Negative stiffness and negative Poisson's ratio in materials which undergo a phase transformation

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Abstract.
Design of adaptive structures can be facilitated if one has access to materials with degrees of freedom beyond those ordinarily anticipated. We consider viscoelastic damping and negative stiffness. Negative stiffness occurs in structures with stored energy, e.g. in some post-buckled elements. Heterogeneous systems containing negative stiffness elements can exhibit extreme values of stiffness or of viscoelastic damping. We consider several designed composite materials in which the negative stiffness arises due to constraint upon a phase transformation. Experiments disclose material properties greater than those of either constituent, and exceeding conventional bounds. We also examine the viscoelastic damping in two polycrystalline model materials which undergo a phase transformation. The notion of partial constraint of negative stiffness of crystals is explored. To that end, dynamic mechanical properties (dynamic modulus and damping, tan δ) were observed in an indium-21 at% thallium alloy and in barium titanate ceramic through their phase transformations.

§1 Introduction

For most elastic systems, stiffness is positive. This means that a deformed object experiences a force in the same direction as the deformation. Negative stiffness can occur in systems such as pre-strained objects including post-buckled elements, which contain stored energy [1]. Heterogeneous systems with one constituent of negative stiffness are predicted to give rise to high damping and stiffness [2], higher than that of either constituent. Experimentally, high viscoelastic damping and negative axial stiffness was observed [3] in lumped systems containing post-buckled viscoelastic rubber tubes. High viscoelastic damping has also been observed in metal matrix (Sn) composites containing particulate ferroelastic VO_2 inclusions [4]. Ferroelastics are of interest in this context since they are predicted to, if constrained, exhibit negative stiffness below the transformation temperature. Ferroelastics, if not constrained, undergo a shear instability in which the crystal structure changes form as temperature is lowered. In the Landau theory of phase transformations, the free energy has a relative maximum, corresponding to unstable equilibrium, below the material's transformation temperature T_c [5]. Since the curvature of this energy function corresponds to a modulus, negative moduli are predicted. These negative moduli are not observed in blocks free of constraint since the material forms bands or domains due to the instability. Multi-domain blocks of material have positive stiffness as is observed experimentally.

The continuum theory of elasticity provides guidance as to the kinds of instability to be expected. In isotropic elastic solids, the 'allowable' range of Poisson's ratio ν is

$$-1 < \nu < 0.5. \quad (1)$$

This corresponds to the requirement that the shear (G) and bulk (K) moduli [6] be positive for *stability* of an unconstrained block of material. This condition corresponds to a surface traction boundary condition in elasticity theory; this condition means the surface forces are specified. Most isotropic materials have Poisson's ratios close to 0.3; rubbery materials have Poisson's ratios close to 0.5. Negative Poisson's ratio, though counter-intuitive is possible. Foams [7, 8] with ν as small as -0.8 have been conceptualized, fabricated and studied. The composites of Milton [9] offer the intriguing possibility of stiff materials with a negative Poisson's ratio. The stiffness of one the two constituents must be at least 25 times greater than that of the other constituent to obtain a Poisson's ratio less than zero. A Poisson's ratio approaching the stability limit -1 requires constituents which differ even more in stiffnesses: one phase becomes very soft, tending to 'empty space' in its properties. Microporous polymers with negative Poisson's ratio have been developed [10]. Another intriguing possibility is that of creating solid polymer negative Poisson's ratio materials by design on the molecular scale [11].

The range of properties associated with stability of a *constrained* object is that of strong ellipticity. The range of elastic constants, is [12] for isotropic solids,

$$G > 0 \text{ and } \nu < 0.5 \text{ or } \nu > 1 . \quad (2a,b)$$

Since $E = 2\,G\,(1 + \nu)$, and $K = 2G(1 + \nu)/3(1 - 2\nu)$, negative Young's modulus E and bulk modulus K, are allowed. Specifically

$$-\infty < E < \infty \text{ or } -4G/3 < K < \infty. \quad (3)$$

Negative Poisson's ratios below the usual stability limit of -1 are possible. Strongly elliptic materials are stable with respect to formation of domains or bands. An inclusion in a composite is partially constrained. Recently it has been shown that the range of material properties associated with such a situation is intermediate between positive definiteness and strong ellipticity [13].

