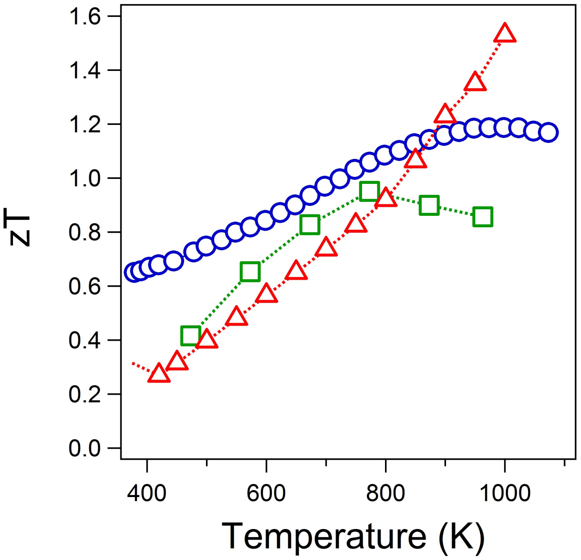

Figure 4.1: zT data for $Cu_{1.97}Ag_{0.03}Se$ (TPM-217) as extracted from JPL status reports. Blue circles are data from 3M Corporation tests. Green squares are data from JPL tests [71]. Red triangles represent data from Liu *et al.* [122].

block diffused in and out of the bulk sample.(See Figures 1 and 2 of reference [181]) Electrical conductivity and thermopower were measured via a four-point technique. Thermal conductivity was directly measured by steady-state direct calorimetry, as was typical then, [81] rather than by separate measurement of thermal diffusivity and heat capacity, as is done in modern thermoelectric laboratories. The material was also evaluated over a ten year period by the General Atomics corporation. Most of the information in the General Atomics reports evaluates $Cu_{1.97}Ag_{0.03}Se_{1+y}$ in a device setting, with particular focus on high-temperature (1000 K to 1200 K) stability and operation under typical device thermal gradients with a cold-side at 400 K to 600 K and a hot side at 1000 K to 1200 K, as well as under conditions of applied current and in segmented legs and devices. These tests revealed problems that were not reported in $Cu_{1.97}Ag_{0.03}Se_{1+y}$ original material testing at 3M.

The biggest problem observed was material loss rate, see Figure 4.1. At 1200 K the loss rate under zero current was found to be $10^{-4}\,\mathrm{g \cdot cm^{-2} \cdot hr^{-1}}$, and under conditions of applied current the loss rate was measured as high as $10^{-2}\,\mathrm{g \cdot cm^{-2} hr^{-1}}$ at $iL/A = 8.6\,\mathrm{A/cm}$ [40]. For a reasonable sample geometry, these loss rates would

