Nonmetallic Materials and Composites at Low Temperatures 3

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PREFACE

This was the third meeting in the series of special topical conferences on Non-Metallic materials at low temperatures. The first meeting was in Munich in 1978, the second in Geneva (1980) and so Heidelberg 1984 seemed an obvious time to review some of the hopes and objectives of the earlier meetings. It is also appropriate to consider the changing needs of the cryogenic community and how best the theory and practice of Non-metallic materials can be applied to suit this dynamic young science.

The aims and objectives of the International Cryogenic Materials Board in sponsoring this meeting remain the same. Namely, to provide a forum where practicing Engineers can meet with materials suppliers and researchers in an attempt to ensure that a real understanding exists between the two sides of the Cryogenic Materials Community. In this atmosphere, real problems can be addressed together with full discussions of tried and tested practical solutions. It is in this way that knowledge and confidence may grow hand in hand with the logical growth of the industry.

The first volume in this Non-metallic series noted that - "Cryogenics is an emerging technology, filled with promises." The second volume considered the 'delicately balanced relationship between knowledge and experience,' together with the hope that ..." year by year the application of non-metallic materials to the low temperature environment advances to the stage of a science". This, the third volume, reflects the urgent need that was so strongly evident in the panel discussion at the end of the conference. A need for further characterization of standard materials, and for formulators and materials scientists to ensure that well characterized composite materials are available to the cryogenic community.

It is clear that the science of cryogenic materials is still in its infancy but this latest volume, containing as it does a world wide collection of the latest works on the subject, continues the aims and objectives outlined in the previous volumes, progress through full understanding, detailed and frank discussion and careful application.

In many ways 1984 was an important year for the cryogenic industry and this truly international meeting was timely and of equal importance. Non-metallic materials have an important role to play in the rapidly expanding 'industrial' cryogenic world, and the world should know, with confidence, that the many aspects of this role are being researched and documented with care and enthusiasm.

David Evans
Günther Hartwig

CONTENTS

THERMAL EXPANSION OF NON-METALS

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ABSTRACT

The thermal expansion of a solid is determined by two factors, namely the internal stress generated by temperature change and the elastic stiffness. In many non-metallic crystals both these factors show considerable anisotropy which leads to expansion coefficients and associated Grüneisen parameters varying greatly with temperature and from one material to another. Experimental data extending down to 2 K are available for many materials of the common crystal structures such as rock-salt, fluorite, zincblende, rutile, caesium chloride, rare gas solids (f.c.c.). Data are scarce for most anisotropic crystals, mixed systems and composites. A brief review is given of the available experimental data for non-metallic crystals and some glasses and polymers.

INTRODUCTION

There are three thermal properties which are of practical interest in cryogenic design, namely heat conductivity, heat capacity (C) and thermal expansion. This paper reviews briefly (see Barron *et al*[1] for fuller treatment) what is known esperimentally of the expansion behaviour below room temperature of solids which are representative of common crystal structures, some glasses and polymers, and a few mixtures and composites.

Before considering the individual categories, there are general background features to remember:

1. Firstly, the volume coefficient of expansion, β, depends on the product of two factors: one is the anharmonicity or internal pressure P generated in a solid as the temperature T is changed and the other is the compressibility χ. That is

$$\beta = (dV/dT)_P/V = \chi_T(dP/dT)_V.$$

Other things being equal, soft materials expand more than hard ones, as shown by linear coefficient, α, in Figure 1.

2. Thermal expansion is a property (like heat capacity) which is in-

trinsic to the host lattice and therefore is relatively insensitive to trace impurities (say $\leqslant 1$ mole percent) except at temperatures well below the Debye characteristic temperature, θ_D. At temperatures $T \leqslant \theta/10$, magnetic impurities or localised modes of heavy impurity atoms may have an energy per atom which is larger than that of the host lattice and so be significant. From an engineering aspect this is not important as the significant practical changes in dimensions occur at high temperatures.