In viscoelastic materials, one may express the behaviour in the context of the dynamic viscoelastic moduli. The complex dynamic Young's modulus is $E^* = E' + iE'' = E'(1 + i \tan \delta)$, with $E' = \mathrm{Re}\{E^*\}$ and $\tan \delta \equiv \mathrm{Im}\{E^*\}/\mathrm{Re}\{E^*\}$; δ is the phase angle between the stress and strain sinusoids. The primes are standard notation for the real and imaginary part respectively; they do not represent derivatives. The dynamic modulus is a function of frequency. In composite materials it depends on constituent properties and morphology. A representative stiffness-loss map for well-known materials is shown in **Fig. 1**. The product $E' \tan \delta$ is a figure of merit [14] for the damping of structural vibration. Most known materials [15], including commercial damping layers, exhibit maximum $E' \tan \delta < 0.6$ GPa. Some composites with values as much as an order of magnitude higher have been developed [16] [17]; selected results are also shown in Fig. 1.

In the present work we explore the role of negative stiffness constituents in composites and constrained negative stiffness in the grains of polycrystals in achieving high damping in materials.

§2 Experimental methods

§2.1 Material preparation

For InTl alloy, indium wire (Alfa Aesar, 99.9985% metals basis) and thallium granules (Alfa Aesar, 99.999% metals basis) were weighed, mixed, and cast in a steel mould to form a In-21at%-Tl alloy. The mould cavity was rectangular (8.0 cm long, 1.9 cm wide, and 1.5 cm deep) and was provided with tapered surfaces to allow easy removal of the ingot. Specimens were cut using a low speed abrasive saw from the cast ingot into rectangular cross sections, typically on the order of 3 x 4 x 30 mm. Specimens were cut and polished and observed using light microscopy.

Solid rods of barium titanate ceramic were obtained from two sources. Prof. Smay, of Oklahoma State University synthesized a cylindrical rod 73 cm long and 21 cm in diameter by sintering from from Ticon-HPB powder (Ferro Electronic Materials, Niagara Falls, NY) at 1350°C for 1 hour. Testbourne Ltd. (Hampshire, UK) provided five rods of about 6 cm long and 12 cm in diameter. These as received rods had tapered ends, which were sectioned off using a diamond saw. The ends were then polished to achieve approximate parallelism.

Viscoelastic properties of specimens of InTl and of composites were determined in torsion or bending using broadband viscoelastic spectroscopy (BVS) [[18]]. The instrument was provided with temperature control and the ability to measure slow, large amplitude free end deformation associated with spontaneous strain. The method is capable of frequency dependent measurements over eleven orders of magnitude of frequency to about 100 kHz. In the present studies, temperature dependence is emphasized since temperature allows one to tune the behaviour of ferroelastic solids. Torque upon the end of the specimen was generated via the action of a Helmholtz coil on a high intensity magnet cemented to the end. The fixed end of the specimen was clamped to a 25 mm diameter steel support rod by tungsten adapters and set screws. Angular displacement of the free end was determined by reflecting a laser beam from a mirror cemented to drive magnet, upon a split diode light sensor. The sensor electrical signal was input to a lock in amplifier: viscoelastic damping and modulus measurements were taken using a Stanford Research Systems lock-in amplifier (SR850 DSP) by measuring the phase angle between the sinusoidal torque and displacement signals. Constant frequency tests with variable temperature were conducted at various frequencies well below the specimen resonance (typically about 2 kHz in torsion). Spontaneous strain and other manifestations of instability were studied by splitting a portion of the laser beam and directing it to a wide angle, 2 axis photodiode position sensor (Pacific Silicon Sensor Inc. DL100-7PCBA, Westlake, CA) with a detector area of 1 cm^2. Specimen temperature was measured using a type-K (Omega) thermocouple about 1 mm from the base of the specimen in the stream of heated air. Output voltage was recorded by a digital oscilloscope.

