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SUBJECT: Observations on the effects of inclusions in thermoelectric materials
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This memo concerns the expected effect of inclusions on the thermoelectric figure of merit (Z). Based on an expected reduction in the lattice thermal conductivity, extensive experiments to incorporate inclusions in SiGe are underway at TTC . Gerry Stapfer has complained that my predictions for the Z of a matrix of standard SiGe with fine (20 Å radius) inclusions should not continue to increase with increasing inclusion content. As usual, Gerry's common sense is more accurate than my detailed calculations and in fact Z must eventually degrade with increasing inclusion content (unless, of course, the inclusion has a better Z than SiGe). This memo is in partial response to Gerry's concerns. Paul Klemens addresses related issues in a memo to John Beaty of TTC dated 12/30/91. In resolving this issue several points have arisen which I think you may find of interest. I will briefly summarize the main points here, although a more detailed paper will eventually be required.

Classical Effects alone can't improve Z

The first point is to distinguish between what D.J. Bergman would call quantum and classical effects. By classical effects I mean the effect of merely mixing two materials into a composite, such as might be achieved by hot pressing a mixture of two relatively coarse powders. Bergman has proven that such a composite can never have a Z better than the best of the components. This is just what Gerry Stapfer's common sense required: if you add alumina (or whatever) to SiGe, eventually Z must go down.

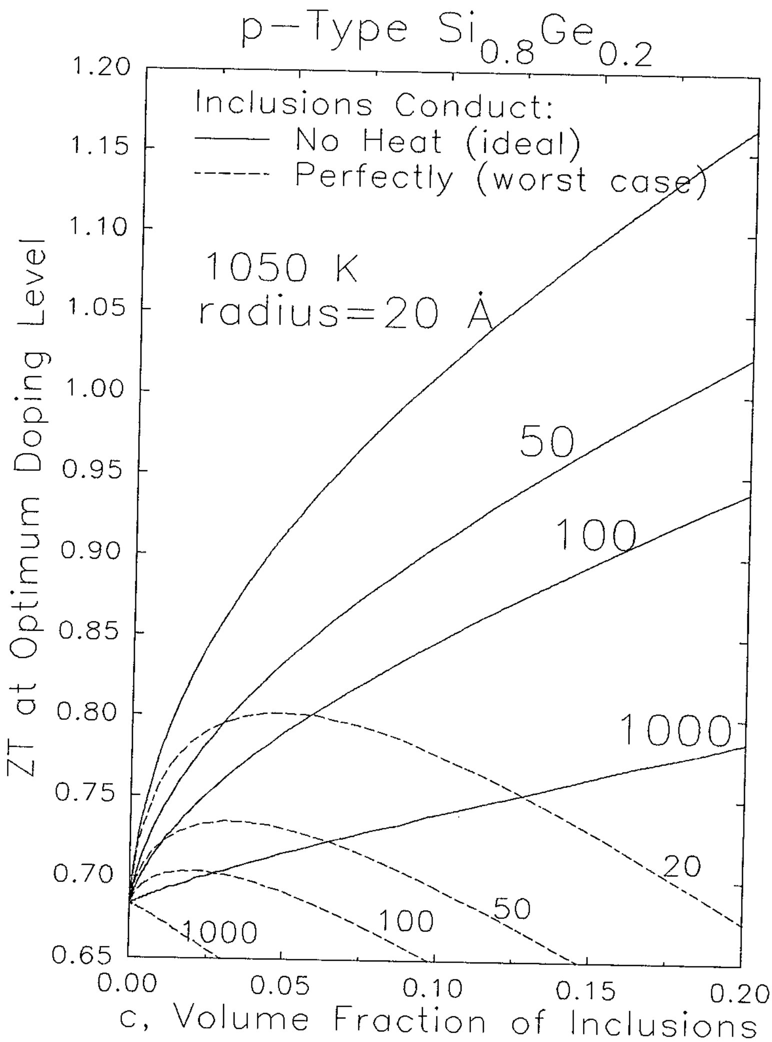
Quantum Effects can improve Z

By quantum effects I mean things that affect the scattering rates of the heat or current carriers. In this case, the very small size of the inclusion is necessary to increase the scattering rate of the phonons, lower the thermal conductivity and thereby increase Z. Many other quantum effects are also possible. SiGe itself might be viewed as a composite of Si and Ge mixed at the atomic level. Classically, such a composite would have a Z no higher than the Z of Si or Ge alone, but the purely quantum effect of mass fluctuation scattering increases Z tremendously. In effect, inclusion experiments are similar, except that the inclusions will affect a different range of phonon wavelengths.

