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Pressure Dependence of the Thermoelastic Quotient for Three Glasses[1]

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The interrelationship between the mechanical work done on a material in the elastic range and changes in its thermodynamic properties, that is, between stress and strain, on the one hand, and temperature and entropy, on the other, is known as the thermoelastic effect. The phenomenon is exactly adiabatic and is characterized by the thermoelastic quotient commonly referred to as thermoelastic constant. The thermoelastic effect can be used for stress analysis by monitoring the stress fluctuations by means of infrared radiometry. Also, it can be applied to study the anharmonicity in materials by measuring the temperature changes associated with adiabatic pressure changes. In this paper thermodynamic expressions are derived for the pressure derivative of the thermoelastic quotient under adiabatic as well as isothermal conditions. The derived expressions are applied to investigate the thermoelastic effect for the three glasses, namely, silica glass, soda-lime silica glass, and lead-silica glass. The isothermal pressure derivative of the thermoelastic quotient is evaluated for the three glasses. The isothermal volume derivative of the Gruneisen function is calculated.

KEY WORDS: anharmonicity; Gruneisen function; stress analysis; thermoelastic quotient.

1. INTRODUCTION

The thermal-mechanical coupling between temperature and stress is known as thermoelastic effect. Under adiabatic conditions the temperature of some materials is decreased by the application of a tensile stress and is increased by compression. All materials which have a positive thermal expansion coefficient behave in this manner. The thermoelastic effect has

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attained significance in recent years as researchers in engineering and solid-state physics have utilized the effect for important applications such as monitoring stress fluctuations in materials [1] and evaluating the Gruneisen function for materials [2–4].

Under adiabatic conditions the change in stress, $\Delta\sigma$, applied to a material and the resulting temperature change, ΔT, are related as follows:

$$\Delta\sigma = \left(- \frac{\Delta T/T}{K} \right) \tag{1}$$

where T is the absolute temperature of the material and K is the thermoelastic quotient, usually referred to as the thermoelastic constant. In the case of compression, the sign of the temperature change is the same as that of the change in pressure for materials having a positive thermal expansion coefficient.

Recent experimental [5] and theoretical [1, 6] investigations revealed that the thermoelastic quotient for a material subjected to a cyclic stress is stress dependent; the temperature response to changes in stress varies with the mean stress and contains a second harmonic. However, the theoretical investigations [1, 6] contained several approximations. The latest theoretical findings [7] on the stress dependence of the thermoelastic quotient reveal that it is the isothermal stress dependence of the thermoelastic quotient that determines the effect of mean stress on the temperature response of the material, while the adiabatic stress derivative determines the magnitude of the second harmonic. Exact thermodynamic expressions are derived in the latest theoretical study [7] to describe the temperature response of a material subjected to oscillating stress or pressure, and the magnitudes of the thermoelastic effect are evaluated for various materials.

In this paper, thermodynamic expressions are derived for the pressure derivative of the thermoelastic quotient under adiabatic as well as isothermal conditions. The isothermal pressure dependence of the thermoelastic quotient for silica glass, soda–lime silica glass, and lead–silica glass is investigated. Also, the isothermal volume derivative of the Gruneisen function is evaluated for the three glasses and is compared with the corresponding experimental values.

2. THEORY

The thermoelastic quotient for a material subjected to change in applied pressure under adiabatic conditions is expressed by the following relation:

$$K=\frac{1}{T}\left(\frac{\partial T}{\partial P}\right)_S \tag{2}$$

where K is the thermoelastic quotient, T is the absolute temperature of the material, and S is the entropy. The Maxwell relation gives

$$\begin{aligned}\left(\frac{\partial T}{\partial P}\right)_S&=\left(\frac{\partial V}{\partial S}\right)_P=V\left(\frac{\partial \ln V}{\partial T}\right)_P\left(\frac{\partial T}{\partial S}\right)_P\\&=\left(\frac{\beta VT}{C_{\mathrm{P}}}\right)=\gamma\chi_{\mathrm{S}}T\end{aligned} \tag{3}$$

where V is the volume, β is the coefficient of volumetric expansion, C_{P} is the heat capacity at constant pressure, γ is the thermodynamic Gruneisen function, and χ_{S} is the adiabatic compressibility. So the thermoelastic quotient K may be expressed as

$$K=\frac{1}{T}\left(\frac{\partial T}{\partial P}\right)_S=\frac{\gamma}{B_S} \tag{4}$$

where B_S is the adiabatic bulk modulus.