Polycrystalline ceramic $BaTiO_3$ was studied using pulsed wave ultrasound, and by mechanical testing. Both longitudinal and shear wave transit times were measured ultrasonically at 1 MHz, and engineering moduli were calculated using the theory of isotropic elasticity. After ultrasonic testing, the rods were provided with SK-09-125TM-350 strain gauge T-rosettes using standard M-bond-610 strain gauge cement. Thermal expansion tests were done by heating and cooling the rods in a furnace, and monitoring the strain. Specimen temperature was measured using a type-K (Omega) thermocouple in contact with the specimen Strain results were corrected for expansion mismatch between gage and ceramic. A differential scanning calorimetry (DSC) test was done on granules of barium titanate obtained from Alfa Aesar. Some granules were plated with nickel for later use as inclusions in composites; these were also examined in the DSC. Compression tests upon solid rods of barium titanate were conducted on a MTS (Minneapolis, MN) 20,000 lb capacity servo-hydraulic frame. To achieve thermal isolation, aluminum oxide rods 2.54 cm in diameter and 10 cm long were placed between the specimen and the steel test frame platens; also, a swivel joint was added between the actuator and the lower alumina isolation rod. As above, phase and magnitude measurements were conducted using a Stanford Research Systems lock-in amplifier (SR850 DSP). Mechanical testing using this frame was done at 1 Hz. Phase calibration was done with 6061 aluminum alloy which has a tan δ on the order of 10^{-5}. Based on measured phase for this alloy, a phase shift correction of about 0.01 rad at 1 Hz was applied to compensate for overall shifts in the servo-hydraulic system electronics.

§3 Composites

§3.1 Theory

In composite materials there are several exact analytical solutions for composite properties in terms of inclusion properties and geometry. Within these solutions one can allow the modulus of an inclusion to become negative and calculate the composite properties. If the matrix is much stiffer than the inclusion, the situation approximates that of constraint of surface displacement in which strong ellipticity suffices for stability. This allows negative bulk modulus. Negative shear moduli are excluded. In real materials, domains form at temperatures below the point at which a shear modulus softens to zero. In crystals which are sufficiently small, surface energy, not incorporated in the continuum theory, results in single domain single crystals.

The Voigt formula, corresponding to fibers or laminae aligned in the direction of a uniaxial stress, is

$$E_c = E_1 V_1 + E_2 V_2, \tag{4}$$

in which E_c, E_1 and E_2 refer to the Young's modulus (stiffness) of the composite, phase 1 and phase 2, and V_1 and V_2 refer to the volume fraction of phase 1 and phase 2 with $V_1+V_2 = 1$. Negative stiffness of one phase can give rise to a small or zero composite stiffness.

The Reuss formula is, in terms of the compliances, e.g. $J_1 = 1/E_1$,

$$J_c = J_1 V_1 + J_2 V_2, \tag{5}$$

Negative stiffness of one phase can give rise to a large composite stiffness, even a stiffness which tends to infinity. The corresponding composite geometry consists of laminae orthogonal to the direction of a uniaxial stress. This configuration is unstable under load control but it can be stabilized in displacement control for a range of constituent properties. The Voigt and Reuss formulae represent bounds provided that both phases are described by a positive definite strain energy. Although this excludes negative stiffness for interpretation of formulae as bounds, they remain exact analytical solutions for the corresponding composite morphologies when constituents assume negative moduli.

The Hashin-Shtrikman formulae [[19]] apply for isotropic composites. They are bounds provided that both phases are described by a positive definite strain energy, which excludes negative stiffness. The lower bound for the shear modulus G_L of an *elastic* composite is,

$$G_L = G_2 + \frac{V_1}{\dfrac{1}{G_1 - G_2} + \dfrac{6(K_2+2G_2)V_2}{5(3K_2+4G_2)G_2}} \quad . \tag{6}$$