3. The ratio β/C is rather constant for most materials at temperatures $T > \theta/2$ as Grüneisen observed in his classic experiments over sixty years ago.

Grüneisen introduced the dimensionless proportionality factor or anharmonicity parameter

$$\gamma = \beta V/\chi_T C_V = \beta V/\chi_S C_P$$

where $\chi_T(\chi_S)$ is isothermal (adiabatic) compressibility and $C_V(C_P)$ is heat capacity at constant volume (pressure) of a molar volume V. γ is sometimes erroneously called a <u>constant</u>. In fact it is a weighted average of the values $\gamma_i = -(V/\omega_i)(d\omega_i/dV)$ for individual lattice vibrational modes of frequency ω_i. Since γ_i for many non-metal crystals varies from -2 or -3 (for some transverse 'guitar-string' modes of vibration) to +3, the weighted average will vary with the relative excitation and importance of different modes as the temperature changes.

At elevated temperatures where all modes are excited we should expect $\gamma_\infty = \langle\gamma_i\rangle$ to be sensibly constant. This appears to be true and C_V and βB_T are also fairly constant at these higher temperatures ($B = 1/\chi$).

4. At the Cryogenic Materials Conference in 1983, I reviewed briefly[2] the expansion behaviour of metals and pointed out that excepting those metals with strong magnetic interactions, γ does not change more than 20% or so on cooling. This is because γ_i values do not vary so greatly in close packed systems. In such cases it can be useful for design calculations to assume $\gamma \approx$ constant and calculate changes in length ℓ or volume V using tabulated heat capacities or Debye Functions. Of course, if $\alpha(T)$ is known experimentally this is unnecessary.

As an example of this calculation for a non-metal, consider polycrystalline (isotropic) alumina for which γ only varies from <u>ca</u> 1.25 ($T \to 0$) to 1.35 (1000 K). Cooling α-alumina from 293 K down to 77 K would give a contraction of

$$\Delta\ell/\ell = \Delta V/3V = (1/3)\int_{77}^{293} \beta dT = (1/3)\int_{77}^{293} \gamma\, C_V \chi_T dT/V$$

$$\simeq (\gamma\chi_T/3V)\,[\,U_{293} - U_{77}\,].$$

U is the internal energy which is tabulated in terms of Debye functions, e.g. see American Institute of Physics Handbook, Third Edition, 1972, p.4-112. Using $\gamma = 1.3$, $\theta_D \approx 950$ K, $V = 25.6\ \mathrm{cm}^3$, $\chi_T = 4 \times 10^{-12}\,\mathrm{Pa}^{-1}$ leads to $\Delta\ell/\ell = 0.34 \times 10^{-6} \times [\,1850-20\,] = 620 \times 10^{-6}$. Compare this calculated value with the observed average[3] for sapphire of 628×10^{-6}. The agreement is so close as to be fortuitous.

5. As we shall see below, $\gamma(T)$ can vary greatly particularly for the

more open crystal structures which favour low-lying transverse accoustic modes having negative values of γ_i.

In the low-temperature limit, only long waves are excited and ultrasonic measurements at different pressures (or volumes) lead to the limiting value, γ_0. This may be calculated for cubic materials from the weighted average of the pressure derivatives of the principal elastic stiffnesses c_{11}, $c' = (c_{11}-c_{12})/2$ and c_{44} using

$$\gamma_i = -\frac{1}{6} + \frac{d\ell n c_i}{dP}/2\chi \text{ (see appendix}^1\text{).}$$

For anisotropic crystals θ_0 may be calculated from the appropriate c_{ij} at two or more pressures (or volumes) and then differentiated numerically to give

$$\gamma_0 = - d\ \ell n\ \theta_0 / d\ \ell n\ V.$$

CLOSE-PACKED RARE GAS SOLIDS. (Coordination number CN = 12)

Solid neon, argon, krypton are not of much concern to most cryogenic engineers but are an example of close-packed non-metals. They show remarkably small variation in γ_i with either direction, polarisation or wave-number. For example, neutron scattering experiments on neon crystal show γ_i to all lie within the range 2.5 to 3.1 and the average $\gamma(T)$ from expansion data only varies between 2.58 and 2.7.