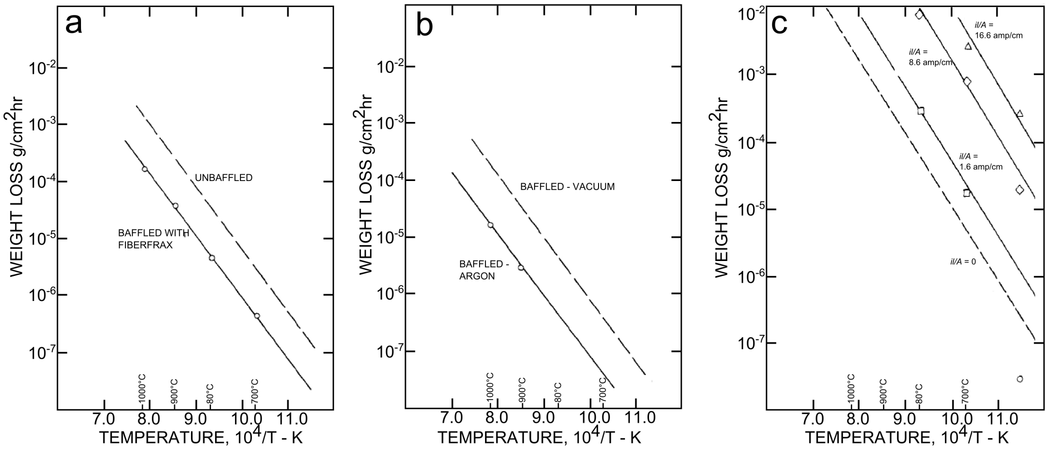

Figure 4.2: Weight loss rates for TPM-217 as a function of temperature. Figures 6, 7, and 8 from reference [183]. (a) Comparison between unprotected and baffled TPM-217. (b) Comparison between TPM-217 in vacuum and in 750 mbar argon atmosphere. (c) Loss rates at different applied currents. Il/A ranges from 0 A/cm to 16.6 A/cm.

cause rapid deterioration of the material. Quantitatively the fraction loss rate per hour is a function of the loss rate (LR), the geometric density (ρ) and the leg radius (r) as:

$$fLR = \frac{2LR}{\rho r} \tag{4.1}$$

This gives for a 1 cm radius leg a loss of mass equal to 0.3% of total mass per hour under applied current. The mechanism for this loss was believed to be evaporation of Se at the hot end.[9] As thermal and electrical potential gradients created a Cu concentration gradient with a low concentration of copper at the hot end, the Se activity increased and thereby increased its vapor pressure. The evaporation of the selenium causes the solid state precipitation of the copper there. Under conditions of applied thermal and electrical gradient, it was found that the percent excess selenium in the material varied with temperature. 3M and JPL found that excess selenium percent increased by the factor of 0.0095 iL/A over the zero-current concentration with iL/A in Acm. To mitigate this problem the p-leg was partitioned with a diffusion barrier. This diminished the problem of Se evaporation but also decreased zT by 25% [181].

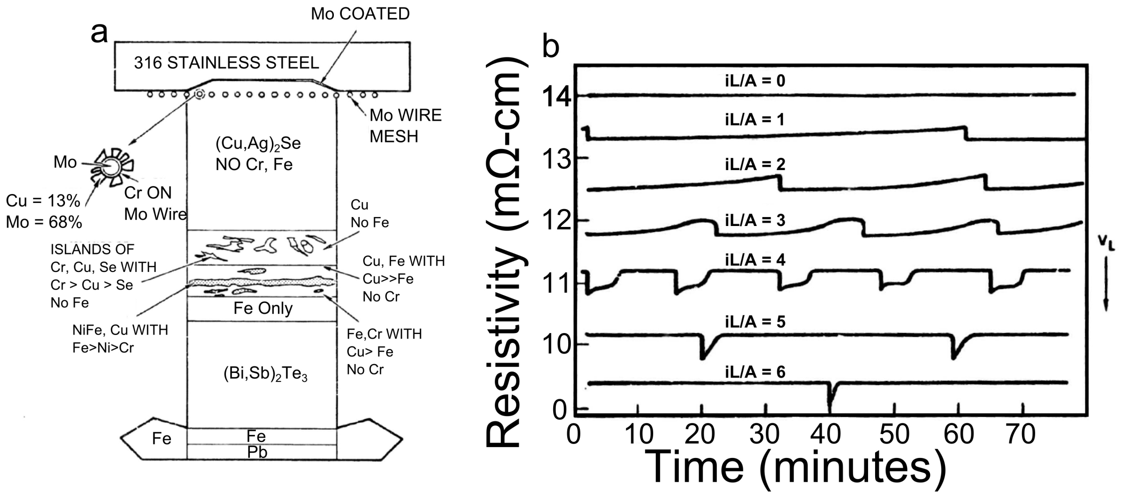

Figure 4.3: Degradation of segmented modules. Data from General Atomics final report [57], representing Figure 2-21 and Figure 2-31. (a) Depiction of chemical degradation after isothermal test of p-type leg after 2490 hr at a 1027 K/380 K thermal gradient. (b) Depiction of resistivity ratcheting under conditions of applied current. iL=A is in units of A/cm. $T_h = 1023\,K$, $T_c = 473\,K$.