in which K_1, K_2, G_1 and V_1, and G_2 and V_2 are the bulk modulus, shear modulus and volume fraction of phases 1, and 2, respectively. Both shear and bulk moduli must be positive for this and related formulae to be bounds [20]. Upper and lower Hashin-Shtrikman formulae for bulk modulus are attained via a hierarchical morphology in which the composite is filled with coated spheres of different size but identical ratio of sphere size to coating thickness. The attainment is *exact* for the bulk modulus [21] and approximate for the shear modulus. The shear modulus formula is attained *exactly* by hierarchical laminates [22]. Since they are exact solutions, they may be used in predictions of behaviour of composites with negative stiffness constituents. For viscoelastic solids, the moduli or compliances in the above equations become complex following the elastic-viscoelastic correspondence principle. If negative moduli are allowed in these formulae, mechanical damping of the composite can approach a singularity; sigmoid shaped anomalies are predicted in the composite moduli as a function of inclusion modulus.

§2.2 Experiment

High damping composite materials can be achieved in several ways. The simplest approach is to embed inclusions of a stiff, low damping phase in a matrix of more compliant high damping material. The optimal inclusion shape, considering various inclusion morphologies, is a sphere of stiff material coated with a layer of high damping material forming the hierarchical morphology referred to above. [15] Spherical or near spherical inclusions of similar size will suffice for most purposes. If anisotropy is tolerable, a Reuss laminate provides better results in this context than a Voigt laminate. Representative results of this approach are shown in the map in **Fig. 1**.

Negative stiffness or modulus allows larger damping, even damping tending to infinity, to be achieved, as predicted theoretically [2] via the above equations. Experimental realization was achieved in a lumped system involving buckled tubes [3]; damping increases of orders of magnitude were observed. As for distributed systems, several experimental studies have been conducted in the Sn-VO_2 system [4] [23] [24]. Vanadium dioxide is a ferroelastic material; it undergoes a phase transformation from monoclinic to tetragonal at T_c = 67 °C. The domain size is typically about 10 μm. The rationale is that in single domains of ferroelastic material, domain formation is suppressed by surface energy considerations. Therefore single domain particles, when constrained by a sufficiently stiff composite matrix, can be stable. Inclusions were prepared with a particle size distribution including granules of size smaller than 10 μm. Composites with 1% volume fraction of inclusions, a value close to the calculated stability limit, exhibited large peaks in mechanical damping (tan δ), and large anomalies in stiffness. Anomalies in stiffness and damping in the composites are much larger than they could be for inclusions of any positive stiffness or damping. Composites with higher concentrations of inclusions exhibited multiple peaks in damping, and manifestations of instability including episodes of negative damping and a thrashing instability. Current experiments as of this writing deal with barium titanate as an inclusion. The experiments upon bulk barium titanate described below are motivated in part by the desire to characterize the material for inclusions. The role of negative stiffness of crystallite grains in polycrystalline material is also explored.

§4 Polycrystals

§4.1 Theory

The rationale for existence of negative stiffness in polycrystals is as follows. Many materials in the vicinity of a solid to solid phase transformation, display a decrease (softening) to zero of one or more of the elastic constants. for example, in single crystal In-Tl, the $(1/2)(C_{11}-C_{12})$ shear modulus approaches zero [25,26] as the martensitic transformation temperature is approached during heating or cooling. In polycrystals, a grain or crystal which has a negative modulus can be constrained, hence stabilised, by the surrounding grains. This situation is similar to a negative modulus inclusion in a composite; the difference is that composite inclusion concentration can be made dilute to achieve stability, but in a polycrystal the concentration of grains is 100%.

Polycrystal properties may be predicted using bounding formulae. Upper, G_U , and lower, G_L,, bounds [27] for cubic materials are given by

$$G_L = G_1 + 3\left\{\frac{5}{G_2 - G_1} + 4\,\frac{3}{5G_1}\,\frac{K + 2\,G_1}{3K + 4G_1}\right\}^{-1}, \tag{7}$$

$$G_U = G_2 + 2\left\{\frac{5}{G_2 - G_1} + 6\,\frac{3}{5G_2}\,\frac{K + 2\,G_2}{3K + 4G_2}\right\}^{-1}. \tag{8}$$

Similar analyses have also been conducted for materials of lower symmetry [28].