CAESIUM CHLORIDE STRUCTURE (CN = 8).

The caesium halides are also almost 'perfect' Grüneisen solids with $\gamma \approx 2.0$ from 2 to 300 K. This is a happy accident as they are elastically anisotropic and theoretical models indicate γ_i values ranging from 1 to 3.

ROCK SALT STRUCTURE (CN = 6)

Extensive measurements on alkali halides with this structure show γ_∞ lies between 1.4 and 1.7 for all but γ_0 drops from 1.65 for LiF to ca 1.0 for Na halides, 0.3 to K halides and 0 for Rb halides. This drop is associated with weakening of the c_{44}-type shear stiffness and the fact that γ_i for such modes becomes small and then negative for K and Rb-halides, i.e. they soften under pressure.

Figure 2 illustrates the behaviour of $\gamma(T)$. MgO also has this structure but γ is sensibly constant with value of 1.5.

FLUORITE STRUCTURE

Data for the alkaline earth fluorides, PbF_2 and ThO_2 give the picture of $\gamma(T)$ in Figure 3. In the progression from Ca to Sr to Ba, the ion size increases and associated with this is decrease in shear stiffness c' and softening of the mode, particularly in the (110) direction. The peak in γ for PbF_2 may arise from a nearly TA ferroelectric optic mode.

ZINCBLENDE STRUCTURE (CN = 4)

In this tetrahedrally-bonded family there are also low-frequency TA modes controlled by the shear stiffness c' which can soften under pressure. $\alpha(T)$ and $\gamma(T)$ become more negative as we grogress from group IV (Ge, Si) to III-V to II-VI and finally to a I-VII compound (CuCl) for which $\gamma_0 \sim -2$ (Fig. 4). The progressive change seems to be linked to the increasingly ionic nature and reduced angular rigidity of the bonding.

Cu_2O consists of two interpenetrating zincblende lattices sharing common oxygen atoms and shows even more extreme negative values of α and γ. The expansion coefficient α is negative from 0 to 270 K, reaching $\alpha_{min} = -3 \times 10^{-6}\ K^{-1}$ at 80 K.

WURTZITE STRUCTURE

These are also tetrahedrally bonded but have hexagonal symmetry and are therefore anisotropic. Limited thermal data for ZnO, Cds, ice and β-AgI all indicate that β and γ are negative at low temperatures.

ANISOTROPIC-AXIAL SYMMETRY

For crystals of hexagonal, rhombohedral or trigonal structure two linear coefficients are necessary to define the expansion. One is parallel to the symmetry axes ($\alpha_{||}$) and the other is normal to it ($\alpha_\perp$). These in turn depend on a product of a Grüneisen parameter and an elastic compliance s_{ij}

so $\alpha_{||} = [\gamma_{||} s_{33} + 2 s_{13} \gamma_\perp]\ C_p/V$

and $\alpha_\perp = [\gamma_\perp (s_{11} + s_{12}) + s_{13}\gamma_{||}]\ C_p/V$.

In either case, the second term in the square bracket can give rise to a negative expansion via cross-contraction, if the first term is small. The compliance s_{13} is normally negative.

Important examples are the layered materials, graphite and boron nitride, for which there is strong covalent bonding within layers and weak van der Waals forces between layers. This results in s_{33} being larger (soft) than $s_{11} + s_{12}$. The parallel coefficient $\alpha_{||}$ is large and positive. $\alpha_\perp$ is negative partly due to cross-contraction and partly from negative value of $\gamma_\perp$. Other examples are the chain-like solids, including polymers and tellurium and selenium. Here the weak forces are between chains so that $\alpha_\perp$ is large and positive. Strong bonding occurs along the chains so that s_{33} is small and $\alpha_{||}$ is negative, at least at low temperatures.