To address this issue, General Atomics developed systems to suppress the evaporation of Se. They would baffle the $Cu_{1.97}Ag_{0.03}Se_{1+y}$ with boron nitride and boron oxide glassy coatings [79]. With greater baffling thickness they would find a reduction in material loss rate of up to two orders of magnitude, but this baffling decreases device efficiency by acting as a thermal short. This provides a limiting condition on the thickness of the baffling that can be effectively added to the module. They further found that they could suppress the weight loss rate by one order of magnitude if they operated in a low (2.5 torr) atmosphere of Argon instead of in vacuum [79]. The combination of these effects reduced the loss rate to a level that allows potential operation of the leg for multiple years without significant degradation. Another option for reducing the effect might be to decrease the hot end temperature, as evaporative material loss was is an exponential function of that temperature.(Figure 4.1)

The second major problem was the chemical degradation of the material and device, particularly under conditions of applied current. In the original 3M studies, these effects were obscured by the use of Cu as both hot and cold-side contacts. General Atomics found that at elevated temperature the Cu in $Cu_{1.97}Ag_{.03}Se_{1+y}$

would react with the Fe in 316 stainless steel contacts [79]. Tungsten, molybdenum, and tungsten-rhenium were found to be chemically unreactive to $\mathrm{Cu_{1.97}Ag_{0.03}Se_{1+y}}$. However, these materials showed a coefficient of thermal expansion one-fifth that of $\mathrm{Cu_{1.97}Ag_{0.03}Se_{1+y}}$, resulting in micro-cracks through which Cu could diffuse at elevated temperatures [79]. It is also possible that these cracks were related to the approximately 1.4% volume expansion at the 410K phase transition of the material [191]. In the final General Atomic tests during the late 1970s, $\mathrm{Cu_{1.97}Ag_{0.03}Se_{1+y}}$ was used as the low temperature segment. Fe was used as the diffusion barrier for the segmented tests, because it was known to be compatible with $(\mathrm{Bi,Sb})_2\mathrm{Te}_3$ [80] During isothermal tests it was found that the Fe reacted with the Cu in $\mathrm{Cu_{1.97}Ag_{0.03}Se_{1+y}}$, see Figure 4.1a. A region of mixed Cu and Fe was found in between the $\mathrm{Cu_{1.97}Ag_{0.03}Se_{1+y}}$ and the Fe, as well as a region of $\mathrm{Cu_{1.97}Ag_{0.03}Se_{1+y}}$ with inclusions of Cu, Fe, and Cr from the coating of the 316 Stainless Steel end caps. Under conditions of applied current these segments failed dramatically. At different factors or IL/A ranging from 0 to 6 A/cm the segments were measured to have a resistivity ranging from 15 to 9 $\mathrm{m\Omega \cdot cm}$ when $\mathrm{T_h} = 1023\,\mathrm{K}$ and $\mathrm{T_c} = 473\,\mathrm{K}$. The measured Seebeck coefficient and electrical resistivity would also show ratcheting behavior: at regular intervals the transport quantity would suddenly increase for a short period of time and then decrease down to the baselin, see Figure 4.1b. The ratcheting frequency depended on applied current, but was typically on order one ratchet per 15 minutes. These results were interpreted as being due to an irregular electrochemical process — plate out of copper followed by reabsorption of copper. Work done at 3M indicated that under accelerated conditions (Il/A = 15 A/cm), contact resistance increased to up to 700% of leg resistance after 100 hours. Upon thermal cycling, the device was restored to its original contact resistance. After these tests, the TPM-217 project was terminated [80].