Assuming the shear modulus G_1 to become negative provides several predictions for the polycrystalline behavior. The upper Hashin-Shtrikman formula, equation (8), predicts a singularity in internal friction and a sigmoid shaped curve for the polycrystalline shear modulus.

As for the bulk modulus of the grains, for cubic symmetry, the bulk modulus of the polycrystalline aggregate is the same as that of the crystals.

Consider modulus elements $C_{11} = 1$, $C_{12} = 1$, $C_{44} = 1(1 + 0.05i)$

In the cubic system, the bulk modulus is $K = (C_{11} - 2C_{12})/3$. Suppose the temperature scale is normalized so that the transformation temperature T is 1 in normalized units. Then let the bulk modulus soften according to

$$K = [(C_{11} - 2C_{12})/3\}\,[1000(T - 1)]$$

and can become negative below T. Suppose further that the shear modulus G_1 above softens according to

$$G_1 = 0.2\,[460|T - 1|]\,[1 + 10^{-5}\,|T - 1|^{-2}] + 1.$$

Here the shear modulus softens, but not to zero, and is not allowed to go negative, since the crystal grains are assumed to be sufficiently large that many domains form within them. An imaginary, temperature dependent part is allowed for the modulus to account for viscoelastic dissipation. Results of this analysis are shown in **Fig. 2**. There is a peak in mechanical damping as the material is cooled, then damping becomes negative, corresponding to instability, hence spontaneous strain. In considering this as a model for barium titanate, a free crystal of material undergoes a phase transformation from cubic to orthorhombic at the Curie point. In a polycrystalline ceramic or in a composite, there is some constraint on each crystal. Therefore the crystal will remain cubic over some range of temperature below the Curie point, so the analysis is likely to be applicable over a range of temperature down to and somewhat below the Curie point.

§4.2 Experimental results

Results are presented for polycrystalline ceramic $BaTiO_3$; for comparison, selected results for polycrystalline InTl are presented as well. Further details regarding the InTl results and their interpretation are provided elsewhere [*23*]. Viscoelastic damping tan δ at 100 Hz of In-21 at% Tl alloy during cooling is shown in **Fig. 3**. Shown for comparison are single crystal results from Li et al. [29]. **Fig. 4** shows shear modulus and damping for polycrystalline InTl at two different cooling rates.

The large peak in the tan δ of polycrystalline InTl differs from the usual internal friction peaks in polycrystals, which are broader and weaker than those of single crystals. The usual broadening of damping peaks in polycrystalline solids is attributed to a superposition of contributions from different crystals to the viscoelastic behavior [30]. Martensitic bands occur in both polycrystals and single crystals, so interface theories cannot readily account for the higher peak. Moreover, the high temperature portion of the damping peak occurs above the temperature at which martensitic bands are observed, therefore this portion cannot be due to the motion of interfaces such as twin boundaries. Spontaneous strain, a manifestation of instability, is shown in **Fig. 5**. Constrained negative moduli of the constituent crystallites can account for this damping, as well as for amplification of viscoelastic damping peaks in these polycrystals. Sigmoid shaped anomalies in the shear modulus vs. temperature at high cooling rates are not predicted by prior analyses of phase transformation but are predicted by analysis of polycrystal properties allowing negative moduli of individual crystallites.

As for barium titanate, room temperature ultrasonic testing at 1 MHz revealed the tensorial C_{11} modulus and shear modulus. From these it was calculated that the thin rods from Testbourne had a Young's modulus of about 100 GPa, a shear modulus of 38 GPa and a Poisson's ratio of 0.34. The "normal" value of Poisson ratio supports the notion of isotropy for the polycrystalline specimens. The thicker rod was somewhat less stiff, with E of about 76 GPa, G of 26 GPa, and a Poisson's ratio of about 0.3. The difference is attributed to imperfect consolidation during preparation of the ceramics. Indeed, the thinner rods had a density of 5.8 g/cm^3, and the thicker rod had a density of 5.54 g/cm^3. By contrast, the accepted density for $BaTiO_3$ in the absence of porosity is 5.85 g/cm^3.