POLYMERS

A chain-like crystal of polyoxymethylene (POM), was measured down to 2 K and results were qualitatively similar to those for Se and Te : $\alpha_\perp$ is large and positive while $\alpha_{||}$ is negative below 100 K.

Recently, polyethylene has been measured down to 2 K for samples of varying crystallinity and degree of orientation[4]. Values for sample of 80% crystallinity and a draw ratio of 11 gave values for $\alpha_{||}$ and $\alpha_\perp$ which should approach those of the single crystal. As seen in Fig. 5, the $\alpha(T)$ curves are somewhat similar to those of Se and Te.

Choy[5] has reviewed the expansivity of oriented polymers giving data on PS, PMMA, POM, PVC etc, down to 100 K. Volume 13 of the Thermophysical Properties of Matter[6] gives much data for isotropic polymers including epoxy resins at temperatures above 70 or 80 K.

MINERALS AND LOW-EXPANSION CERAMICS

Most of the common minerals in the earth's mantle are silicates for which there is a marked lack of experimental knowledge at low temperatures.

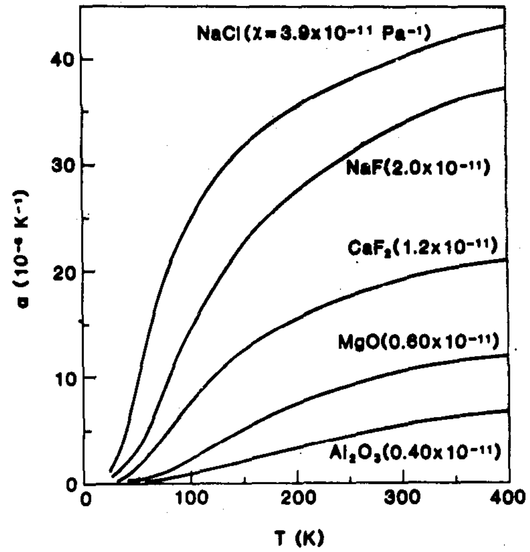

Fig. 1. $\alpha(T)$ for solids of different compressibility χ.

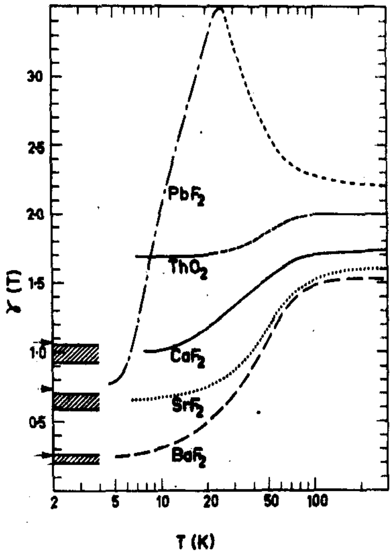

Fig. 3. $\gamma(T)$ for some fluorites.

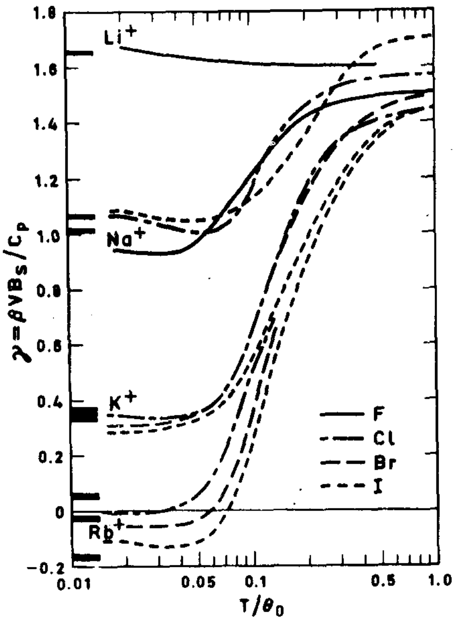

Fig. 2. $\gamma(T)$ for alkali halides.