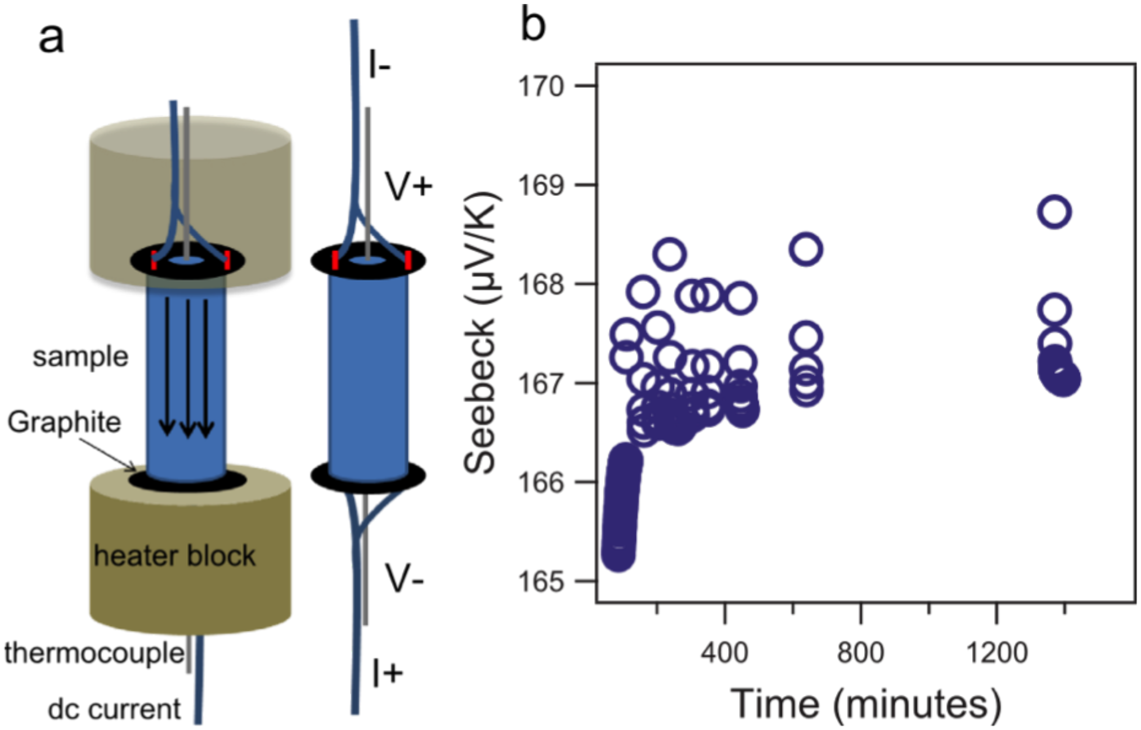

Figure 4.4: (a) Thermopower measurement apparatus with modification to allow operation with applied current. Conductive graphite contacts are used for the current source and sink. (b) Seebeck coefficient stability during measurement of sample under conditions of applied current and temperature gradient. It is unclear whether the transients represent instrument error or relaxation of the concentration gradient produced by turning off the current source immediately before the measurement.