The isothermal pressure derivative of the thermoelastic quotient is given by the following expression:

$$\begin{aligned}\left(\frac{\partial K}{\partial P}\right)_T&=\left(\frac{\partial}{\partial P}\left(\frac{1}{T}\frac{\partial T}{\partial P}\right)_S\right)_T=\left(\frac{\partial}{\partial P}\left(\frac{\gamma}{B_S}\right)\right)_T\\&=\frac{1}{B_S}\left[\left(\frac{\partial \gamma}{\partial P}\right)_T-\frac{\gamma}{B_S}\left(\frac{\partial B_S}{\partial P}\right)_T\right]\end{aligned} \tag{5}$$

The adiabatic pressure derivative of the thermoelastic quotient may be derived as follows:

$$\left(\frac{\partial K}{\partial P}\right)_S=\left(\frac{\partial K}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_S+\left(\frac{\partial K}{\partial P}\right)_T \tag{6}$$

The volume derivative of the thermoelastic quotient is

$$\begin{aligned}\left(\frac{\partial \ln K}{\partial \ln V}\right)_T&=-B_T\left(\frac{\partial \ln K}{\partial P}\right)_T\\&=\left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T-\left(\frac{\partial \ln B_S}{\partial \ln V}\right)_T=q-\left(\frac{\partial \ln B_S}{\partial \ln V}\right)_T\end{aligned} \tag{7}$$

B_T is the isothermal bulk modulus. The above expression can be used to estimate q, the isothermal volume derivative of the Gruneisen function.

3. ESTIMATION OF THE THERMOELASTIC QUOTIENT AND ITS ISOTHERMAL PRESSURE DERIVATIVES

The thermoelastic quotient, K, and its isothermal pressure dependence are evaluated for three glasses: silica glass, soda–lime–silica glass, and lead–silica glass. Sato and Anderson [4] measured $(\Delta T/\Delta P)_S$ and evaluated the adiabatic Gruneisen parameter, γ_{ad}, as a function of pressure using the relation

$$\gamma_{\mathrm{ad}} = B_S \frac{1}{T}\left(\frac{\Delta T}{\Delta P}\right)_S \tag{8}$$

for the three glasses. Their experimental results are used in this paper to study the pressure dependence of K. Also, the isothermal volume derivative of the Gruneisen function, q, is evaluated for the three glasses using Eq. (7). The calculated values of q are compared with the experimental values. Table I lists the values of γ_{ad} and B_S from Ref. 4, and the calculated values of K. The value of $(\partial\gamma/\partial P)_T$ is calculated by fitting the experimental values of γ_{ad} to the theoretical relationship

$$\gamma_{\mathrm{ad}} = e^{(aP+b)} \tag{9}$$

The coefficient of pressure P is

$$a = -\left(\frac{q}{B_T}\right) \tag{10}$$

The above relationship follows from the thermodynamic relation:

$$\left(\frac{\partial\gamma}{\partial P}\right)_T = -\frac{V}{B_T}\left(\frac{\partial\gamma}{\partial V}\right)_T \tag{11}$$

$(\partial B_S/\partial P)_T$ is obtained by fitting the experimental values of B_S to a quadratic function of pressure. Average differences between the experimental values and the fitted values for the three glasses are about 1% or less for γ_{ad}, and for B_S the average differences lie within 0.05%. Table II gives the values of the isothermal bulk modulus, B_T [4], $(\partial \ln K/\partial P)_T$, $(\partial \ln B_S/\partial P)_T$, and q values calculated in the present work, which are compared with those reported in Ref. 4.