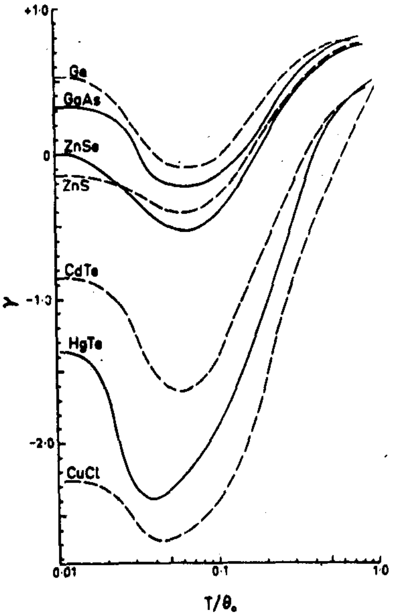

Fig. 4. $\gamma(T)$ for zincblende structure.

An exception is α-quartz which consists of SiO_4 tetrahedra linked by shared oxygen atoms and having trigonal symmetry. The linear expansion is positive and large compared with vitreous silica, silicon or germanium. The coefficient increases markedly with T up to the α-β transition above which β-quartz has a small or negative expansion[7]. The expansion of α-quartz at normal temperatures is believed to be largely due to cooperative rotation of the tetrahedra and associated increase in the Si-O-Si angle.

Very-low-expansion materials are of technical importance both at low and high temperatures. The lithium alumino-silicates of β- spodumene, also described as substituted β- quartz structure, appear to have negative expansion behaviour and contribute to the 'zero-expansion' character of some ceramic glasses such as Zerodur[7] and CerVit.

Cordierite ($2\,MgO.\ 2A\ell_2O_3\ .\ 5SiO_2$) is a aluminosilicate which has been measured at normal temperatures where α_c is negative and nearly twice the magnitude of α_a (positive) so that β is near zero[8].

Slack and Huseby[9] have discussed the expansion of some phenacite-type compounds including Zn_2SiO_4, Si_3N_4, Be_2SiO_4 and suggest that some of these might have negative expansions at low temperatures. They are open structures with tetrahedral bonding.

Related to the phenacite-structure is the olivine structure of Mg_2SiO_4 (forsterite) where the Mg ions are six-coordinated. The expansion of this orthorhombic mineral has been measured to low temperature with α_a, α_b and α_c all being positive[10]. The principal γ-values lie between 1.0 and 1.5 from 0 to 1000 K. At room temperature the average

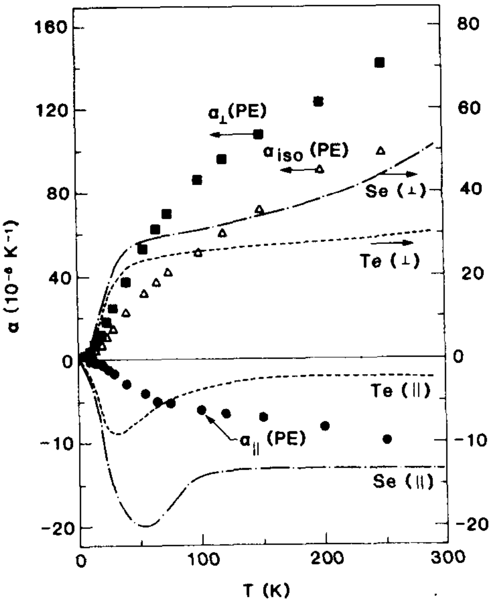

Fig. 5. α(T) for selenium, tellurium and polyethylene.