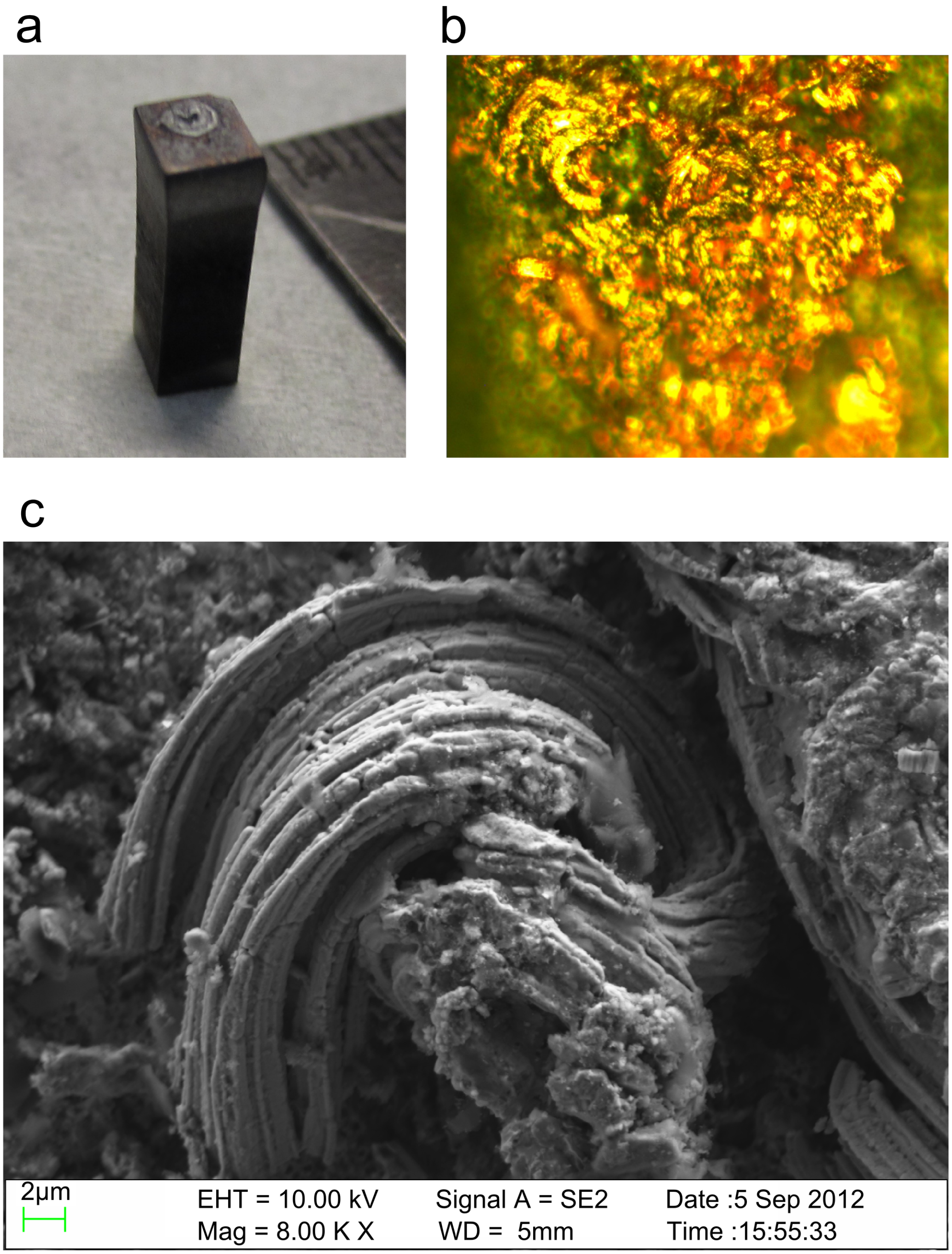

Figure 4.5: (a) Sample after applying current for 24 h. (b) Optical microscopy image of the current-sink face of the sample after applying a current for 24 h. Copper can be clearly seen precipitated on the surface. (c) SEM micrograph of top surface of sample after applying current for 24 h. The electromigrated copper grows into nanowire bundles (whiskers).

4.2 Degradation Testing of Cu_2Se

In order to understand these results and test their applicability to stoichiometric Cu2Se, we performed a short electro-migration experiment. A piece of copper selenide with cross-sectional area of 11.47 mm^2 and length of 10.7 mm was placed in a modified Seebeck apparatus, see Figure 4.2a. This Seebeck apparatus allows for simultaneous measurement of voltage and temperature and application of a current of up to 10 A. The sample was placed under a thermal gradient of 275 K for 16 hours with $T_h = 795\,K$ and $T_c = 520\,K$. The sample was not visibly affected. Current was varied from 0 to 10 A under the same thermal gradient as before. The resistivity did not depend upon applied current, in contradiction to the General Atomics reports [57]. The sample was then run under the same temperature gradient and in current continuously for 24 hours. The magnitude of this current was such that the voltage it induced was half the thermoelectric voltage. The direction was such that it transported Cu^+ in the opposite direction of thermal diffusion; Cu^+ should electromigrate to the hot-side and thermally diffuse to the cold side. The applied current was 1A. The applied current density was $j = 9\,A/cm^2$. There was no noticeable degradation of the average Seebeck coefficient over this period (Figure 4.2,b), which is consistent with the reports by JPL, 3M and General Atomics. When the sample was removed, visual inspection showed that it had undergone deformation at the hot end. Copper residue was visible on the face that had been against the hot-side heater and the current sink. The copper residue was inspected via optical microscope (Figure 4.2ab) and SEM (Figure 4.2c). The non-uniformity of the surface copper may have been due to spatial inhomogeneity in the contact resistivity between the current electrodes and the sample face. The SEM image reveals that the copper grows as bundles of nanowires. The result is a clear indication that electromigration drives physical degradation of Cu_2Se.