Table I. Calculated Values of the Thermoelastic Quotient ($T = 297$ K) of Three Glasses

Pressure (kbar)	B_S (kbar)	γ_{ad}	K (10^{-3} kbar^{-1})
		Silica glass	
0.5	357.5	0.058 ± 0.000	0.162 ± 0.000
1.012	354.5	0.062 ± 0.002	0.175 ± 0.000
1.494	351.7	0.064 ± 0.002	0.182 ± 0.000
1.983	348.8	0.076 ± 0.002	0.218 ± 0.001
2.461	346.0	0.084 ± 0.000	0.243 ± 0.001
2.953	343.1	0.093 ± 0.002	0.271 ± 0.002
3.438	340.2	0.104 ± 0.000	0.306 ± 0.002
3.932	337.3	0.114 ± 0.003	0.338 ± 0.002
		Soda–lime–silica glass	
0.510	461.0	0.623 ± 0.002	1.351 ± 0.008
0.985	462.2	0.627 ± 0.005	1.357 ± 0.008
1.489	463.5	0.636 ± 0.001	1.372 ± 0.008
1.986	464.8	0.634 ± 0.005	1.364 ± 0.007
2.465	466.0	0.634 ± 0.002	1.361 ± 0.007
2.950	467.3	0.639 ± 0.003	1.367 ± 0.007
3.451	468.6	0.641 ± 0.002	1.368 ± 0.007
3.929	469.9	0.637 ± 0.002	1.356 ± 0.007
		Lead–silica glass	
0.614	348.5	0.514 ± 0.004	1.475 ± 0.008
1.193	350.1	0.516 ± 0.008	1.474 ± 0.008
1.780	351.7	0.521 ± 0.005	1.481 ± 0.008
2.368	353.4	0.522 ± 0.008	1.477 ± 0.008
2.953	355.0	0.528 ± 0.006	1.487 ± 0.008
3.541	356.7	0.526 ± 0.001	1.475 ± 0.008
3.949	357.8	0.528 ± 0.003	1.476 ± 0.008

Table II. Calculation of the Parameter q for Three Glasses

	B_T	$\left(\frac{\partial \ln B_S}{\partial P}\right)_T$	$\left(\frac{\partial \ln K}{\partial P}\right)_T$	$q = \left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T$	
	(kbar)	(10^3 kbar^{-1})	(kbar^{-1})	Present work	Ref. 4
Silica glass	360.5	-0.017 ± 0.000	0.225 ± 0.010	-74.98 ± 3.82	-135 ± 25
Soda–lime–silica glass	456.9	0.006 ± 0.000	0.001 ± 0.001	-3.20 ± 0.52	-3.2 ± 0.9
Lead–silica glass	345.4	0.008 ± 0.000	0.003 ± 0.003	-2.87 ± 0.39	-3.0 ± 0.4

4. DISCUSSION

In the case of soda–lime–silica glass and lead–silica glass there is a spurious fluctuation of experimental values of γ_{ad} with pressure. This has resulted in a high uncertainty in the estimation of $(\partial\gamma/\partial P)_T$ and $(\partial \ln K/\partial P)_T$ for these two glasses. The values of $(\partial\gamma/\partial P)_T$ and $(\partial \ln K/\partial P)_T$ have a maximum uncertainty of 14 and 100%, respectively.

In the case of silica glass K steadily increases with increase in the pressure. The thermoelastic behavior of soda–lime–silica glass and that of lead–silica glass is similar; there is no steady change in K with pressure in both these glasses. The q value for the three glasses is calculated from Eq. (7). The anomalous behavior of silica glass is reflected by q, which has a large negative value, -74.98. There seems to be a discrepancy in the q value reported in Ref. 4 for silica glass. The value of a obtained from fitting γ_{ad} to the theoretical relationship given in Eq. (9) is -0.21 for silica glass. From Eq. (10), the q value is found to be -75.7. The q values for silica glass calculated using Eq. (7) and Eq. (10) are in very good agreement with each other. This suggests that the value of q for silica glass reported in Ref. 4, -135 ± 25, is incorrect. The q values calculated for the other two glasses agree well with those reported in Ref. 4.

5. CONCLUSION

The thermoelastic behavior of the silica glasses is investigated using thermodynamic theory. The exact thermodynamic expressions are useful in studying the thermoelastic effect in materials. It would be more interesting to study the temperature response of the materials subjected to fluctuating pressure and also to investigate the variation of the thermoelastic quotient with temperature. Such an attempt has not been made in this paper due to lack of experimental data.

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