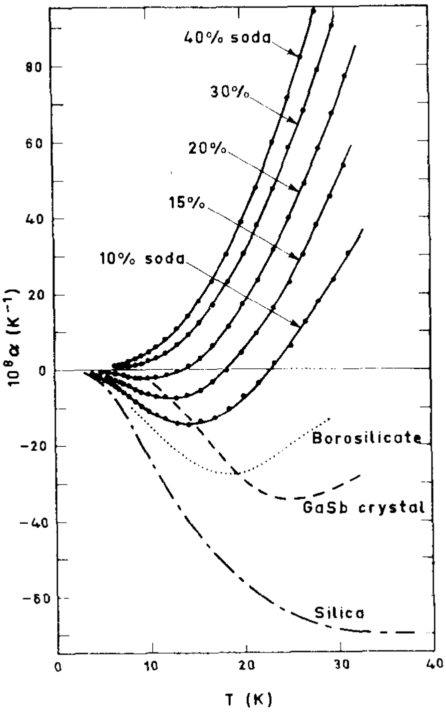

Fig. 6. α(T) for silicate glasses.

$\alpha \simeq 9 \times 10^{-6}\ K^{-1}$ compared with 12×10^{-6} for α- quartz and 10×10^{-6} for for MgO.

For the purposes of designing low-expansion mixtures or composites, it would be useful to have much more data at cryogenic temperatures on a variety of silicate minerals.

GLASSES

Glasses have been of practical interest for a very long time, but their thermal properties are still somewhat of a mystery. For example, vitreous silica, whose density is about 20% smaller than that of α-quartz, has an expansion coefficient which is negative below 150 K. The magnitude of α for SiO_2 depends on the thermal history (and density), being generally smaller in magnitude at high density. Other tetrahedrally bonded glasses such as GeO_2, BeF_2 also show negative expansion but of much smaller magnitude. Most non-tetrahedrally-bonded glasses, e.g. B_2O_3 and As_2S_3, have positive coefficients except perhaps below 2 K.

For SiO_2, additions of a few percent of network modifiers such as B_2O_3 (in Vycor) do not change this negative character significantly. Indeed the addition of 7.4 wt% TiO_2 which Corning use in their ULE silica enhances the negative α by about 30% below 50 K and yields a near-zero coefficient at room temperature.

However, network filling materials like soda, potash etc, reduce the negative component and so make α(T) much more positive (Fig. 6). Presumably the network filters inhibit those transverse modes which contribute to the contraction of the SiO_2 lattice.

MIXTURES AND AGGREGATES

There does not appear to be much data at low temperatures on well-defined mixed (2-component) systems which would allow comparison with theoretical models. Data on sintered mixtures of UO_2/ThO_2 at 283 K and 30 to 90 K indicate a roughly linear relation between α and relative concentration. The model of Turner[11] gives for an isotropic mixture

$$\alpha = \sum_i \alpha_i B_i V_i / \sum B_i V_i$$

where V_i is the relative volume occupied by the i^{th} component and α_i and B_i are the corresponding expansion coefficient and bulk modulus.

Measurements on equimolar BaF_2/CaF_2 polycrystal (p. 662[1]) gave values from 300 down to 80 K which were much closer to BaF_2 than to CaF_2.

The analyses of effective thermal expansion coefficient of a polycrystalline aggregate of anisotropic constituent crystals is rather similar to the Voigt and Reuss averaging of eleastic moduli. Upper and lower bounds have been calculated recently by Hashin[12] for a number of metals but comparison with experiment is made difficult by the presence of preferred orientation in metals. For non-metals, the best data are probably for α-alumina. It is not particularly anisotropic (e.g. $\alpha_{||}/\alpha_{\perp} \approx 1.2$ at 200 K). The polycrystalline and the single crystal average ($= 2\alpha_{\perp} + \alpha_{||}/3$) agree within experimental error of ± 1%[3].

Technically important are the composites comtaining one or more crystal phases in an isotropic matrix. Calculations have been made by Levin, Hashin, Rosen[12], but well-defined experimental systems do not seem to have been measured. Yates and collaborators[13] have measured a number of graphite-epoxy systems which are of interest but are not readily comparable with theoretical models. It seems desirable to have good data on, for example, randomly distributed anisotropic particles (of known expansion) in an isotropic matrix (of known expansion), also high-density compacts of isotropic particles having very different α-values would be of interest.

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