Thermal deformation results for barium titanate are shown in **Fig. 6**. A spontaneous strain was observed near the Curie point transformation temperature 120 °C during cooling. The corresponding jump in strain during heating occurred near 140 °C. Such hysteresis is known in this system. The hysteresis is also manifested in differential scanning calorimetry (DSC) as shown in **Fig. 7**. Viscoelastic behaviour of barium titanate in load control is shown in **Fig. 8**. The damping peak associated with phase transformation is typical. The damping peak begins and reaches its maximum at a temperature well above the corresponding temperatures associated wtih the instability of spontaneous strain and with the peak in the DSC curve. As with the InTl, the peak in the barium titanate damping appears in a regime where there are no domain wall interfaces. A role for negative modulus of crystallites is therefore suggested in this case as well. A moderate softening of modulus occurs below the Curie point. The ripples in properties near 60 °C are notable. We hypothesize they represent an effect of constraint by surrounding grains upon transformation of crystallite grains.

§5 Discussion

For adaptive structures, the spontaneous strain associated with phase transformations can be of interest, not only in shape memory materials, also in actuators and ceramics. Snap through can be done via macroscopic or composite structure, e. g. tape springs [31], alternatively it can be done in connection with phase transformations in composites. In the negative stiffness paradigm, interface deformation is amplified via the balance between positive and negative stiffness. This interface may be between inclusion and matrix in a composite or between adjacent crystallites in a polycrystalline metal or ceramic. As for composites, the spontaneous volumetric strain which occurs in the free expansion of the ceramic offers potential that negative bulk modulus may occur if this transformation is subjected to volumetric constraint. Among the many possible areas of application are high damping layers for vibration abatement, and materials with enhanced piezoelectric or thermal [32] properties.

§6 Figures

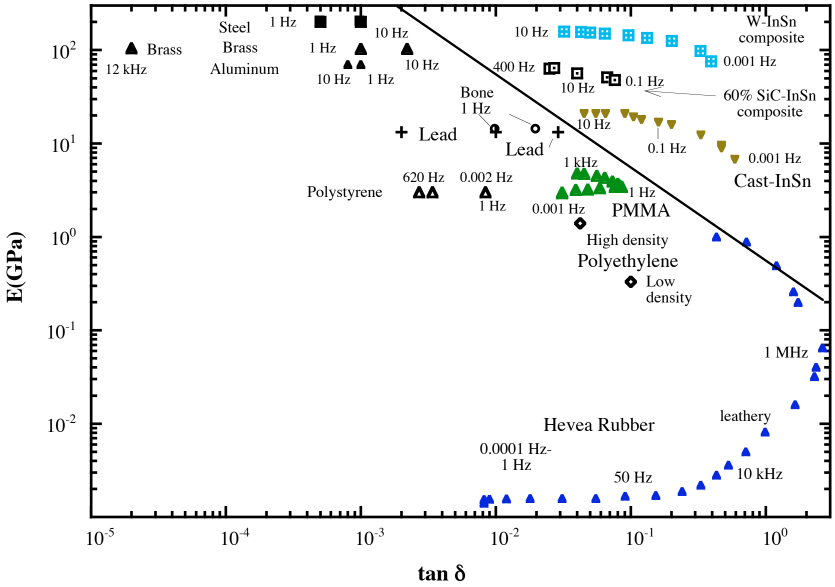

Fig. 1 Stiffness-loss map. Properties of selected materials inluding designed particulate composites.