To go any further, estimates of the magnitude of both of these effects are needed.

Case 1: Inclusions are perfect electrical and thermal insulators

In this case, which really corresponds to voids in SiGe, the classical effects decrease both the electrical and thermal conductivity by the same factor of $(1-\frac{4}{3}c)$, where *c* is the volume fraction of the inclusions. The Seebeck coefficient will be unaffected and, classically, so will Z. The thermal conductivity is reduced even more by including the effect of scattering on the phonons and this effect does increase Z. Both of these effects have been incorporated in the calculations shown by the solid lines in the Figure. Z really would continue to increase with increasing inclusion content regardless of the size of the inclusion, so long as the SiGe matrix remains interconnected throughout the sample.



Case 2: Inclusions are perfect electrical and thermal conductors
This case may be something of a surprise. Classically, the electrical and thermal conductivities will both be increased by the same factor of $(1+\frac{4}{3}c)$. Note that there is no effect corresponding to 'circulating currents' around the inclusions. The assumption of a perfect thermal conductor means the inclusion is isothermal, hence there is no driving force for circulating currents. There is also no effect on the Seebeck, so classically Z is unaffected. The inclusion, however, should still scatter phonons and the net effect on Z should be essentially the same as in case 1 and given by the same solid lines in the Figure.

Case 3: Inclusions are perfect thermal conductors and perfect electrical insulators (Worst Case)
Classically, this is the worst possible case (except for an inclusion with a large Z of opposite sign Seebeck to the matrix). The electrical conductivity is reduced by the factor $(1-\frac{4}{3}c)$, while the thermal conductivity is increased by $(1+\frac{4}{3}c)$. The Seebeck is unaffected, but classically Z will be decreased by $(1-\frac{8}{3}c)$. The only factor working to improve Z is the phonon scattering mechanism. The dashed lines in the Figure show this effect, which still shows a gain in Z, but the effect is significantly smaller than either case 1 or 2.

Differences with Klemens memo of 12/30/91
In his memo, Paul Klemens considers what I have called the classical effects of the inclusions on the electrical properties and prefers to leave the total thermal conductivity of the composite as a subject for another calculation. I believe the discussion above is essentially in agreement with Klemens memo, although I need to resolve a difference in the numerical factors (5/3 vs. 4/3) in a few places.

Klemens also points out that my calculations overestimate the effect of inclusions on long wavelength phonons, resulting in an overly optimistic enhancement in Z by perhaps 5%. I agree completely and intend to correct this defect in the near future.

Summary
Until recently the bulk properties of the inclusions have been neglected entirely, corresponding to case 1. Materials with thermal conductivity values much lower than our matrix material of SiGe are hard to find. Even voids conduct heat by radiation at high temperatures, so case 1 will be very hard to achieve.

I have also been under the mistaken impression that electrically conducting inclusions would be bad, due to both shorting out the Seebeck voltage and increasing heat conduction via circulating currents. Thus, in the search for selecting inclusions the experiments have emphasized refractory electrical insulators.

In fact these electrical insulators are mostly excellent thermal conductors, corresponding most closely to case 3, the worst case. Metallic inclusions (case 2), in fact, appear to offer the best hope for improved Z. Coincidentally, these are also the easiest materials to prepare using the TTC process.

Finally, the experimental situation is made significantly more complex do to defects in the SiGe matrix (grain boundaries, oxygen, etc.) introduced by the preparation process. Such defects can reduce the electrical conductivity by factors much greater than the direct effect of the inclusions, obscuring any potential improvements in Z.

Conclusion

The Figure shown above may be regarded as bounding the improvement in Z due to inclusions. The recent results of Bergman on the properties of thermoelectric composites has allowed improved estimates of the classical effects of the inclusions. These classical effects represent the common sense expectation that composites will, eventually, degrade Z. Nevertheless, improvements in Z by inclusions still expected.