It has yet to be shown that liquid-like thermoelectrics based on fast-ion conductors can be used effectively in thermoelectric devices. The historical work by General Atomics, the 3M Corporation, Teledyne Energy Systems, and the NASA Jet Propul-

$\bar{T}$	ΔT	$J(A/cm^2)$	Duration (hr)	Plate out?
$658K$	$275K$	9	16	Yes
$404K$	$23K$	21.7	260	No
$387K$	$19K$	29.3	70	No
$423K$	$6K$	29.3	110	See Text

Table 4.1: Electromigration Experiments on Cu_2Se. No electomigration was observed below the phase transition temperature. When tested slightly above the phase transition temperature there was no plate out observed but there was copper observed on the side of the sample near the hot end.

sion Laboratory gives reason to be cautious in assuming that the excellent material properties observed in Cu_2Se will necessarily lead to a high quality thermoelectric module. There were three major problems observed. The first was electrochemical process resulting in weight loss via selenium evaporation. The 3M and General Atomics reports indicate that this problem was solved via baffling of the thermoelectric leg and operation in an Argon atmosphere. JPL and Teledyne expressed skepticism that the problem had been sufficiently reduced to prevent mechanical and chemical degradation of the thermoelectric generator. The second major problem was that of chemical reactivity at high temperature. In the view of all four major organizations involved in this work, this problem was never solved. Changes in contact resistance over time due to chemical process at interfaces between $(Ag, Cu)_2Se$ and diffusion barriers and bond pads led to unacceptable degradation of overall module performance. This last problem appears to be the principle reason the program was cancelled in 1979. If Cu_2Se is to be used for thermoelectric generators, these problems must be solved or evaded. Possible solutions would be the development and use of different diffusion barriers and contact materials, and the operation of the material only at lower temperature. The authors own work shows that physical degradation of Cu_2Se can be induced with currents similar to those needed to build a practical thermoelectric generator.

Fortunately these problems are eliminated below the phase transition temperature. The author performed high current density plate-out tests at three additional temperaturesm, the results of which are summarized in table 4.1. Currents and durations far in excess of that applied above the phase transition resulted in no observed copper plate out or altering of the transport properties. A further test was performed just above the phase transition temperature. It also showed no whisker-growth or plate out at the end of the sample, however there was a small quantity of Cu on the side of the sample near the hot end. This may result from loss of selenium due to evaporation or the piezodiffusion of Cu_2Se that has been noted by prior authors [107].

Why should copper excrescence growth occur and why should it only in the high temperature phase? Korzhuev provides a compelling answer [106, 103] that relies on the comparative thermodynamics of the solid, super-ionic, and melt phases. The sub-lattice melting and super-ionic transition causes a decrease in the melt entropy of transition of the super-ionic phase. He prepared two samples of nominal composition $Cu_{1.77}Se$ and Cu_2Se [106]. Denote the entropy of transition of the super-ionic transition as (ΔS_C) and that of the melt transition as (ΔS_m) and their sum $(\Delta S_T = \Delta S_C + \Delta S_M)$. ΔS_T differed by less than 2% between the two samples. In the Cu_2Se 62% of the total was released at the superionic transition, while in $Cu_{1.77}Se$ only 29% was released. This resulted in a significant change in melt morphology between the two samples. Korzhuev also suggested [103] that the entropy of the Cu in the superionic phase might be larger than that in the liquid phase. Therefore the material under external force (e.g. piezodiffusion, electrodiffusion) may be extremely unstable and tend to copper excrescence growth.

In general the super-ionic phase, in addition of course to its elevated ionic conductivity, is thermophysically quite distinct from the low temperature phase. It shows ultrafast chemical diffusion [107, 102, 108] and superplasticity [177]. In this context it is unsurprising that the ion-ordered phases do not show the same thermophysical instability as the super-ionic phase.