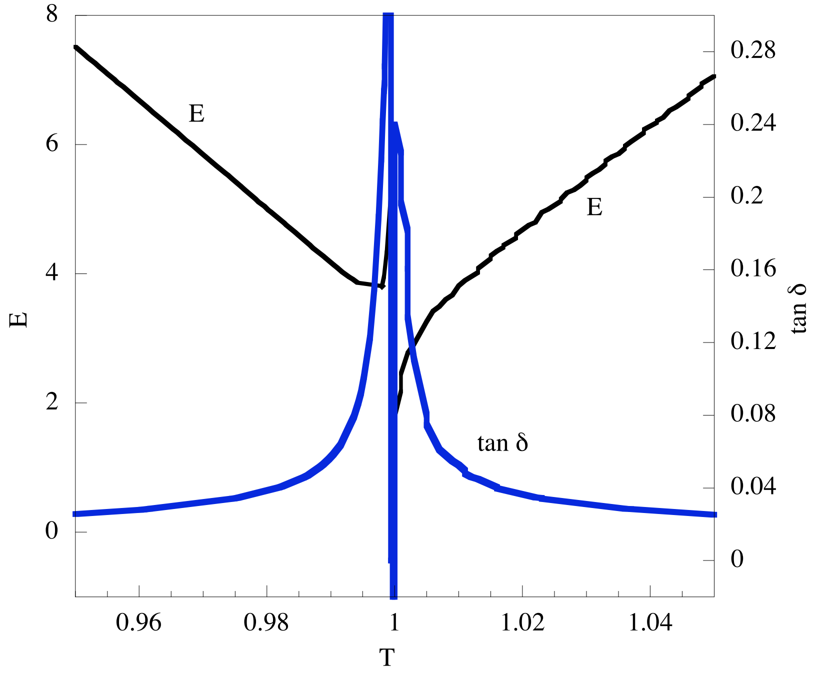

Fig. 2 Modulus (arbitrary units) and damping predicted in a polycrystalline solid in which the bulk modulus softens to zero at normalized temperature T = 1, then to negative values, and in which the shear modulus softens to a positive value.

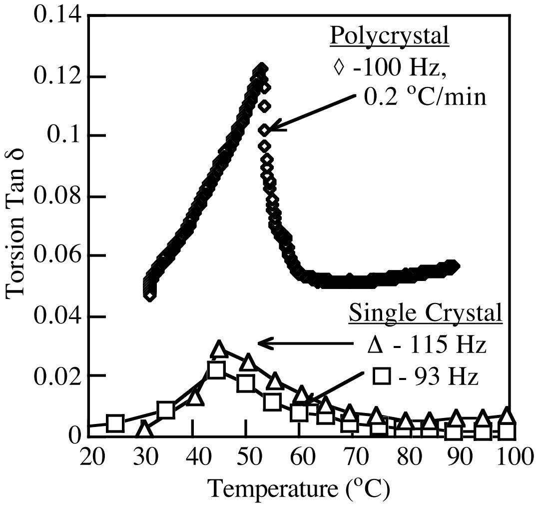

Fig. 3 Damping peak during cooling at 100 Hz for polycrystalline InTl in comparison to single crystals of similar composition from Li et. al., after Ref. [*23*].

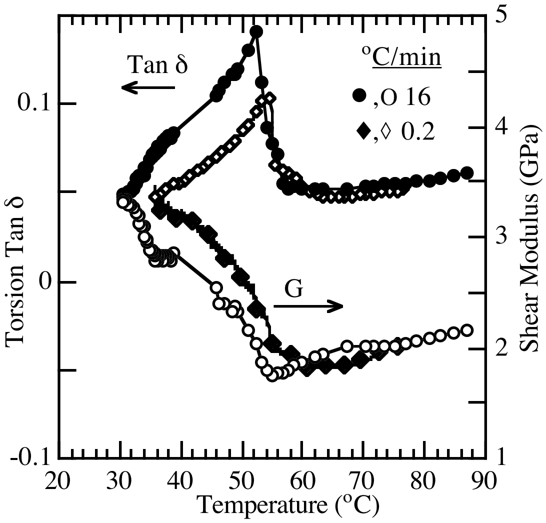

Fig. 4 Modulus and damping during cooling at 100 Hz for polycrystalline InTl for several cooling rates, after Ref. [*23*].

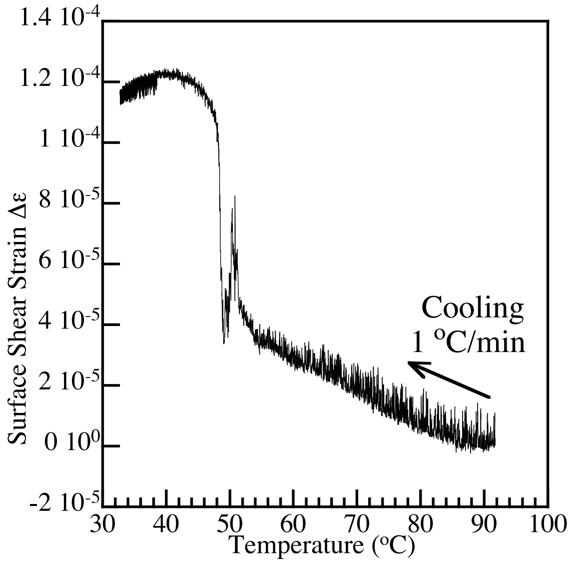

Fig. 5 Spontaneous strain in polycrystalline InTl, after Ref. [*23*].

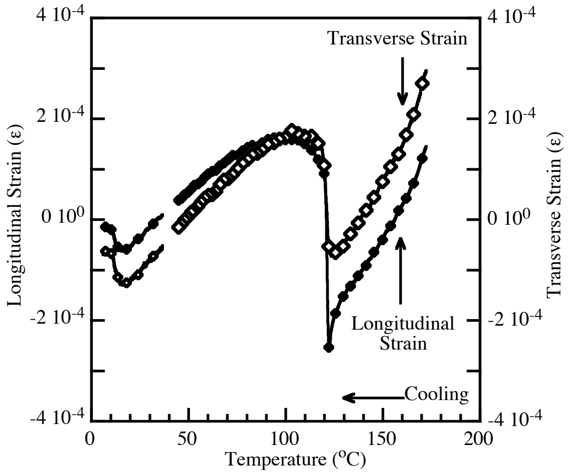

Fig. 6 Free thermal deformation during cooling for polycrystalline barium titanate showing spontaneous strain both the cubic to tetragonal transition near 125°C, and the tetragonal to orthorhombic transition near 15°C for this material.

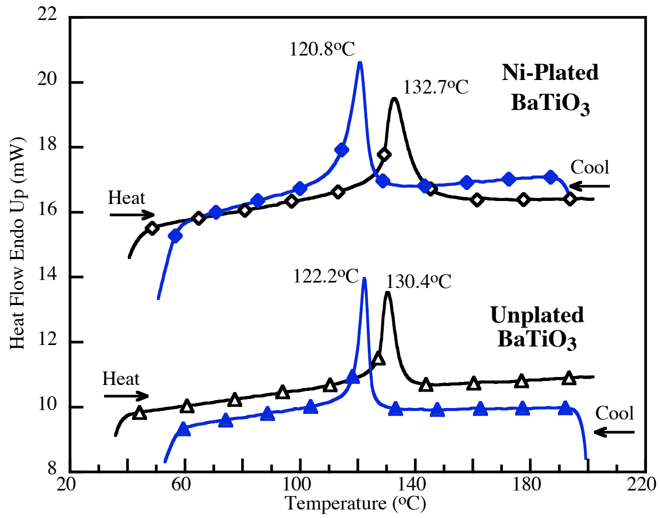

Fig. 7 Differential scanning calorimetry (DSC) of polycrystalline barium titanate. Endo refers to endothermic.

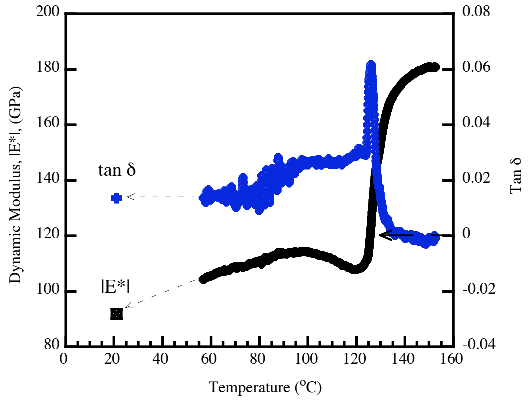

Fig. 8 Young's modulus and tan δ for polycrystalline barium titanate at 1 Hz as a function of temperature.

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